THÈSE

Pour obtenir le grade de

Docteur

Délivré par **L'Ecole Nationale Supérieure de Chimie de Montpellier**

Préparée au sein de l'école doctorale
Sciences Chimiques Balard (ED459)
Et de l'unité de recherche
ICGM-IAM (UMR 5253)

Spécialité : **Chimie et Physicochimie des Matériaux**

Présentée par **Adrien Cornille**

Substitution des Isocyanates dans les Polyuréthanes pour l'Elaboration de Matériaux Adhésifs et Expansés

Soutenue le Jeudi 24 Novembre 2016 devant le jury composé de

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Préface

Remerciements

Ces travaux de thèse ont été réalisés au sein de l'équipe Ingénierie et Architectures Macromoléculaires (IAM) de l'Institut Charles Gerhardt (UMR 5253) et ont été financés par l'Agence Nationale de la Recherche à travers le projet CYRRENAS.

Je souhaite tout d'abord remercier M. Patrick Lacroix-Desmazes pour m'avoir accueilli au sein de l'équipe IAM et m'avoir permis de conduire ces travaux.

Je remercie particulièrement M. Henri Cramail, et M. Christophe Detrembleur qui ont accepté d'être rapporteur de ce mémoire.

Je remercie également M. François Tournilhac, M. Bernard Boutevin, M. Patrick Lacroix-Desmazes ainsi que M. Stéphane Fouquay qui me font l'honneur de juger ces travaux en qualité d'examinateur.

Je tiens à remercier Mme Fatoumata Camara d'avoir accepté de participer à ce jury de thèse et d'avoir pris le temps de lire ce mémoire.

Je souhaite exprimer ma plus sincère reconnaissance et toute ma sympathie à M. Sylvain Caillol et M. Rémi Auvergne qui ont dirigé ces travaux de thèse. Je souhaite joindre également M. Bernard Boutevin à ces remerciements. Ces trois personnes ont su me guider habilement dans un sujet riche tout en m'accordant leur confiance. Leurs compétences et leurs enthousiasmes ont été des sources permanentes de soutien et de motivation au cours de ces trois années.

J'associe à mes remerciements Mme Marine Blain, Mme Claire Negrell, Mme Sylwia Dworakovska, Mme Sofia Benyahia, et M. Vincent Froidevaux avec qui j'ai eu le plaisir de collaborer à plusieurs reprises.

J'exprime également mes remerciements à M. Stéphane Fouquay, Frédéric Simon et Guillaume Michaud de l'entreprise Bostik ainsi que Mme Corinne Roqueta de l'entreprise Arkema, pour avoir participé à ce projet, de leurs conseils lors de nos nombreuses réunions et de m'avoir accueilli au sein de leurs équipes de recherche.

Je remercie mes stagiaires (Camille, Patricia, Julien et Maxime) et les mini-projets pour leur aide dans la réalisation de ce travail.

Un grand merci à tous les membres de l'équipe IAM, permanents comme non-permanents, nouveaux et anciens, pour leur aide et cette très belle ambiance de travail.

Enfin, je ne remercierai jamais assez mes parents, mon frère, Lucie, Yvan, Josette ainsi que mes amis pour tout ce qu'ils m'ont apporté et m'apporteront dans ma vie.

Abréviations

A

AHEW	Amine Hydrogen Equivalent Weight ($g.eq^{-1}$)
APTS	*p*-Toluenesulfonic Acid

B

BADGE	Bisphenol A Diglycidyl Ether
Bis-C5-Ether	4,4'-(butane-1,4-diyl)bis(1,3-dioxolan-2-one)
Bis-MPA	2,2-Bis(hydroxyMethyl)Propionic Acid

C

C_5-Acetate	(2-oxo-1,3-dioxolan-4-yl)methyl acetate
C_5-Benzoate	(2-oxo-1,3-dioxolan-4-yl)methyl benzoate
C_5-Butane	4-butyl-1,3-dioxolan-2-one
C_5-Ethyl-Ester	ethyl 2-oxo-1,3-dioxolane-4-carboxylate
C_5-Ethyl-Ether	4-(ethoxymethyl)-1,3-dioxolan-2-one
C_5-Phenyl-Ether	4-(phenoxymethyl)-1,3-dioxolan-2-one
C_6-Allyl-Ether	5-((allyloxy)methyl)-5-ethyl-1,3-dioxan-2-one
C_6-Benzoate	(5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl benzoate
C_6-Ethyl-Ester	ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate
C_6-Trimethylhexanoate	(5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate
CaO	Calcium Oxide
CBMA	1,3-cyclohexanebis(methylamine)
CBMI	1,3-bis(isocyanatomethyl)cyclohexane
CC5	5-membered Cyclic Carbonate
CC6	6-membered Cyclic Carbonate

CCs	5-membered Dithio-Cyclic Carbonate
$CDCl_3$	Deuterated Chloroform
CEW	Carbonate Equivalent Weight ($g.eq^{-1}$)
CH_2Cl_2	Dichloromethane
$CHCl_3$	Chloroform
CMR	Carcinogenic, Mutagenic, Reprotoxic
CNSL	Cashew Nut Shell Liquid
CO_2	Carbon Dioxide
CS_2	Carbon Disulfide
C_s-Ethyl-Ether	5-(ethoxymethyl)-1,3-oxathiolane-2-thione

D

D	Thermal Diffusivity
DBTDL	DiButylTin DiLaurate
DMA	Dynamic Mechanical Analysis
DMF(-d_7)	(Deuterated) Dimethylformamide)
DMSO(-d_6)	(Deuterated) Dimethylsulfoxyde
DSC	Differential Scanning Calorimetry

E

E’	Storage modulus
E’’	Loss modulus
EDR-148	2,2’-(ethylenedioxy)bis(ethylamine)
EEW	Epoxy Equivalent Weight
Esterified TMP 1	2,2-bis(hydroxymethyl)butyl 3,5,5-trimethylhexanoate
Esterified TMP 2	2,2-bis(hydroxymethyl)butyl benzoate
Et_3N	Triethylamine

EtOAc	Ethyl Acetate

F

FTIR	Fourier Transform Infrared Spectroscopy

G

GC	Gel Content

H

HCL	Hydrochloric acid
Hd	Hardness
HDI	Hexamethylene diisocyanate
H-NIPU	Hybrid Non Isocyanate Polyurethane
HU	Hydroxyurethane

I

IOH	Hydroxyl Content ($mgKOH.g^{-1}$)
K_2CO_3	Potassium Carbonate

L

LiBr	Lithium Bromide

M

M	Molar Mass ($g.mol^{-1}$)
Methanol(-d_4)	(Deuterated) Methanol
$MgSO_4$	Magnesium Sulfate

N

N_2	Diazote
$NaHCO_3$	Sodium Bicarbonate
NC-514	Diepoxydized Cardanol
NCOEW	Isocyanate Equivalent Weight ($g.eq^{-1}$)
NIPU	Non Isocyanate Polyurethane
NMR	Nuclear Magnetic Resonance (^{1}H: Proton, ^{13}C: Carbon, ^{19}F, Fluor)

O

OHEW	Hydroxy Equivalent Weight ($g.eq^{-1}$)

P

PGTE	Phloroglucinol Tris-Epoxy
PHU	Polyhydroxyurethane
PPOBC	Poly(propylene oxide) bis-carbonate
PPODGE	Poly(propylene oxide) diglycidyl ether
Protected TMP	(5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol
PU	Polyurethane

R

REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RT	Room Temperature

S

SEM	Scanning Microscopy Electron
Sh A	Shore A

SH D	Shore D
SI	Swelling Index

T

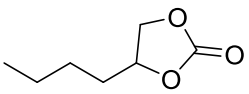
Tan δ	Loss Factor
TBD	1,5,7-Triazabicyclo[4.4.0]dec-5-ene
$Td_{30\%}$	Temperature at 30% of lost mass
$Td_{5\%}$	Temperature at 5% of lost mass
TDI	Toluene DiIsocyanate
Tg	Glass Transition Temperature
Tg_0	Initial Glass Transition Temperature
TGA	ThermoGravimetric Analysis
TGA/IR	ThermoGravimetric Analysis coupled Infrared Spectroscopy
TGA/MS	ThermoGravimetric Analysis coupled Mass Spectrometry
THF(-d_8)	(Deuterated) Tetrahydrofurane
TMP	Trimethylolpropane
TMP 1	(5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate
TMP 2	(5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl benzoate
TMPAE	Trimethylolpropane allyl ether
TMPTC	Trimethylolpropane tricarbonate
TMPTGE	Trimethylolpropane triglycidyl ether
Tα	Mechanical Glass Transition Temperature

GREC

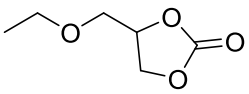
λ	Thermal Conductivity
ν_e	Crosslinking Density ($mol.m^{-3}$)
ρ	Density

Structures Chimiques

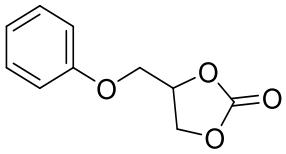
Carbonate Cyclique



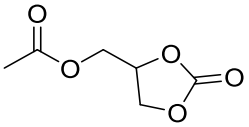
C_5-Butane



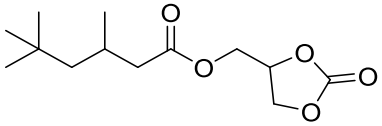
C_5-Ethyl-Ether



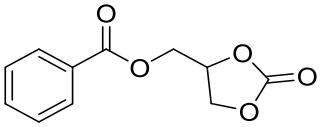
C_5-Phenyl-Ether



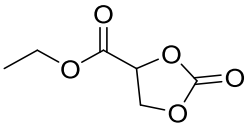
C_5-Acetate



C_5-Trimethylhexanoate



C_5-Benzoate



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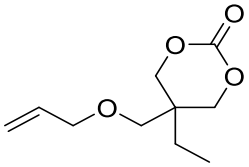
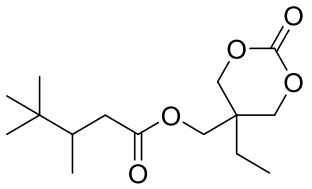
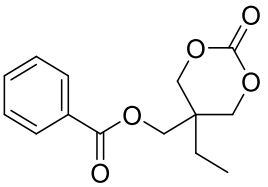


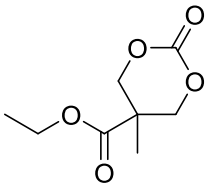
C_6-Allyl-Ether



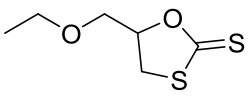
C_6-Trimethylhexanoate



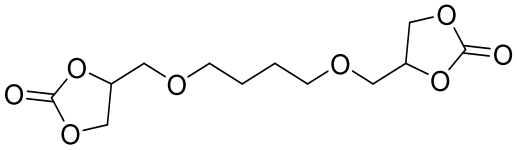
C_6-Benzoate



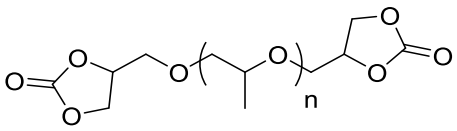
C_6-Ethyl-Ester



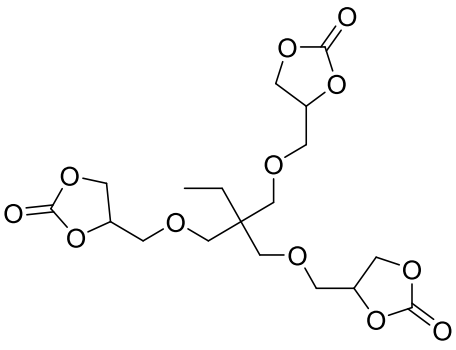
Cs-Ethyl-Ether



Bis-C_5-Ether

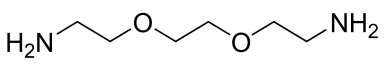


PPOBC380 (n=3) PPOBC640 (n=7)

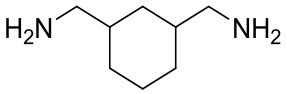


TMPTC

Amine

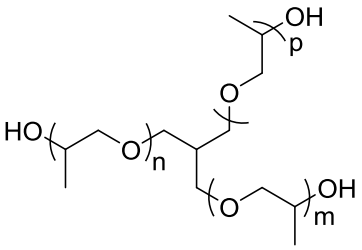


EDR-148



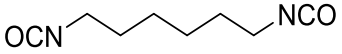
CBMA

Polyol

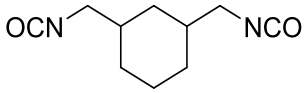


Triol420

Isocyanate

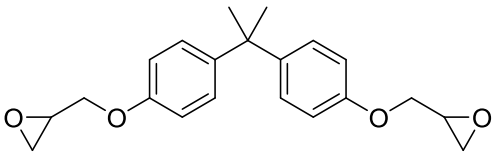


HDI

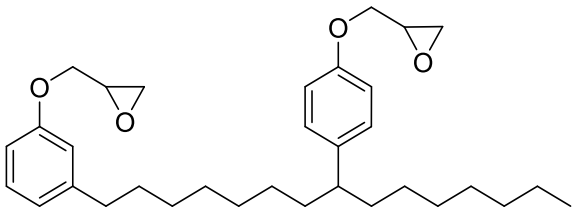


CBMI

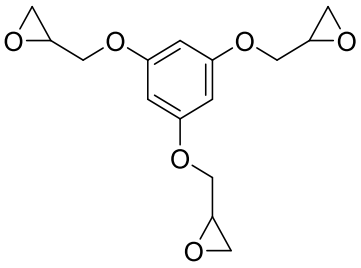
Epoxy



BADGE

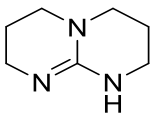


NC-514

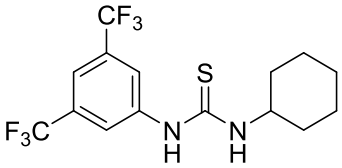


PGTE

Catalyseur

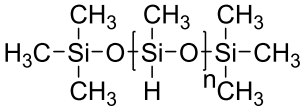


TBD



Thiourée

Agent Moussant



MH 15

Introduction Générale

Introduction Générale

Depuis leur découverte par le chimiste Allemand Otto Bayer en 1947, les polyuréthanes (PUs) occupent une place de choix dans le domaine des polymères en raison à la fois de leur nature très diversifiée et de leurs nombreuses applications telles que les mousses, les revêtements, les adhésifs, les vernis les peintures, les élastomères ou encore les fibres textiles (Figure 0-1). En 2016, leur production mondiale atteint les 18 millions de tonnes.

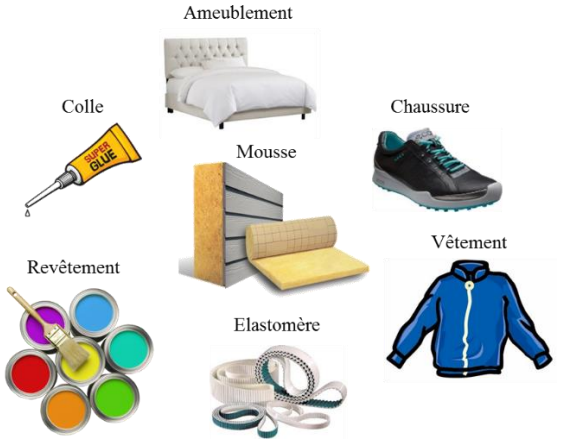


Figure 0-1: Exemples d'applications des matériaux PUs

Ces polymères sont généralement produits par la réaction entre un polyisocyanate et un polyol selon une polymérisation par polyaddition (Figure 0-2). Une large variété de polymères ramifiés ou réticulés peut être obtenue en choisissant et en ajustant la fonctionnalité de chacun des réactifs. Les polyisocyanates utilisés peuvent être aromatiques, aliphatiques, cycloaliphatiques ou polycycliques. Les plus utilisés dans l'industrie sont le diisocyanate de toluène (TDI), le 4,4'-diisocyanate de diphénylméthylène (4,4'-MDI) et le diisocyanate d'hexaméthylène (HMDI). Les structures « polyols » utilisées sont, quant à elles, nombreuses, couvrant une large gamme de masses molaires et pouvant être de différents types ; le plus souvent il s'agit de polyols de type polyester ou polyéther. Ainsi, cette flexibilité dans le choix des réactifs engendre à un large éventail de propriétés physiques.

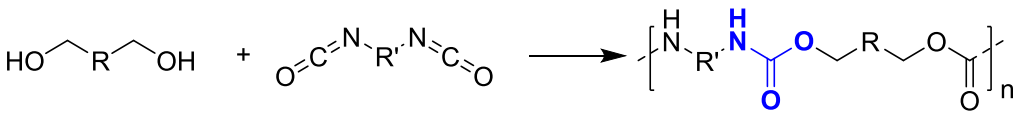


Figure 0-2: Voie d'accès aux PUs par réaction polyol/polyisocyanate

Néanmoins, du fait de leur nocivité et de leur dangerosité, aussi bien lors de leur synthèse qu'au moment de leur manipulation et utilisation, ainsi qu'en fin de vie des polyuréthanes, les

isocyanates constituent une réelle menace pour l'environnement et la santé. Le TDI et le MDI, qui sont parmi les isocyanates les plus utilisés dans l'industrie, sont obtenus par phosgénation respective du toluène diamine et de 4,4'-diaminodiphénylméthane. La synthèse de ces composés implique de ce fait l'utilisation du phosgène, un gaz mortel par inhalation, notamment utilisé comme gaz de combat lors de la première guerre mondiale. En outre, le TDI et le MDI sont classés CMR (Cancérigène, Mutagène, Reprotoxique) et une exposition prolongée à ces deux substances présente un risque majeur pour la santé des opérateurs et des utilisateurs. Enfin, les matériaux polyuréthanes présentent un risque lors de leur fin de vie. En effet, lors de leur combustion, des composés isocyanate sont libérés et se décomposent principalement en HCN, une substance mortelle pour l'homme. Lors de leur enfouissement, les PUs subissent une réaction d'hydrolyse et donnent des amines aromatiques toxiques. A cause des problèmes de toxicité que présentent les isocyanates, ces derniers sont surveillés par la réglementation REACH. En effet, le MDI est entré dans l'annexe XVII (Restriction List) de la réglementation qui vise à restreindre sa fabrication et sa mise sur le marché.

En 2014, la prise de conscience mondiale concernant la nécessité de protéger l'environnement et d'assurer la sécurité, la santé et le bien-être des salariés et des consommateurs, a été à l'origine du montage du projet CYRRENAS (new CYclocarbonate building blocks Reactive at Room temperature for ENvironment friendly polyurethane Adhesives and Sealants). Ce projet financé par l'Agence Nationale de la Recherche, est un projet collaboratif entre deux équipes de recherche : le laboratoire OMC (Organometallics : Materials & Catalysis) de l'Institut des Sciences Chimiques de Rennes et le laboratoire IAM (Ingénierie et Architectures Macromoléculaires) de l'Institut Charles Gerhardt de Montpellier, ainsi que deux entreprises : Bostik et Arkema. Le projet CYRRENAS vise à substituer les composés isocyanates des formulations polyuréthanes afin de concevoir des matériaux polyuréthanes sans isocyanate, communément appelés NIPUs (Non-Isocyanate Polyurethanes). Les bénéfices attendus sont importants, tant académiquement qu'industriellement, puisque ce projet vise au développement d'une nouvelle génération de matériaux sans isocyanate, un avantage non négligeable sur un marché mondial extrêmement innovant et concurrentiel.

Parmi les voies d'accès aux NIPUs, la réaction d'ouverture des carbonates cycliques par les amines semble être la voie la plus prometteuse (Figure 0-3). Au cours de ces dernières années, de nombreuses recherches se sont intéressées à cette réaction notamment pour la synthèse de poly(hydroxyuréthane)s (PHUs). Cette voie extrêmement innovante, semble être la plus intéressante sur le plan environnemental, physique et chimique, et en terme de sécurité. En

effet, aucun composé ayant une toxicité équivalente ou supérieure aux isocyanates n'est utilisé et les carbonates cycliques employés peuvent être issus de substances naturelles renouvelables telles que le glycérol, lui-même issu de la synthèse d'esters méthyliques par transestérification d'huiles végétales servant de carburant sous la dénomination de biodiesel.

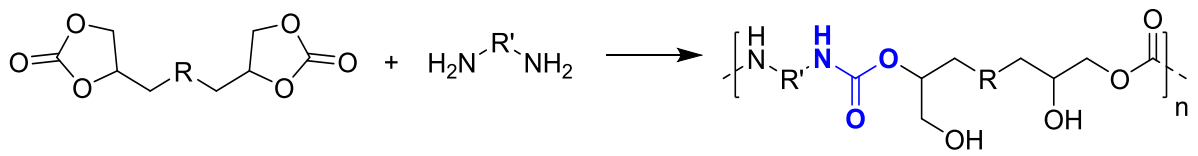


Figure 0-3: Voie d'accès aux PHUs par réaction carbonate cyclique/amine

Néanmoins, cette technologie présente deux verrous scientifiques à lever : la faible réactivité des carbonates cycliques à température ambiante ainsi que les faibles masses molaires des matériaux PHUs résultants de cette réaction. Pour répondre à ces deux problématiques, les objectifs scientifiques et technologiques du projet incluent :

- la conception et la préparation de synthons comportant des carbonates cycliques selon des procédés économiquement et écologiquement viables,
- la compréhension du mécanisme de formation des PHUs à partir de ces synthons ainsi que des paramètres influençant leur réactivité,
- le choix judicieux de la structure interne de ces composés carbonates cycliques, pour accéder à des matériaux PHUs aux propriétés thermomécaniques ajustables à différentes applications et mimant aux mieux les propriétés des PUs traditionnels.

Par ailleurs, l'objectif principal de l'entreprise Bostik s'inscrit dans une démarche d'innovation durable avec la mise en place de formulations de mastics et d'adhésifs NIPUs bi-composante utilisant les couples carbonates cycliques / amines les plus adaptés et ce, à partir des travaux de recherche effectués antérieurement. A noter que la société Bostik est un des leaders mondiaux de la fabrication d'adhésifs et de colles trouvant des applications dans de nombreux domaines qui peuvent être regroupés en trois secteurs tels que le grand public, la construction et l'industrie.

De surcroît, parmi les applications des matériaux PUs précédemment citées, deux tiers du marché mondial concernent les mousses, flexibles et rigides, utilisées dans de nombreux domaines tels que l'automobile et le transport, le mobilier, le bâtiment, l'industrie navale, l'aéronautique, les articles de sport, les appareillages domestiques et industriels, les chaussures ou encore l'emballage. Cette grande diversité d'applications est due aux propriétés

exceptionnelles de ces matériaux notamment dans les domaines de l'isolation thermique et acoustique, l'absorption d'énergie, et la protection contre les chocs. A partir des études préalables, menées au sein du projet CYRRENAS, la compréhension des spécificités du système carbonate cyclique / amine a été permise et ce, tout en restant dans une optique de développement durable et de protection des employés de l'industrie et des consommateurs. Ces travaux de thèse se sont de ce fait intéressés à la substitution des monomères dangereux dans les formulations des mousses polyuréthanes en élaborant pour la première fois des mousses flexibles à base de PHUs.

Cette thèse a été réalisée au sein de l'équipe IAM de l'institut Charles Gerhardt de Montpellier (ICGM) qui dispose d'une grande expertise dans le domaine de la chimie des carbonates cycliques et de la synthèse des PHUs. Ce travail a été mené en collaboration avec la société Bostik, qui dispose du savoir-faire industriel pour la synthèse d'adhésif polyuréthane, ainsi que l'entreprise Arkema spécialisée dans la synthèse des résines acryliques et qui souhaite développer une nouvelle gamme de produits polyuréthanes sans isocyanate.

Ce mémoire de thèse est divisé en quatre parties. Le premier chapitre propose, par l'intermédiaire d'un article scientifique de perspectives, un état de l'art des voies d'accès aux NIPUs et de la réaction carbonate cyclique/amine ayant pour but de remplacer les systèmes actuels sans avoir recours aux isocyanates et ce, pour la formulation des PHUs. Cette première partie permet également de faire le bilan des limitations de cette technologie pour ainsi proposer des alternatives pour les années à venir.

Le deuxième chapitre de ce mémoire est dédié à l'étude et à la compréhension de la réactivité des carbonates cycliques et des amines. Des études cinétiques, suivies par spectrométrie RMN sur des réactions modèles ou à partir de polymérisation de composés polyfonctionnels étudiés par DSC, ont été à la base de ce travail. Ces deux études ont eu pour but de montrer les raisons de l'obtention des faibles masses molaires des PHUs et de proposer ainsi des voies d'amélioration.

Le troisième chapitre traite de la formulation de matériaux PHUs réticulés à partir de composés polyfonctionnels pour des applications adhésives et des mousses flexibles. Ces matériaux ont été caractérisés du point de vue structurel, thermique, mécanique et thermomécanique, et leurs propriétés ont été comparées à des matériaux polyuréthanes de référence.

Enfin, dans un quatrième chapitre, une nouvelle approche de formulation de matériaux polyuréthanes sans isocyanate est décrite afin de pallier les limitations des PHUs. Ces nouveaux matériaux appelés H-NIPUs (Hybrid Non-Isocyanate PolyUrethanes) sont élaborés à partir de la réaction carbonate cyclique/amine pour former des pré-polymères amino-téléchéliques contenant des groupements hydroxyurethanes et combinés dans un deuxième temps à des extendeurs de chaînes époxydés bio-sourcés.

Ce manuscrit de thèse est rédigé sous la forme d'une compilation d'articles scientifiques acceptés ou soumis dans des journaux à comité de lecture.

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Chapitre I. Contexte et état de l'art des polyuréthanes sans isocyanate

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Comme indiqué dans l'introduction générale de ce manuscrit, ces travaux de thèse ont pour objectif principal d'éviter l'utilisation d'isocyanates dans les polyuréthanes en proposant des polymères plus respectueux de l'environnement, n'utilisant pas de réactifs dangereux pour la conception de matériaux techniques et contenant des groupements uréthanes mimant au mieux les caractéristiques des PUs classiques.

Pour cela, un état de l'art approfondi est primordial afin de prendre connaissance de toutes les voies d'accès disponibles, de leurs avantages, de leurs limitations, et de sélectionner celles qui semblent les plus viables économiquement et écologiquement. Cet état de l'art sur ce sujet est déjà disponible à travers plusieurs revues publiées ces dernières années par Cramail *et al.*, Figovsky *et al.*, Muelhaupt *et al.*, Rokicki *et al.* et nous même[1-7]. Ces revues scientifiques rassemblent de manière extrêmement détaillées tous les travaux de recherche effectués ces dernières années à travers le monde et le lecteur pourra aisément retrouver ces informations dans ces revues scientifiques. C'est pourquoi nous n'avons pas effectué un nouveau travail de recensement qui n'aurait pas apporté plus d'informations que celles présentées dans ces articles scientifiques.

Il nous a paru en revanche beaucoup plus pertinent d'effectuer une lecture critique de ces revues et d'en proposer une vision synthétique et prospective en 2016 autour de la problématique de l'utilisation des isocyanates dans les polyuréthanes, des voies d'accès pour les remplacer, en sélectionnant les plus prometteuses pour en étudier les intérêts, les limites et les enjeux à envisager dans les prochaines années afin d'accéder à des matériaux proposant des propriétés comparables ou supérieures aux PUs actuels.

Cet article scientifique, soumis sur invitation dans *European Polymer Journal*, constitue une plateforme à ces travaux de thèse en décrivant de manière non conventionnelle le contexte et l'état de l'art de ce projet. Cette production scientifique a été rédigée en fin de doctorat ce qui explique les références récentes.

A Perspective Approach to Sustainable Routes for Non-Isocyanate Polyurethanes

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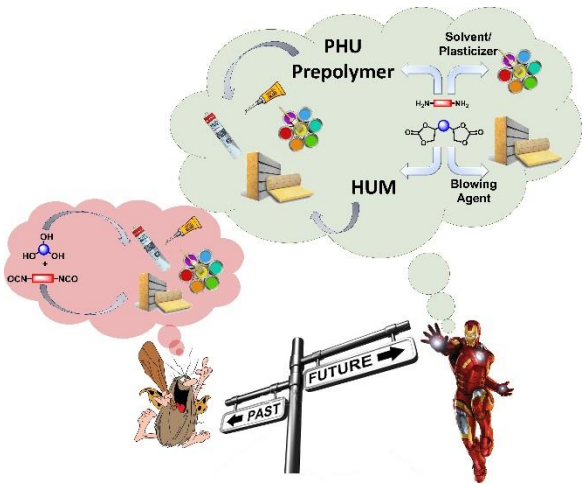
I. Abstract

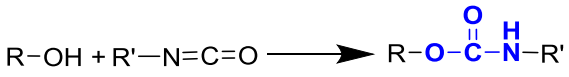
Sustainable routes for the synthesis of polyurethanes with industrial applications are discussed in this article. Polyurethane is currently one of the most commonly used polymers worldwide for various applications such as rigid and flexible foams, coatings, elastomers, adhesives and sealants. However, isocyanate precursors are very harmful at each stages of the life cycle of the polymers. Hence, new synthesis routes for isocyanate-free polyurethanes are reported in literature, but most of them suffer from significant lacks that prevent any industrial application. This feature article focuses on the new challenges and new opportunities of these routes. A first part is dedicated to the market, the manufacture and the hazards of polyurethanes. In a second part, this article deals with the synthesis routes leading to non-isocyanate polyurethane. Hence, the advantages and limits of these routes are reported and discussed. Finally the outlooks for a future and industrial use of non-isocyanate polyurethane in industry are examined.



II. Polyurethane, interesting materials for various applications

II.1 Brief history

Polyurethanes were invented back in the 1930's by Otto Bayer and coworkers [8] from the works of Wûrtz, who discovered in 1849 the reaction between alcohol and isocyanate yielding urethane (carbamate) groups (Scheme I-1). These polymers were developed to obtain materials with properties similar than polyamide fibers (nylon) discovered earlier but protected by American patents. The versatility of polyurethanes, and their ability to substitute to other materials, stimulated the development of numerous applications. Around mid-50's, polyurethanes (PUs) found applications in coatings, adhesives, elastomers and rigid foams. In the next years, the development of polyol polyether at low cost allowed to obtain flexible polyurethane foams for applications in furnishing and automotive areas. Nowadays, PUs find applications everywhere in everyday life: furnishing, cars, clothing, shoes, elastomers, coatings, wall and roofing insulation, etc.



Scheme I-1: Synthesis of urethane compound

II.2 Polyurethane market

The value chain of polyurethanes involves three key players. The first ones are the industrial chemists that produce the raw materials for the synthesis of polymers. The second players are the formulators that produce polyurethanes from raw materials; and the last ones are assemblers, who include polyurethanes in their final products. The economic players are involved in one, two or these three sectors. In 2016, with a global production of 18 Mt, PUs rank 6th among all polymers based on annual worldwide production. The major part of this production is performed in Asia with around 8 Mt, then in Europe with around 4 Mt and finally in the United States of America with around 3 Mt. The global market of polyurethane is valuated around 53 billion euros and the five first Companies, BASF, Bayer, Dow, Huntsman and Yantai Wanhua, account for over 35% share of the total market (Figure I-1).

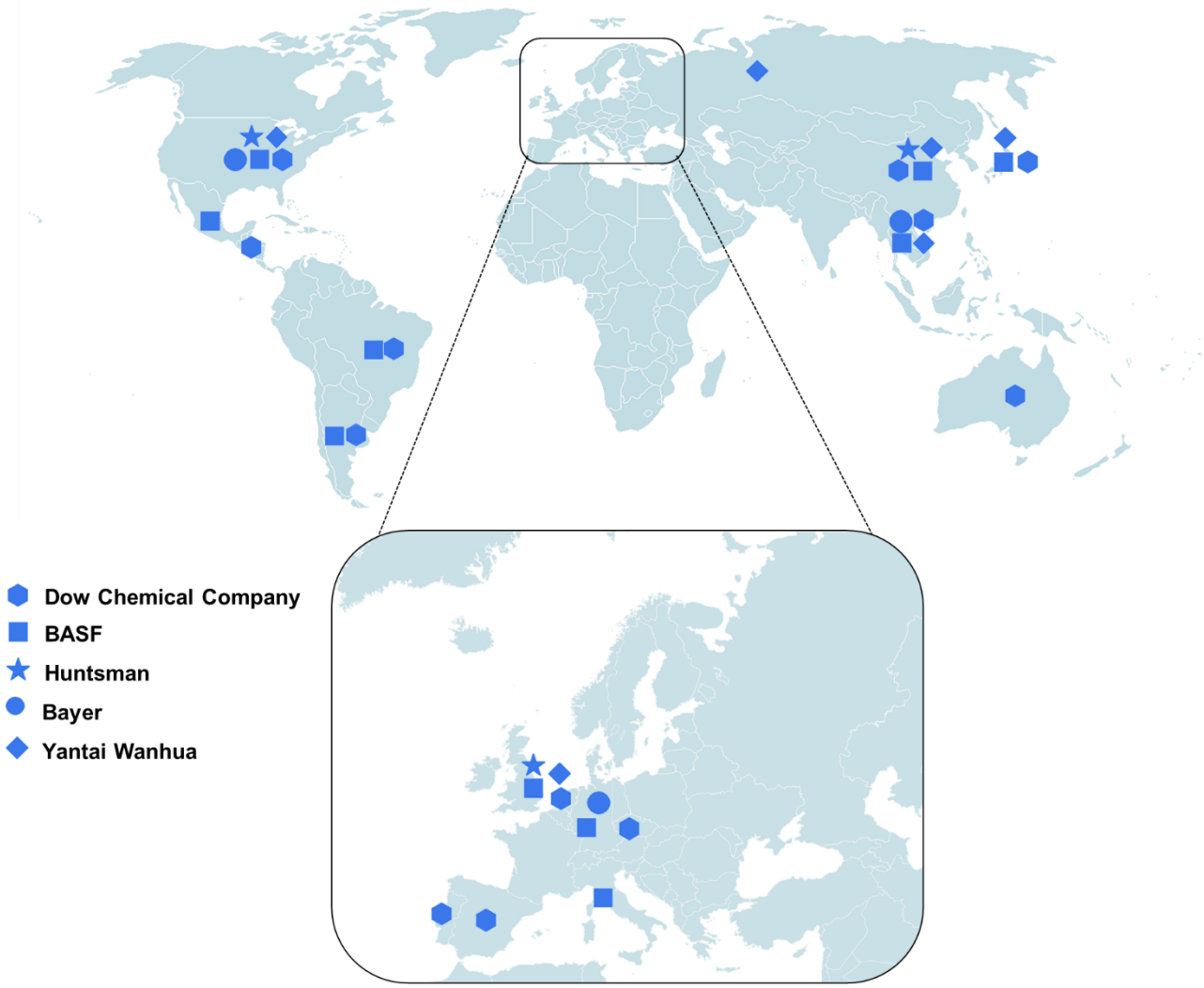


Figure I-1: Geographical area of the polyurethane production

II.3 Polyurethane properties

Due to the diversity of isocyanates and polyols, various polyurethanes can be synthesized, therefore the term "polyurethane" represents actually an important range of products with different macromolecular structures. The polyurethane market is segmented in three large product families: flexible foams, rigid foams and non-porous materials. This classification corresponds to PU density and rigidity (Figure I-2). The non-porous PUs find applications in coatings, adhesives, sealants, elastomers and binders. Polyurethanes RIMs are materials obtained by Reaction-Injection-Molding and consist of poly (urethane-urea) copolymers. The rigid foams are mainly used as insulation panels for building, fridge-freezer while the flexible foams find applications in mattresses, seats, sofas, automotive …

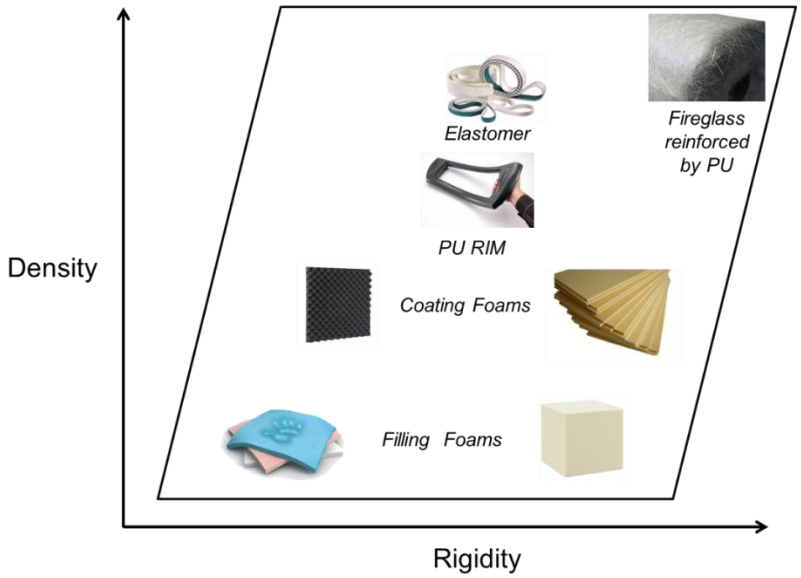
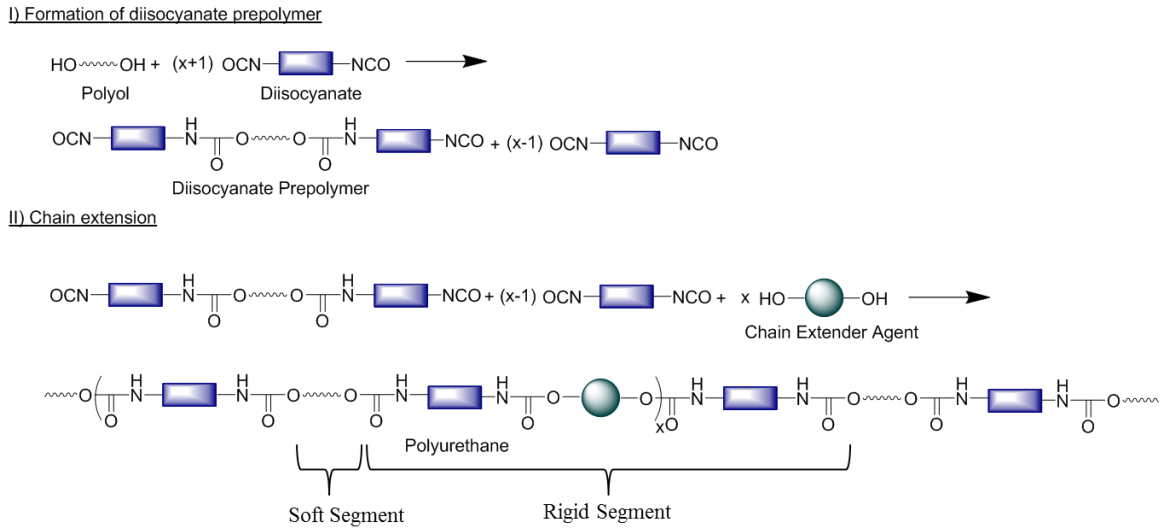


Figure I-2: Properties of polyurethane range [9]

II.4 Polyurethane manufacture

Currently, most of the polyurethanes are synthesized by a two-step process (Scheme I-2) [10]. The first step corresponds to the reaction between a polyol and an excess of diisocyanate which yields a polyurethane prepolymer with NCO end-groups. The second step consists in the reaction of this prepolymer with another polyol as chain extender or crosslinking agent. This two-step process allows to circumvent the difference of reactivity between polyols and consequently to improve the material properties. The resulting polyurethanes then composed of soft and rigid segments.



Scheme I-2: Synthesis of polyurethane in 2-step process

II.5 Hazards of polyurethanes synthesis

Environmental impacts of chemical substances are evaluated through three stages of life cycle of a polymer: during the synthesis of the monomers; during the polymerization and at the end of life of materials. Hence, polyurethanes present hazards at these three stages.

Firstly, the synthesis of isocyanates requires the use of phosgene, which is a lethal gas, to convert amines into isocyanates. Moreover, the two most widely used isocyanates in PU industry, MDI (methylene diphenyl diisocyanate) and TDI (Toluene diisocyanate), are classified as CMR (Carcinogenic, Mutagenic and Reprotoxic). These substances have harmful effects on human and environment. Prolonged exposure to them presents dramatic health risks such as asthma, dermatitis, conjunctives and acute poisoning [11, 12]. In conjunction with these serious health concerns, the environmental regulations limit or banish the use of some isocyanates [13]. Finally, end of life PUs are either burnt or put into landfills. However, during combustion, polyurethanes are degraded and release isocyanates that decompose mainly in HCN, a poisonous substance [14-17]. In the landfills, polyurethanes undergo hydrolysis reaction that yields toxic amines. To summarize, polyurethanes exhibit hazards during their whole life cycle, mainly due to the presence of harmful precursors such as isocyanates and phosgene. Therefore, in Europe, with REACH regulation, isocyanates will be progressively banned [13]. Therefore, this context urges the development of isocyanate-free polyurethane. Thus, considerable works were reported in literature on the synthesis of isocyanate-free polyurethanes, but until now, the various technologies that were proposed have pros and cons and none of them was chosen and developed by industry. The objective of this article is to summarize the state of the art and to propose, for the first time, a perspective approach for the choice of a sustainable route to isocyanate-free polyurethanes, based on industrial expectations and scientific challenges.

III. Substitution of isocyanates in polyurethanes

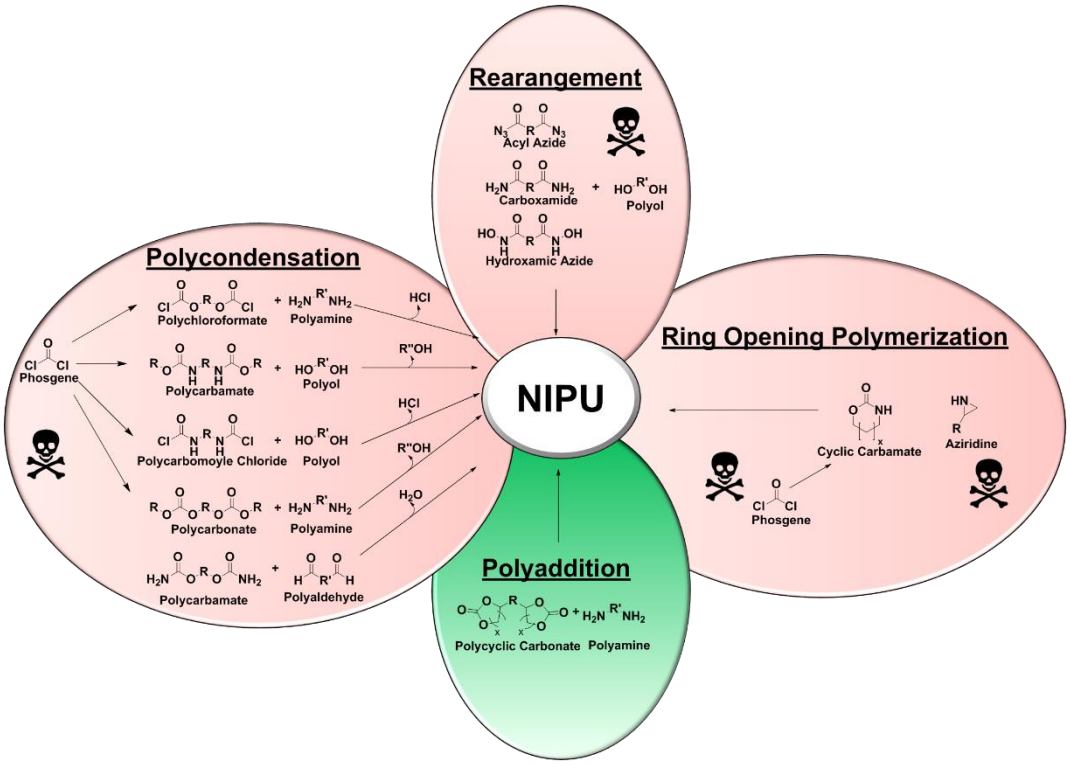
III.1 Nomenclature

In the literature, several names are given to isocyanate-free polyurethanes: NIPU, PHU, H-NIPU. Therefore, nomenclature should be defined for the rest of this article. The name NIPU (Non-Isocyanate PolyUrethane) corresponds to the generic name of isocyanate-free polyurethanes. Among the NIPUs, the PHUs (PolyHydroxyUrethane) are a kind of NIPUs obtained by reaction between cyclic carbonate and amine that yields hydroxyurethane

repeating units. Finally, recently, the new terms HUM (Hydroxy Urethane Modifier) and H-NIPU (Hybrid Non-Isocyanate PolyUrethane) emerged in the literature in order to to describe respectively monomers and co-polymers of NIPU with other polymers such as polyacrylates or polyepoxides.

III.2 Synthesis routes to isocyanate-free polyurethanes

For the past several years, NIPUs have gained a great deal of attention in scientific community. Literature reports four synthesis routes: polycondensation, rearrangement, ring-opening-polymerization and polyaddition. All these routes are summarized in Scheme I-3. Recently, some interesting reviews dedicated to the synthesis of NIPU were published [2, 4-6, 18, 19] and provided a complete overview of all these methods.



Scheme I-3: NIPU routes

Among polycondensation routes, we can find the reactions between polychloroformate and polyamine, polycarbamate and polyol by transurethanization, polycarbamoyl chloride and polyol, and polycarbonate and polyamine. Nevertheless, these routes require the use of phosgene or derivatives for the synthesis of precursors. Moreover, during polycondensation, side-products, such as HCl or alcohols, are released, which is a significant limitation to industrial applications. Another polycondensation route consists in the reaction between

polycarbamate and polyaldehyde. This reaction seems interesting but this route, yet little studied, entails also the release of water during polymerization [20].

The synthesis of NIPUs by rearrangement of acyl azides (Curtius rearrangement), carboxamides (Hoffman rearrangement) or hydroxamic azides (Lossen rearrangement) are also described in literature [21-29]. During these rearrangements, isocyanates are produced *in-situ* and in presence of alcohol, polyurethanes are synthesized. These ways still use isocyanates, even if they are produced *in-situ*, but more important, the reactants such as acyl azides, carboxamides and hydroxamic azides, are very harmful substances.

The third way for the synthesis of NIPUs is the ring opening polymerization of aliphatic cyclic carbamates [30-34] or aziridines [35-37]. Although these NIPUs are synthesized without any release of side-products, these reactions are often performed at high temperature and the cyclic carbamates are generally produced from phosgene. The toxicity of aziridines remains also a significant issue.

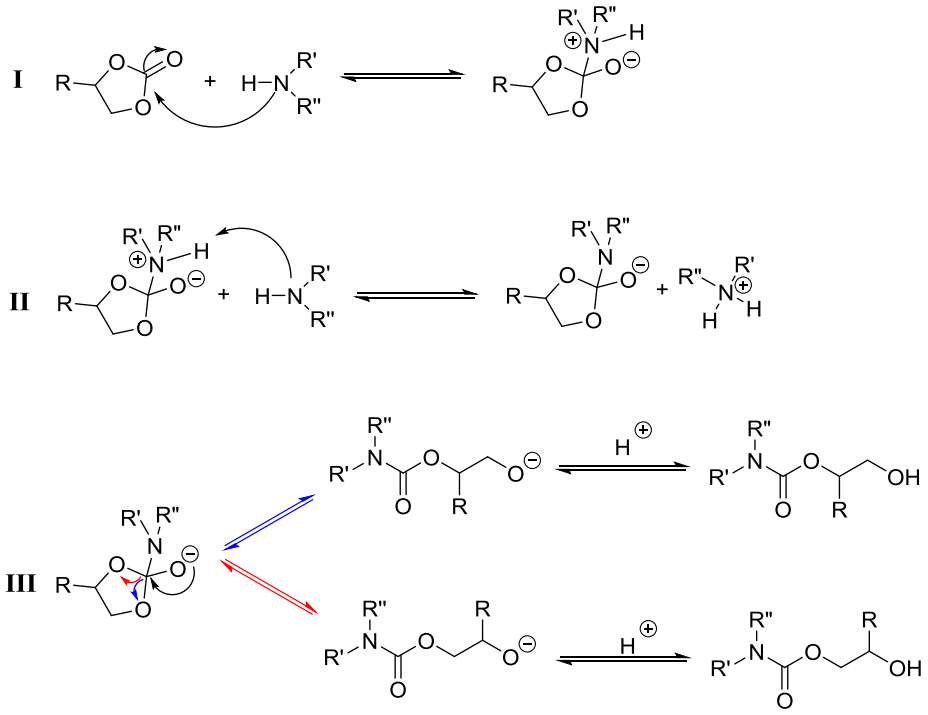
Finally, the last synthesis pathway leading to NIPU is the polyaddition of cyclic carbonates and amines. This reaction seems the best route for the synthesis of NIPUs since it avoids the use of isocyanate and phosgene. Moreover, the cyclic carbonates are not toxic, they are non-moisture sensitive like isocyanates that lead to side products such as urea and CO_2. Therefore their storage does not require any particular caution [2]. Furthermore, the reaction between cyclic carbonate and amine does not release any volatile organic compound which allows the use of this route for coating applications [18]. The resulting polymer is called poly(hydroxyurethane) (PHU) due to the presence of both primary and secondary hydroxyl groups hanging off the main polymer chain. Hence, the structure of PHUs differs from classical PUs. Moreover, the presence of these hydroxyl groups has an influence on the properties of polymers. Indeed, these hydroxyl groups could participate to intra- and inter-molecular hydrogen bonds with carbamate groups, allowing improved chemical resistance to non-polar solvents [1, 2]. This reaction has been studied for 60 years. The first patents were obtained in the 1950's [38]. Very recently, Figovsky *et al.* [7] proposed a comprehensive list of PHU patents showing the huge interest of industrial Companies for these emerging PHUs. However, the authors disagree on the thermal stability of PHUs compared to classical PUs. Some authors claim a higher thermal stability thanks to the extra hydrogen bonds created with hydroxyl groups [1, 2] but other authors report a lower thermal stability due to the influence of hydroxyl groups on the polymer stability [17, 39]. This is also the case for water absorption

properties. Indeed, Nohra *et al.* [40] described in their works a lower water absorption of PHUs compared to classical PUs whereas Tomita *et al.* [41] reported opposite results. Finally, one of the main advantages of PHUs is the possibility to post-functionalize the hydroxyl groups hanging off the chain with chemical and biological functionalities [42].

To summarize, among the numerous pathways leading to NIPUs, the polyaddition of cyclic carbonates with amines seems to be the most interesting route. Moreover, the list of publications, reviews and patents found in literature confirms the large interest of both scientific and industrial communities for this technology. However, this route displays two major drawbacks: the low reactivity of reaction between cyclic carbonates and amines, and a limited degree of advancement of reaction during the room temperature polymerization that leads to low molar mass PHUs. Considerable works were carried out in different research laboratories in Europe (in France, the Universities of Bordeaux, Toulouse, Strasbourg, Rennes; in Belgium, the University of Liège, Mons…; in Germany, the Universities of Freiburg, Aachen, Karlsruhe…), Asia (Kinki University…) and America (University of North Dakota State…) to circumvent the limitations of this reaction. Moreover, the main industrial actors of PU industry such as BASF, DOW and Huntsman [43-59] pay serious attention to this technology to produce PHUs or H-NIPUs. Furthermore, PPG, Solvay, Henkel, Polymate, American Cyanamid, Hoechst, Kansai Paint, Wacker [38, 60-76] also recently filed patent applications in this field. All these international actors (academic and industrial) work in order to increase both the reactivity of cyclic carbonate / amine reaction and the molar masses of PHUs. The rest of this article is focused on the methods to improve this PHU technology and the perspective applications of PHUs.

III.3 The stakes of the reactivity of cyclic carbonates / amines reaction

A 3-step mechanism of the ring opening of cyclic carbonate by amine was proposed by Garipov *et al.* [77] in 2003 (Scheme I-4). The first step of the reaction consists in the nucleophilic attack of the amine on the carbonyl of carbonate which yields a tetrahedral intermediate, and is considered as the limiting step of the reaction. In the second step, a second amine entails the deprotonation of the tetrahedral intermediate. In the third step, the significant electron density initiates the rupture of the carbon-oxygen bond which yield the hydroxyurethane. However, depending on the geometry of intermediate molecules, the opening reaction leads to the production of repeating units with primary or secondary alcohols.



Scheme I-4: Mechanism of cyclic carbonate / amine reaction

Generally, secondary alcohols are favored [78]. Steblyanko *et al.* [79] explained this selectivity since secondary alcohols present a lower energy potential. From the mechanism described in Scheme I-4, several parameters can influence the reactivity, including the nature of solvent, the carbonate structure and the substituents, the structure of amine and the catalysis of reaction.

III.3.1 Influence of solvent on the cyclic carbonate / amine reaction

The solvent (polarity) used for the reaction has an influence on the kinetics of mechanism [77] (Scheme I-4). In aprotic solvents, the first step is the limiting step of reaction. The global order of the cyclic carbonate / amine reaction is 2 [78, 80-85]. However, the first step is more rapid in protic solvents. Indeed, the positive charge on carbonyl carbonate increases due to hydrogen bonds between solvent molecules and oxygen atoms of cyclic carbonate (Figure I-3). Therefore, in this case, the second step which corresponds to the deprotonation of tetrahedral intermediary is the limiting step.

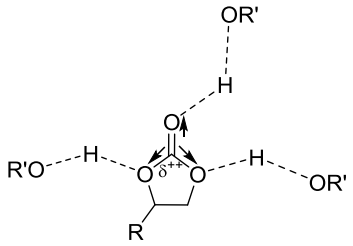


Figure I-3: Increasing of electrophilicity of cyclic carbonate in presence of protic solvent

This phenomenon is interesting to increase the kinetic reaction but most the polyurethanes are formulated in bulk. Therefore, most of researches concerning PHUs are focused on the influence of cyclic carbonate and amine structures on kinetics of reaction and on catalysis.

III.3.2 Influence of the structure of cyclic carbonate

The cyclic carbonate size plays a preponderant role on the cyclic carbonate / amine kinetics of reaction. Actually, syntheses of 5-, 6-, and 7-membered cyclic carbonates were summarized in literature [41, 78, 86, 87]. In 2001, Endo *et al.* [86] compared the reactivity of these carbonates respectively noted CC5, CC6 and CC7. Their works revealed the reactivity order of cyclic carbonate with aliphatic amines according to their structure: CC5<CC6<CC7. The corresponding speed constants (k in $L.mol^{-1}$) are 0.02, 1.19 and 48.5 respectively. Ochia *et al.* [81] observed the same reactivity order between CC5 and CC6. They attributed this difference of reactivity to a stronger ring strain in the case of CC6 compared to CC5. Lamarzelle *et al.* *[83]* showed (Figure I-4-A) the difference of reactivity between CC5 (blue curve) and CC6 (red curve) with the same substituent. He *et al.* [87] synthesized a biscyclic carbonate containing both CC5 and CC6. After reaction with one equivalent of monoamine, the conversion of CC6 was quasi-quantitative which proved, once again, the high reactivity of CC6 compared to CC5. Finally, very recently, Yen *et al.* [88] synthesized the first 8-membered cyclic carbonate (CC8) and compared its reactivity with CC5 and CC6. Their results confirm the previous works: the CC8 is more reactive than CC5 and CC6. Therefore, the reactivity of ring opening reaction increases with the number of members of the cyclic carbonate.

However, the preparation of highly reactive cyclic carbonates (CC6, CC7 and CC8) involves phosgene or its derivatives (ethylchloroformate) which are harmful reactants [78, 80, 86, 87, 89]. Other works presented the preparation of CC6 by carbonation of oxetanes [90, 91] or halohydrins [92] but the reaction yields depend strongly on the structure of precursors and on catalysts.

Despite their low reactivity compared to CC6, CC7 and CC8, the CC5 cyclic carbonates and their synthesis have been extensively studied. Hence, the CC5 can be obtained from linear oligocarbonates [93, 94], diols (with numerous precursors) [41, 78, 95-108], halohydrines [43, 92] olefins [109, 110], substituted propargyl [111], halogenated carbonates [112, 113]. Moreover, the modification of epoxydized compounds with β-butyrolactone [114] can be used to produce CC5. However, the most interesting route for the synthesis of CC5 is the carbonation of epoxides in presence of CO_2 [115-118]. This method presents numerous advantages. Indeed, the use of CO_2 is beneficial regarding both the economic and environmental points of view [119]. CC5 are synthesized with high yields [17, 120, 121] and the CO_2 can be used both as an aprotic solvent and reagent [122]. These particularities explains the growing interest of researchers to produce PHU from CC5 compare to CC6, CC7 or CC8. Finally, CC5 monomers could be synthesized directly from commercial biobased glycerol carbonate which entails great interest in the scientific community [123-125].

Among CC5, cyclic dithiocarbonates noted CC5S, are highly reactive carbonates [126]. Their aminolysis reaction leads to Poly(ThioUrethane) (PTU) with thiol groups hanging off the main chain [127, 128] instead of hydroxyl groups. Indeed, the leaving ability of thiol is higher than alcohol in a nucleophilic substitution reaction [129]. CC5S are directly synthesized by reaction between the corresponding epoxy precursors and carbon disulfide (CS_2) in the presence of catalyst such as neutral metal halides (LiBr) [130-132]. Moreover, CS_2 reacts at room temperature with epoxy precursor, whereas addition of carbon dioxide needs a thermal activation. However, CS_2 is a very toxic substance, is very flammable and suspected of damaging fertility which restricts its use in industry.

To summarize, CC6, CC7, CC8 and CC5S cyclic carbonates are more reactive that C5. However, their syntheses with high yield need harmful precursors such as phosgene, ethylchloroformate or CS_2 that should be banned in a consistent approach to sustainable polyurethanes. Therefore, only CC5 cyclic carbonates can be prepared with safe and economical process (carbonation of epoxide groups or from glycerol). However, if the nucleophilic attack of amine on CC5 is relatively slow, several research groups worked on the influence of substituent groups on the CC5 reactivity.

III.3.3 Influence of substituents on CC5 reactivity

Garipov *et al.* [77] demonstrated that the electron-withdrawing substituents (-I) increase the electophilicity of carbonyl and, therefore, enable nucleophilic attack of the amine.

Conversely, electron-donor substituents (+I) disfavor the opening of cyclic carbonate by the amine. Lamarzelle *et al.* [83] and Tomita *et al.* [80] studied the influence of the substituents on cyclic carbonate reactivity and obtained results in agreement with those of Garipov *et al.* [77] (Figure I-4).

Tomita *et al.* [80] reported the following reactivity order: R=Me<H<Ph<CH_2OH<CF_3 (Figure I-4-B). CF_3 is a promising substituent which allows a quantitative conversion of CC5. Nevertheless, no work has been published on the synthesis of PHUs from fluorinated CC5. These curves show also the partial conversion of cyclic carbonate despite elevated temperature. Such results are reported in numerous publications [78, 86, 133, 134] and are a real drawback of the PHU: low molar masses due to non-quantitative conversion. This point will be discussed later in the part dedicated to molar masses of PHUs.

Lamarzelle *et al.* [83] showed that CC5 with ester substituent exhibits a similar reactivity than CC6 in model reactions with amine and a higher reactivity than CC5 with alkyl or ether substituents (Figure I-4-A). However, amidification side-reaction could occur on ester group, leading to side-products and reducing the molar mass.

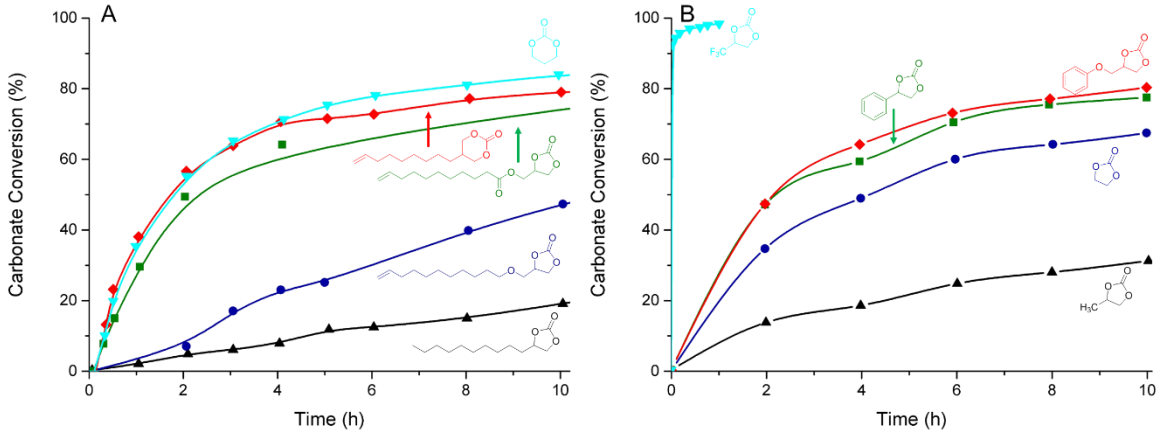


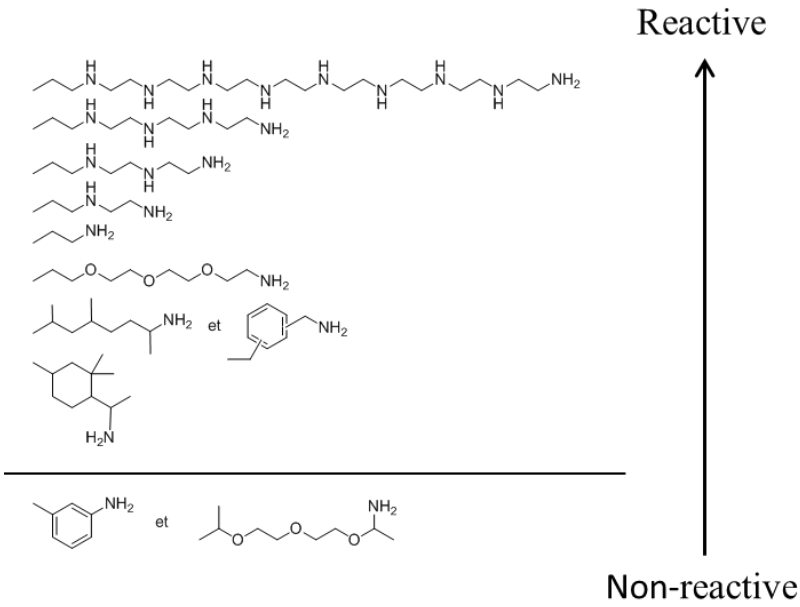
Figure I-4: Time-conversion curves in the reaction with (A) CC5 or CC6 carrier of different substituents (Aliphatic, Ether or Ester) and hexylamine at 50°C, 1 mol.L^{-1} in DMO-d_6 [83] and (B) CC5 carrier of different substituents and hexylamine at 70°C, 1 mol.L^{-1} in DMSO-d_6 [80]

Moreover, He *et al.* [82] modified the position of electron-donor groups on CC5. They showed that more the electron-donor substituent is far from carbonyl group and slower is the reaction. Finally, BASF company filed a patent application on the synthesis of a CC5 with double bonds and its use as reactive diluent for polyepoxide formulations of H-NIPU with epoxides and amino curing agents [51, 55]. The double bond on CC5 is an electron-withdrawing groups

which increases the reactivity of CC5. In order to increase the reactivity of CC5, researches were conducted to graft activating groups on CC5 (CF_3, ester, double bonds). However, the results reported in different works and patents propose the activation with ether group. Indeed, the ether-CC5 is easier to synthesize by direct carbonation of ether-epoxides and doesn't lead to side-reactions. Therefore, the rest of this article will be dedicated to the study of the influence of amine and catalyst on the synthesis of PHUs from ether-CC5.

III.3.4 Influence of the structure of amine

Lots of authors, such as Diakoumakos *et al.* [135], studied the model reaction at room temperature between ether-CC5, and different amines. Their works showed that the structure of amines has a strong influence on reactivity (Scheme I-5). Firstly, aromatic primary amine and secondary amine are non-reactive at room temperature. Concerning primary amines, the main parameters are their nucleophilicity and size. Indeed, the more the amine is nucleophile, the higher is its reactivity [77, 78, 136, 137]. Furthermore, Diakoumakos *et al.* [135] showed that some groups increase significantly the reactivity of the amine: electron-withdrawing groups at α and β position or imino and amino groups (polyamines). These results were confirmed by Webster *et al.* [136]. Tabushi *et al.* [138] showed that primary amines attached to a primary carbon reacts more rapidly than primary amines attached to a secondary carbon. Nohra *et al.* [139] varied the alkyl chain length of aliphatic amine and showed the decrease of amine reactivity with the increase of the alkyl chain length.

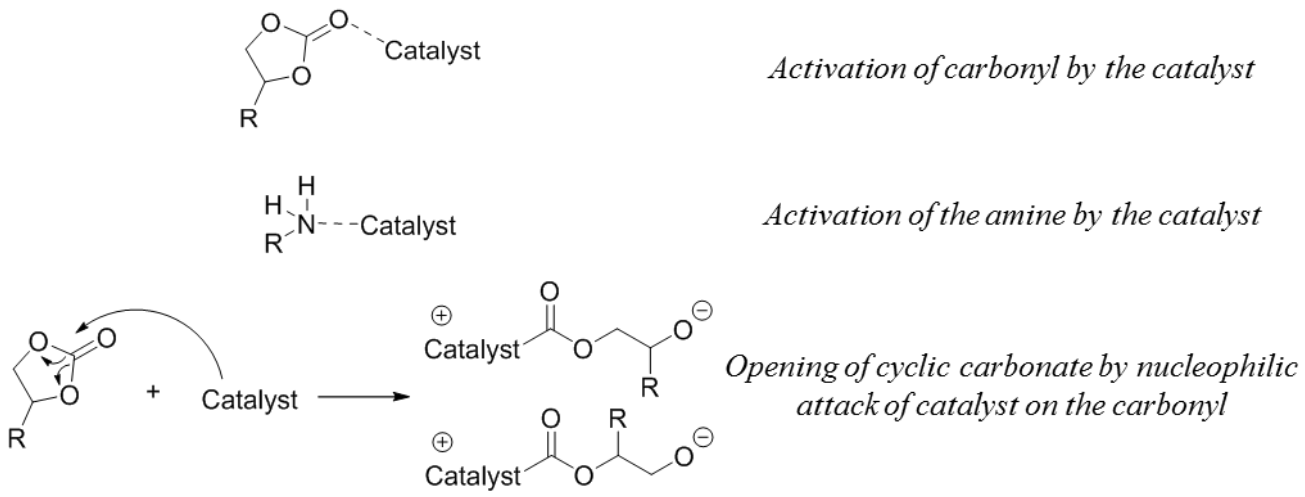


Scheme I-5: Reactivity of various amines toward ether-CC5 at room temperature [135]

Hence, the most reactive amines are primary aliphatic amines attached to a primary carbon with electron-withdrawing groups at α or β position.

III.3.5 Catalyst of cyclic carbonate / amine reaction

Cyclic carbonate could react at room temperature with the most reactive amines. Kinetics studies showed that elevated temperatures activate the reaction [137, 139] and allow the reaction with weakly reactive amines (aromatic or sterically hindered). However, high temperature can lead to side-reaction and formation of side-products, such as ureas [83, 137, 140]. If the reactivity is low at room temperature, it could be increased with the use of catalysts. There are three ways to catalyze the aminolysis of cyclic carbonate (Scheme I-6 the increase of electrophily of carbonyl of cyclic carbonate; the increase of nucleophilicity of amine and the opening of cyclic carbonate with a nucleophilic catalyst.



Scheme I-6: Different catalytic mechanisms of cyclic carbonate aminolysis

Different kinds of catalysts are able to activate the aminolysis reaction by one of these three mechanisms: Lewis acids [141-149], bases [150-152], phosphoric acids [153, 154], carbenes [151, 152, 155-159], phosphines [160], enzymes [161, 162], guanidines [149, 151, 152, 156, 163-165] and thioureas [152, 156, 158, 166-170]. Among all these catalysts, Lambeth *et al.*[164] showed that 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and phenylcyclohexyl thiourea allowed to increase significantly the kinetic of aminolysis reaction. These results were confirmed by Blain *et al.* [171, 172]. Indeed, these studies show that among all catalysts tested, the thiourea and the TBD (Figure I-5) are the most effective catalysts of cyclic carbonate aminolysis.

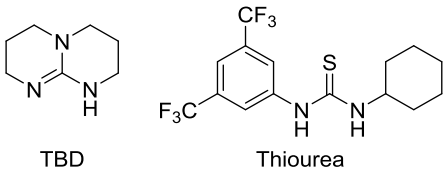


Figure I-5: Structure of TBD and thiourea catalysts

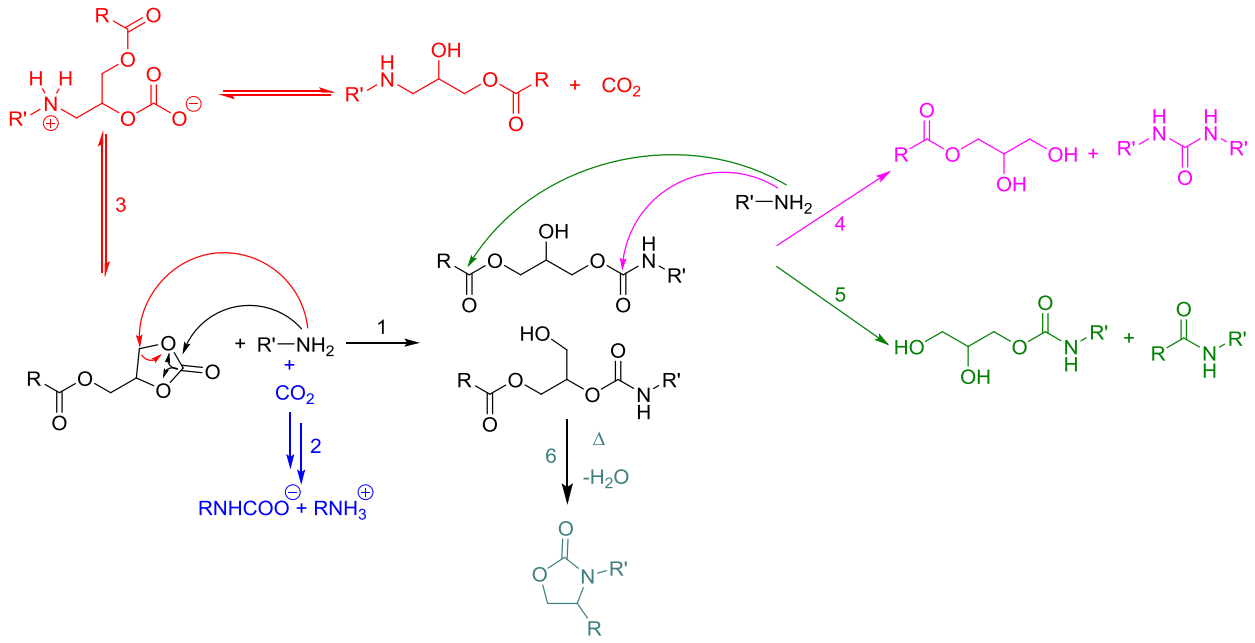
III.4 Influence of reaction parameters on PHU molar masses

Lots of works report the limitations of molar masses of thermoplastic PHUs. In most of the cases, molar masses are determined by size exclusion chromatography ($\overline{M}n$ or $\overline{M}w$). Therefore, in order to compare molar masses, same conditions must be applied (eluent, columns and calibration standards). Most of the authors used DMF with LiBr as eluent and Polystyrene standards, but some of them use other conditions such as THF as eluent and PS standards or DMF with Polymethylmethacrylate standards or DMAC with LiCl and PS standard. Maisonneuve *et al.* [6] summarized the study of thermoplastic PHU molar masses in their review. Among the parameters that influence the molar masses are reported the solvent [173, 174], the structure of monomers [41, 79, 83, 175, 176] and the catalyst [133, 144, 165]. Moreover, the temperature plays also an important role. Indeed, in the reviews of Maisonneuve *et al.*[6] and Rokicki *et al.* [5], no thermoplastic PHU was synthesized with high molar masses at room temperature by polyaddition of CC5 and diamine. . This is probably due to the limitation of advancement of reaction that leads to low molar masses, in agreement with Carothers theory. Indeed, numerous model studies show only a partial reaction, despite a high reactivity at the beginning [78, 80, 86, 133, 134]. Two parameters can explain this phenomenon. The first one is linked to a problem of diffusion of monomers during the polymerization. Indeed, during polyaddition of cyclic carbonates and amines, the viscosity increases with the polymer content. This is an important phenomenon in which are involved the hydrogen bonds created with carbamate groups [177]. Proempers *et al.* [174] reported the polyaddition of non-activated bis-cyclic carbonate (3,4-isopropylidene-D-manitol-1,2:5,6-dicarbonate) with hexamethylene diamine at different temperatures in THF. The molar masse ($\overline{M}w$) of PHUs were 7 $kg.mol^{-1}$ at 25°C and 17 $kg.mol^{-1}$ at 65°C. The increase of the temperature allows to decrease the viscosity, and to increase the mobility, and thus the advancement of reaction and the molar masses.

The second parameter that could explain the limitation of the conversion is a difference of stoichiometry between the monomers consumed by side reactions such as amine carbonation,

in-situ CO_2 production, urea synthesis, amidification reaction or oxazolidinone synthesis. All these side reactions are described in Scheme I-7.

Firstly, the carbonation of amines with CO_2 present in the atmosphere leads to a carbamate anion and an ammonium cation (Scheme I-7-2) [178-180] that reduces the amine concentration. Secondly, Huntsman Company [181] reports the production of *in-situ* CO_2 when the amine attacks on α position of the urethane function, yielding a hydroxyalkylamine with release of CO_2 (Scheme I-7-3). The production of *in-situ* CO_2 can also lead to the carbonation of amine, reducing its availability for aminolysis. Thirdly, the trans-urethanization reaction corresponds to the production of non-reactive urea by nucleophilic attack of amine on carbamate groups (Scheme I-7-4). This reaction was reported in several publications [140, 171, 182, 183] but was observed for temperatures higher than 100°C or in presence of catalyst such as TBD [171]. Furthermore, in the case of aminolysis of ester-CC5, an amidification reaction could occur between amine and ester (Scheme I-7-5). This reaction was reported by Lamarzelle *et al.* [83] and Besse *et al.* [140]. Finally, the production of oxazolidinone was reported by Clements *et al.* [184] and Besse *et al.* [140] (Scheme I-7-6). This side reaction was observed only on glycerol carbonate at 80°C without catalyst.



Scheme I-7: Possible reactions between 5-membered cyclic carbonate and amine: (1) classic aminolysis, (2) carbonation of amine, (3) CO2-in-situ formation, (4) urea formation by trans-urethanization, (5) amidification reaction and (6) oxazolidinone formation by dehydration

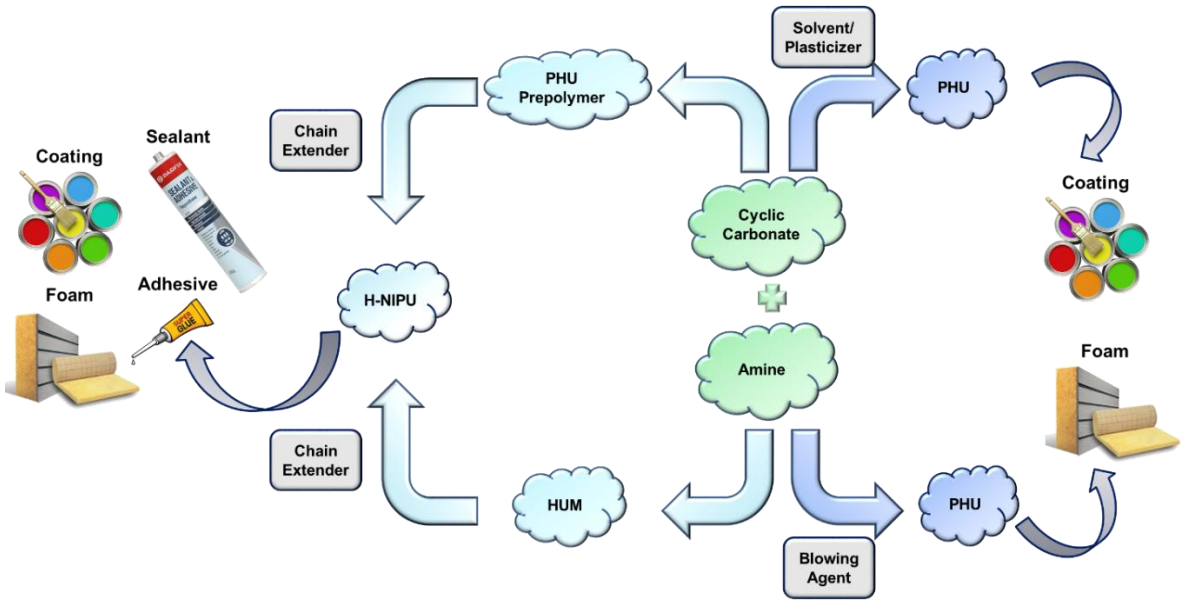
Despite the interest of PHUs, the literature shows the limitations of molar masses obtained by cyclic carbonate aminolysis at room temperature. The next section will focus on solutions that

could help to increase the molar masses of synthesized PHUs, and on the interesting properties that could obtained thereof and guide their applications.

IV. Outlooks for PHUs synthesis and applications

It is obvious from the present article that considerable effort has been made during the last years to develop environmentally friendly processes to produce isocyanate-free polyurethanes, and particularly at room temperature. Hence, the PHU alternative represents a significant opportunity to replace isocyanate in the synthesis of polyurethanes. Despite a lower reactivity, the CC5 cyclic carbonate seems the best compromise in terms of costs, process, stability and hazards to synthesize PHUs. To increase the kinetics of the reaction, it is possible to use activated cyclic carbonate, highly reactive amines and effective catalyst that allow good reactivity of aminolysis reaction. High temperature allows sufficient energy to break inter- and intra-molecular interactions, decrease the viscosity and reach quantitative advancement of reaction and sufficient molar masses. Hence, PHU elastomers [185], adhesives[186, 187], foams[120, 188], coatings [189], hydrogels [190], vitrimers[191] or latexes [192] are of examples of applications. Moreover, Endo *et al.* [193] showed that PHUs have interesting gas barrier properties for food and beverage packaging.

However, in most of the applications, polyurethanes are synthesized at room temperature, therefore, this is a real challenge to propose room temperature routes for the synthesis of PHUs. These ways are reported in the rest of this article and are summarized in Scheme I-8. These ways constitute the outlooks for the synthesis of polyurethane at room temperature for industrial applications in the coming years.

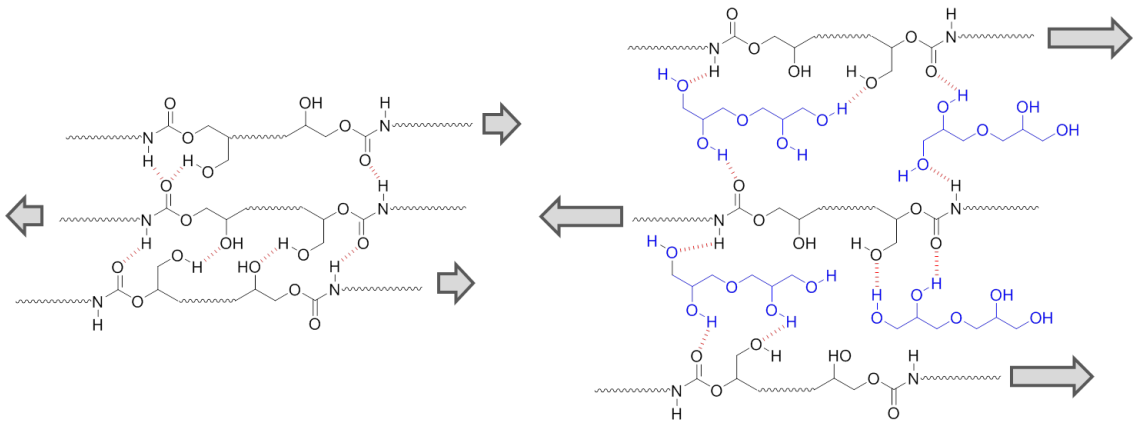


Scheme I-8: Outlooks of synthesis routes for PHUs at room temperature and their industrial applications

IV.1 Access routes to circumvent PHU limitations

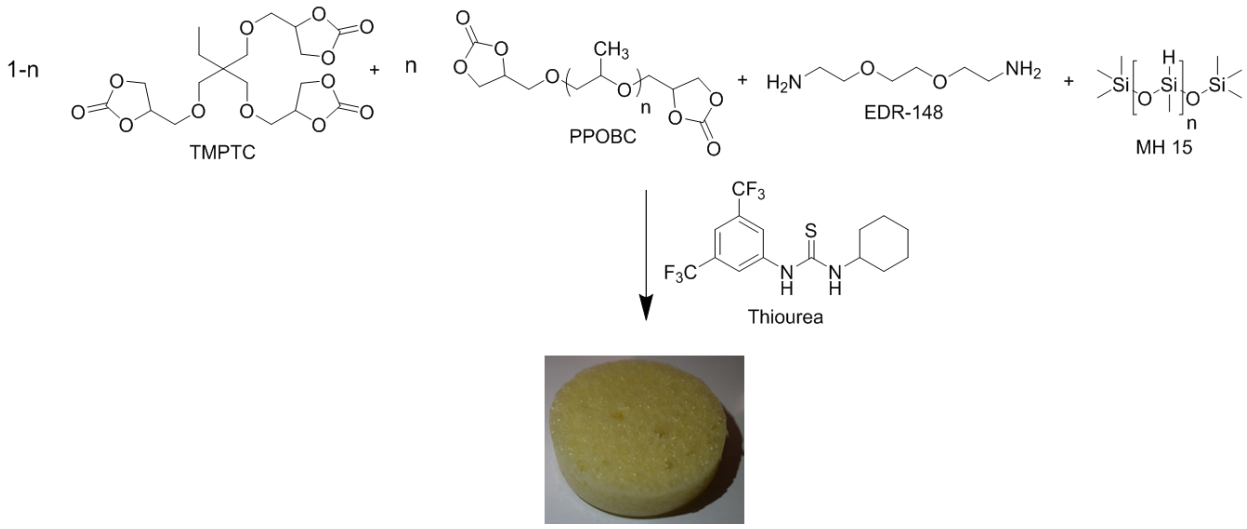
IV.1.1 Synthesis of PHU with additives

The synthesis of PHUs at lower temperature can be performed with additives that will increase chain mobility. Firstly, plasticizers such as alcohols or polyols of low molar masses (methanol, ethanol, di- or tri-glycerol) could create hydrogen bonding with the PHUs and reduce the inter- and intra-molecular hydrogen bonds, and thus increase the mobility of the PHU chains (Scheme I-9). A recent study has highlighted the influence of these plasticizers on the cyclic carbonate aminolysis reaction [194]. Moreover, protic solvents (methanol, ethanol, …) catalyze the cyclic carbonate / amine reaction as mentioned by Garipov *et al.* [77].



Scheme I-9: Diglycerol effect on the PHU chains mobility

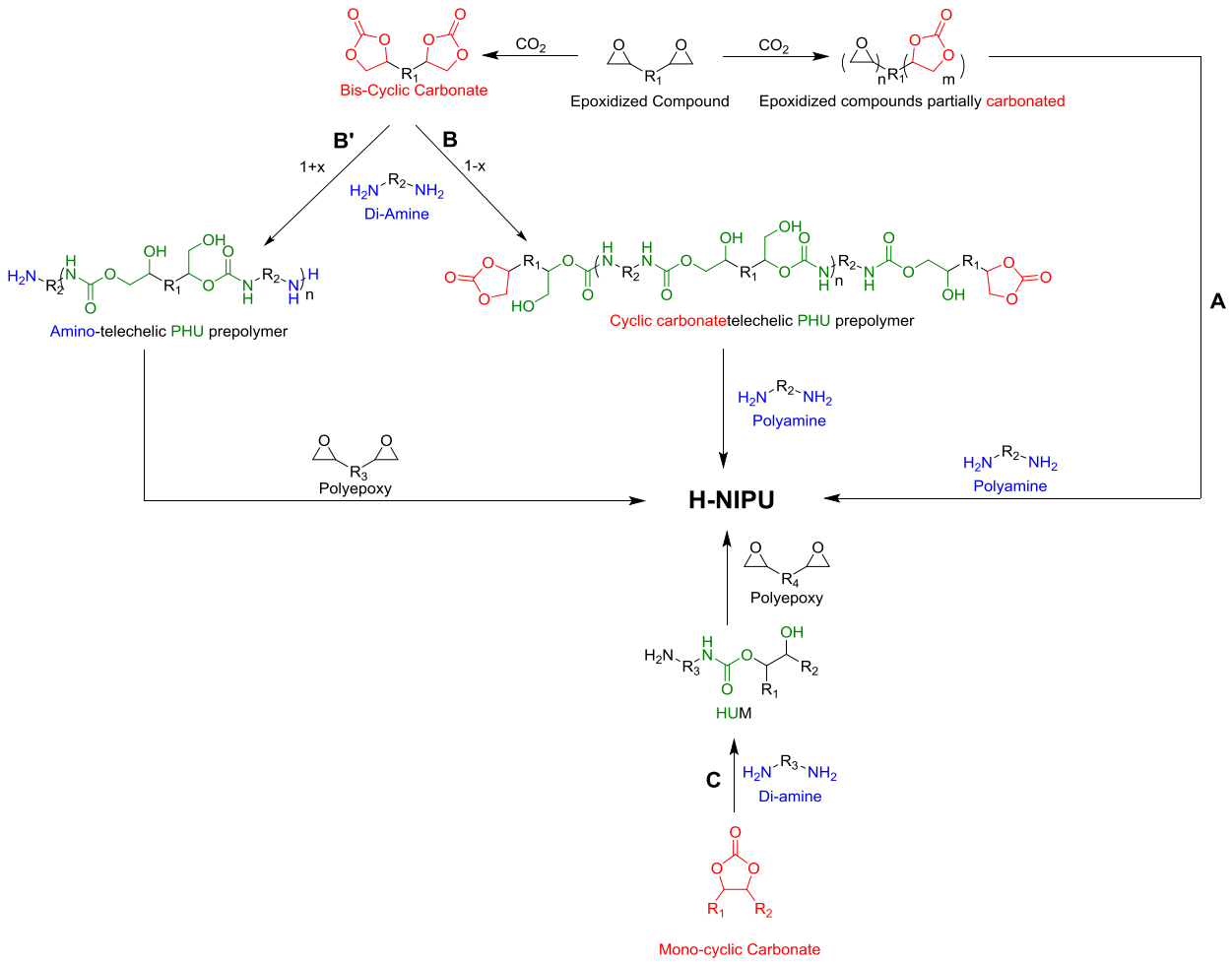
Secondly, the use of a blowing agent that entails chains mobility at microscopic scale allows to increase advancement of reaction at room temperature. This method demonstrated by our team allowed for the first time to obtain quantitative reaction of cyclic carbonate aminolysis at room temperature for the synthesis of porous PHUs [17]. The use of such additives allows to reach a total conversion of monomers and therefore PHU with high molar masses, that will find applications in area such as latexes (synthesis in solvent) or foams (synthesis with blowing agent). In order to cover all applications of polyurethanes, another routes is needed. This new technology consists in the synthesis of Hybrid Non-Isocyanate Polyurethane (H-NIPU).



Scheme I-10: Synthesis of PHU foam by reaction between cyclic carbonates, di-amines, blowing agent (MH 15) and catalyzed with thiourea

IV.1.2 Synthesis of hybrid non-isocyanate polyurethane (H-NIPU)

The most promising method to synthesize PHU at room temperature is based on hybrid non-isocyanates polyurethanes (H-NIPU). Currently, three interesting methods allow the synthesis of H-NIPU: the crosslinking of partially carbonated epoxide monomers (Scheme I-11-A); the crosslinking of PHU prepolymers with carbonate (Scheme I-11-B) or amine (Scheme I-11-B') end groups; or the crosslinking of hydroxyurethane modifiers (HUM) (Scheme I-11-C).



Scheme I-11: Methods to synthesize H-NIPUs from (A) the crosslinking of partially carbonated epoxide monomers; the crosslinking of PHU prepolymers with carbonate (B) or amine (B') end groups; or (C) the crosslinking of hydroxyurethane modifiers (HUM).

IV.1.2.1 Synthesis of H-NIPU by crosslinking of partially carbonated epoxide monomers

This method was widely developed by Figovsky *et al.* [195-197] and consists to the partial carbonation of epoxide monomers. The further reaction with amines allows both aminolysis of cyclic carbonate and ring opening of epoxides that leads to high conversion of monomers. (Scheme I-11). The final interpenetrated network structure is a polyhydroxyurethane cross-linked with polyepoxides. Such H-NIPUs exhibit better mechanical properties than PHUs. The preparation of these H-NIPUs was also studied by Buergel *et al.* [137, 182] and Rokicki *et al.* [198] from oligomerization of bisphenol A diglycidyl ether. A patent claims the methods of making H-NIPU networks for use in composite materials with fiber reinforcement (glass fiber, carbon fiber, basalt fiber, and mixtures thereof), or metal oxide or aluminate reinforcements [199].

IV.1.2.2 Synthesis of H-NIPU by crosslinking of PHU prepolymers

The second route to synthesize H-NIPUs consists to use PHU prepolymers with cyclic carbonate [200] or amine [121] end groups. These PHU prepolymers are subsequently crosslinked with chain extenders able to react with them to give H-NIPUs (Scheme I-11). The main advantage of this route is the ability to obtain materials with a sequence of soft and hard segments as in polyurethanes. In 2015, our team pioneered the synthesis of such H-NIPUs with a sequence of soft and rigid segments. Indeed, in our works [121], H-NIPUs were synthesized from PHU prepolymers with amine end groups, then extended with biobased epoxide monomers such as epoxidized cardanol (NC-514) or epoxidized phloroglucinol (PGTE). Very recently, Carré *et al.* [200] reported biobased thermoplastic PHUs with aliphatic-aromatic architecture from PHU prepolymers with cyclic carbonate end groups. Then, the PHU prepolymers were extended with diamine such as 1,4-butanediamine (BDA) or m-xylene diamine (mXDA). Nevertheless, as showed previously, the cyclic carbonate aminolysis reaction is not quantitative at room temperature and requires a thermal activation or additive to reach total conversion.

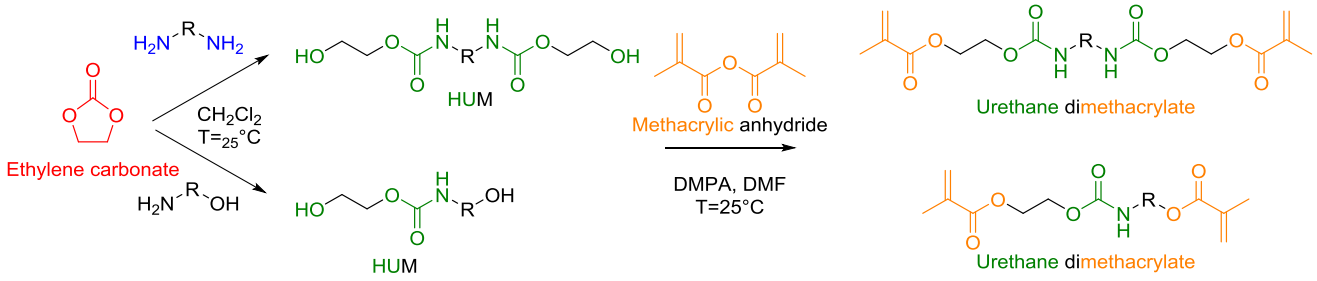
IV.1.2.3 Synthesis of H-NIPU by crosslinking of HUM

Finally, the third pathway to obtain H-NIPU is based on a novel patented concept of multifunctional modifiers: hydroxyurethane modifiers (HUM) (Scheme I-11-C) [72]. The patent application discloses a novel "cold" cure epoxy-amine composition modified with a HUM, which is obtained in a first step, as result of a reaction between a di-amine and a mono-cyclic carbonate. The HUM, having amino-reactive groups, is then added, in a second step, to a polyepoxide. The crosslinking by epoxy / amine reaction leads to an epoxy-amine network with hydroxyurethane groups that confer higher performance compared to classic polyepoxydes resin. In 2014, Polymate Ltd. developed and patented a new H-NIPU polymer with lengthy epoxy-amine chains and pendulous hydroxyurethane units [76]. The patent claimed linear hybrid epoxy-amine hydroxyurethane polymers with controlled numbers of crosslinking nodes. These polymers combine increased flexibility with well-balanced mechanical and physical-chemical properties of conventional epoxy-amine systems. These alternative routes for the synthesis of PHUs at room temperature allow promising applications that are summarized in the following section.

IV.2 Promising applications of PHUs

The synthesis of PHUs with blowing agents could allow to obtain full conversion at room temperature. This is very interesting since foams correspond to 66% of PU applications. Moreover, the synthesis of PHU with plasticizers or solvents covers 20% of the applications of PUs. Furthermore, in 2016, our team showed that the adhesion properties of PHUs were outstandingly higher than the ones of PUs [186]. However, these PHUs were synthesized at high temperature. Hence, H-NIPUs correspond to a real solution to propose PHUs at room temperature and cover the rest of PU applications. In 2012, Birukov *et al.* [73, 201] patented a method of obtaining biobased H-NIPUs at room temperature for adhesive and sealant applications from carbonated-epoxidized unsaturated fatty acid triglycerides (CESBO). From these works, the development of adhesive and sealant H-NIPUs compositions, in particular for bonding metal surfaces, is a promising area for further research. Furthermore, the compositions can apply to the preparation of curable polymer hard and elastic foams [74].

It is also possible to use H-NIPUs with acrylic polymers. Assumption *et al.* [202] synthesized urethane dimethacrylate monomers from hydroxyurethane diol (HUM) and methacrylic anhydride. The HUM were obtained beforehand by the reaction between 3-amino-1-propanol or 2,2-dimethyl-1,3-porpanediamine and ethylene carbonate (Scheme I-12).



Scheme I-12: Synthesis of mono- and bis-urethane methacrylate

Figovsky *et al.* [203] showed that the incorporation of HUM monomers in UV-curable formulation allows improving hardness and wear resistance, while maintaining the other properties of the system. Application is done by spraying, eliminating the negative effects of sunlight during the coating process and uses sunlight during the curing process, which reduces the total polymerization time. Furthermore, the uniqueness of the developed formulation and the possibility of coating concrete without a primer, allows to cover even new areas of application. In order to improve the hydrophobicity, lower the glass transition temperature

and keep thermal stability of the PHUs, the introduction of siloxane in polymers can confer interesting properties. Therefore, H-NIPUs including siloxane functions were synthesized [1, 71]. Figovsky *et al.* [203] developed a highly curable composition at low temperature (10-30°C) from polyepoxide, cyclic-carbonates, amines and acrylate wherein at least one monomer contains alkoxysilanes. The cured composition has excellent adhesion properties on a variety of substrates and resistance properties to weathering, abrasion and solvents.

V. Conclusion

Despite the massive use of PUs in many applications, a great deal of attention is paid to their replacement, particularly to avoid the use of isocyanates that are very toxic substances. Indeed, research efforts were performed both by academic and industrial communities. The most exciting alternative to replace PU could well consist in the cyclic carbonate aminolysis reaction that yields polyhydroxyurethanes PHUs. The most promising routes could be based on the reaction between activated CC5 cyclic carbonate, reactive amines with effective catalysts such as thiourea or TBD. However, this reaction suffers from drawbacks that could limit its development. Particularly, beyond the reactivity, the conversion of reaction at room temperature is limited, which reduces the molar masses and the properties of PHUs. New routes led recently to PHUs or H-NIPUs at room temperature, therefore allowing to cover most of PU applications. Hence, the use of plasticizers (or solvents) allowed quantitative conversion of cyclic carbonate aminolysis at room temperature. Moreover, the use of blowing agent allowed also to open the way to room temperature PHU foams. Furthermore, H-NIPU routes allow to cross-link PHUs with other polymers such as polyepoxide, polyacrylates, polysiloxanes…, to reach quantitative yields and confer improved properties to these hybrid polymers. This technology represents a considerable interest in the coming years in order to target the total replacement of polyurethane in various applications. Polyepoxide-PHU hybrid coatings are currently commercially available under the name Green Polyurethane™ as an isocyanate-free and phosgene-free alternative to conventional coatings and represent a successful application of H-NIPUs. The hydroxyl groups hanging off the main chain of PHU in these hybrid polymers confer unique properties: 30 to 50% higher resistance to chemical degradation, 10 to 30% increased adhesion, 20% increased wear resistance compared to conventional polyurethane without neither solvent nor volatile organic compounds.

VI. References

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Conclusion Générale Chapitre I

Dans ce premier chapitre, les enjeux économiques, la synthèse et la problématique environnementale des matériaux polyuréthanes ont été abordés dans une première partie.

Puis, dans les conditions environnementales actuelles et avec la volonté de développer une chimie plus respectueuse de l'environnement, des utilisateurs et des consommateurs, la substitution des polyuréthanes par des NIPUs a été discutée. Parmi les différentes voies proposées pour leur synthèse, l'aminolyse des carbonates cycliques est retenue par l'ensemble des scientifiques travaillant sur cette thématique de recherche. Cette technique permet de synthétiser des matériaux polyuréthanes sans qu'aucun composé dangereux de type phosgène ou isocyanate n'entre dans la formulation de ces polymères. De plus, la création de groupements hydroxy primaires ou secondaires lors de la réaction d'ouverture des carbonates cycliques par des amines mène à la formation de liaisons hydrogène supplémentaires conférant à ces matériaux des propriétés intéressantes.

Néanmoins, la faible réactivité des précurseurs et les faibles masses molaires des PHUs résultant de cette réaction sont les principaux freins de cette alternative aux PUs. Afin de pallier ces inconvénients, l'amélioration de la cinétique de réaction carbonate cyclique / amine par l'influence du solvant de synthèse, de la structure et des substituants des précurseurs, ainsi que la catalyse de la réaction ont été étudiés dans une troisième partie. Cependant, bien que ces paramètres aient une influence positive sur la réactivité des monomères, les faibles masses molaires des PHUs restent un problème majeur à cette voie de synthèse. Les faibles conversions des précurseurs dues à une limitation de diffusion des espèces par la création d'interactions inter- et intra-chaînes ainsi que les réactions secondaires pouvant avoir lieu entre les précurseurs lors de la polymérisation sont les deux phénomènes pouvant expliquer les faibles masses des matériaux ainsi obtenues.

Bien que cette chimie reste limitée par ces phénomènes, des solutions ont été proposées dans la dernière partie de cette étude. Parmi ces alternatives, l'ajout dans les formulations d'additifs hydroxylés ou d'additifs permettant une micro-agitation au cours de la polymérisation peuvent être envisagés. Une autre solution est la formation de matériaux H-NIPUs utilisant le motif hydroxyuréthane de la réaction carbonate cyclique / amine en l'incorporant à des matrices réactives de type époxy ou autres.

Ces alternatives sont étudiées et décrites dans les trois chapitres suivants de ce mémoire de thèse.

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Introduction Chapitre II

Le chapitre précédent a montré que la réaction d'aminolyse des carbonates cycliques pour la formation de polyuréthanes sans isocyanate a été très étudiée ces dernières années et continue de l'être à l'heure actuelle. Malgré son réel potentiel, il ressort de l'étude bibliographique une double problématique : la faible réactivité des carbonates cycliques lors de leur aminolyse et les faibles conversions obtenues lors de la polymérisation. Ces deux paramètres peuvent être à l'origine des faibles masses molaires des matériaux PHUs linéaires.

Afin de formuler des matériaux polyuréthanes sans isocyanate possédant des propriétés intéressantes, ces problématiques sont investiguées dans ce chapitre à travers une étude approfondie des paramètres de réaction carbonate cyclique / amine à partir de composés modèles monofonctionnels et polyfonctionnels.

L'objectif de ce chapitre est de comprendre les paramètres influençant la réactivité des précurseurs ainsi que les limitations de leur conversion. A partir de ces études, les conditions optimales pour la formulation de nouveaux polymères polyuréthanes sans isocyanate pourront être sélectionnées.

Partie 1 –Réactivité et conversion des carbonates cycliques lors de leur aminolyse à partir de composés modèles

La réaction alcool / isocyanate conduit à des matériaux polyuréthanes dans un temps de réaction relativement court à température ambiante. De plus, cette réaction est très souvent catalysée pour limiter les réactions secondaires des isocyanates avec l'eau mais aussi augmenter la vitesse de réaction. Or, d'après le chapitre bibliographique, la réactivité du système carbonate cyclique / amine est beaucoup plus faible que celle du système alcool / isocyanate. De plus, les faibles conversions des précurseurs conduisent à des matériaux de faibles masses molaires.

Afin d'augmenter la vitesse de réaction et les conversions des précurseurs PHUs, deux alternatives sont envisageables :

- Synthétiser des précurseurs plus réactifs ;
- Catalyser la réaction d'aminolyse des carbonates cycliques.

Cette deuxième alternative a fait l'objet d'une thèse de doctorat menée par Marine Blain et soutenue en mai 2016. Grâce aux études menées au cours de ce doctorat, deux très bons catalyseurs se sont démarqués : la 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourée notée thiourée et le 1,5,7-triaza-bicyclo[4.4.0]dec-5-ene noté TBD (Figure II-1). Néanmoins bien que ces catalyseurs augmentent l'avancement de la réaction, la conversion reste tout de même insuffisante pour obtenir des matériaux de hautes masses molaires.

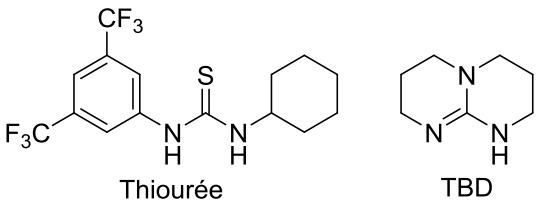

Figure II-1: Structures chimiques des catalyseurs les plus efficaces pour la réaction d'aminolyse des carbonates cycliques

Nos travaux se sont donc portés sur la synthèse et la compréhension de la réactivité des précurseurs carbonates cycliques. Pour cela, un important travail a été mené sur leur structure et la nature de leurs substituants dans le but de sélectionner les meilleurs d'entre-deux. Par la suite, l'étude du blocage de la réaction a également été menée.

Ce travail est présenté sous forme d'une publication scientifique soumise dans *Polymer Chemistry*.

Study of cyclic carbonate aminolysis at room temperature: effect of cyclic carbonates structure and solvent on PHUs synthesis

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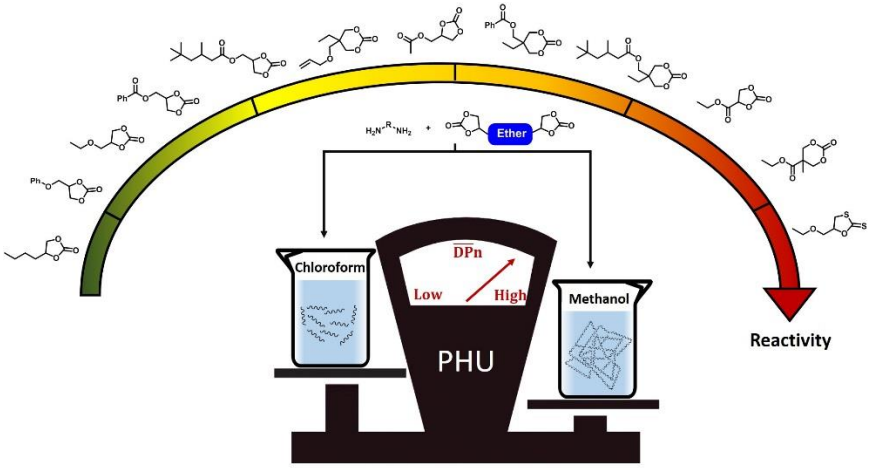
I. Abstract

In recent years, intensive research and development were carried out for the synthesis of isocyanate free polyurethanes from reaction between five-membered cyclic carbonates and amines, called polyhydroxyurethanes (PHU). Despite the interest of safer chemicals, this route presents two major drawbacks: the low reactivity of cyclic carbonates aminolysis and the low molar masses of synthesized PHUs. In order to identify parameters that influence their reactivity, we synthesized various cyclic carbonates with different sizes and structures and studied their aminolysis by ^{1}H NMR. This kinetic study demonstrated a partial conversion of cyclic carbonates which could be responsible of low molar masses of PHU polymers. Investigations showed that these partial conversions is caused mainly by the formation of inter- and intra-chains hydrogen bonds that limit the diffusion of species during the polymerization. A model study displayed that the use of protic solvents improves the reactivity of cyclic carbonates and increases the conversion during their aminolysis. Finally, the effectiveness of protic solvents was evaluated on the synthesis of PHU polymers.



II. Introduction

Since the discovery of the synthesis reaction of polyurethanes (PU) in 1947 by Otto Bayer and coworkers [1], between diisocyanates and polyols, PUs is currently one of the most used polymers in the world for various applications such as rigid and flexible foams, coatings, elastomers, thermosets, adhesives and sealants [2-4]. With an expected global production of 18 Mt in 2016, PUs rank 6th among all polymers based on annual worldwide production [5].

However, the main environmental issue of PUs concerns the use of isocyanate raw materials. Indeed, these substances are harmful for human and environment; therefore, the syntheses of PUs raise increasing health and environmental concerns and become a social issue [6, 7]. For example, methylene-4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), the most widely used isocyanates in PU industry, are classified as CMR (Carcinogenic, Mutagenic and Reprotoxic) [8] and could cause acute poisoning [9].

In recent years, intensive research and development were carried out for the design of isocyanate-free polyurethane (NIPU). Very recent reviews [10-16] reported a comprehensive state-of-the art of these studies and concluded that the reaction between a cyclic carbonates and amines represents one of the most promising alternatives to the conventional synthesis of PUs [10, 17-38]. The resulting polymers are called polyhydroxyurethanes (PHUs). Indeed, the ring opening of cyclic carbonate leads to an additional hydroxyl group (either primary or secondary hydroxyl group) hanging off the main polymer chain close to each urethane function.

However, the main problem of this technology is the low reactivity of cyclic carbonate / amine reaction compared to alcohol / isocyanate system which reacts quit easily at room temperature. In order to overcome this drawback, many studies in the literature have been conducted to design more reactive cyclic carbonates; the influence of several parameters has been studied such as the presence of various substituents [25, 27, 35, 39-47] and the size and structure of the cyclic carbonates with 5-, 6-, 7-, 8-membered (C_5, C_6, C_7 and C_8) or thio-cyclic carbonates (C_s) [34, 38, 45, 48-51]. Nevertheless, the synthesis of C_6, C_7 and C_8 involves phosgene or its derivatives and the synthesis of C_s involves carbon disulfide, which are all harmful reactants.

Although the C_5 are the less reactive cyclic carbonates, they still are the most used for the synthesis of PHUs since they are easily synthesized from corresponding epoxide functions by

simple carbonation [25, 37] or by esterification with bio-based glycerin carbonate [32, 33], without harmful reactants and they are the most stable carbonate for safe storage. In order to increase their reactivity, Tomita *et al.* [35] and Lamarzelle *et al.* [47] varied the nature of substituent on the cyclic carbonate. Catalytic routes were also envisaged to successfully increase their reactivity by Blain *et al.* [52, 53] and Lambeth *et al.* [54] who showed that 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) and cyclohexylphenyl thiourea are the best catalysts for carbonate aminolysis.

However, despite numerous studies dedicated to the enhancement of the reactivity of C_5 / amine reaction, actually, the final conversions do not generally exceed 80%, which corresponds to a degree of polymerization of only 5, based on Carothers' equation. Therefore, in these conditions, only PHUs with low molar masses are obtained. This limitations were always linked in literature to a reduced diffusion of monomers and polymers during the polymerization, due to the creation of the hydrogen bonds between hydroxyl and carbamate group. However, even if this phenomenon was envisaged in literature [47], it has never been demonstrated.

Therefore, the present study is focused on a comprehensive reactivity study of cyclic carbonate and aims to bring to light the phenomenon of hydrogen bonding and propose solutions to overcome it. Hence, we proposed firstly a thorough study of the influence of cyclic carbonate substituents on C_5 and C_6, notably with the synthesis of new structures that never were studied in literature, namely C_5 and C_6 with Ethyl-Ester or trimethylhexanoate substituents. Secondly, a comprehensive kinetic study by NMR of the aminolysis reaction allowed the study and comparison of various cyclic carbonates. Furthermore, a model study allowed to demonstrate that the conversion limitation is due to the diffusion of reactive species during polymerization. From these results, we have investigated a solution to increase the conversion for the synthesis of PHUs.

III. Experimental Section

Materials

2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) noted JEFFAMINE® EDR-148 was obtained from Huntsman. 1,2-epoxyhexane, ethyl glycidyl ether, 1,2-epoxy-3-phenoxypropane, ethyl 2,3-epoxypropionate, 4-(hydroxymethyl)-1,3-dioxolan-2-one (Glycerin Carbonate noted GC), acetic anhydride, benzoyl chloride, 1,1,1-

tris(hydroxymethyl)propane (TMP), *p*-toluene sulfonic acid (APTS), 3,5,5-trimethylhexanoyl chloride, ethyl chloroformate, trimethylolpropane allyl ether (TMPAE), 2,2-bis(hydroxymethyl)propionic acid (Bis-MPA), amberlyst® 15, carbon disulfide (CS_2), 1,4-butanediol diglycidyl ether, 1,3-dibutylurea, N-methylacetamide lithium bromide (LiBr), anhydrous magnesium sulfate ($MgSO_4$), pyridine, trimethylamine (Et_3N), sodium bicarbonate ($NaHCO_3$), calcium oxide (CaO), benzophenone, potassium carbonate (K_2CO_3), hydrochloric acid (HCl 1M), dimethylformamide (DMF), ethyl acetate (EtOAc), dichloromethane (CH_2Cl_2), acetone, methanol, ethanol, tetrahydrofuran (THF) and chloroform were purchased from Sigma Aldrich. Deuterated solvents ($CDCl_3$, Methanol-d_4, DMSO-d_6, DMF-d_7, THF-d_8) were purchased from Euriso-top (Saint-Aubin, France).

Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^1H, ^{13}C, COSY, HSQC, HMBC NMR spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: around 10 mg of product for ^1H, ^{13}C, COSY, HSQC, and HMBC experiment in around 0.5 mL of $CDCl_3$ or DMSO-d_6.

Synthesis of 4-butyl-1,3-dioxolan-2-one: C_5-Butane and a general procedure for epoxy carbonation

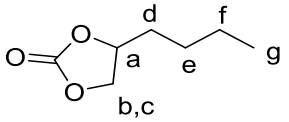


Figure II-2: Structure of C_5-Butane

In a round-bottom flask (100 mL), 1,2-epoxyhexane (5.00 g, 49.92 mmol) and LiBr (0.22 g, 0.25 mmol) were dissolved in DMF (30 mL). The solution was introduced into a reactor and the atmosphere was replaced with CO_2 (P=15 bar). The solution was then allowed to stand at 80°C with continuous stirring for 12 h. DMF was removed by distillation under vacuum (70°C, P= 10 mbar). The crude product was dissolved in ethyl acetate (50 mL) and washed three times with brine. Organic layers were collected, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C_5-Butane was obtained quantitatively as an orange liquid with 91% yield (^1H and ^{13}C NMR spectra, SI - Figure II-1 and SI - Figure II-2).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.61 (*m*, 1H, H_a), 4.43 (*dd*, 1H, *J* = 8.2, 8.2 Hz, H_b), 3.96 (*dd*, 1H, *J* = 8.4, 7.2 Hz, H_c), 1.78 – 1.49 (*m*, 2H, H_d), 1.41 – 1.15 (*m*, 4H, H_{ef}), 0.80 (*t*, 3H, *J* = 7.0 Hz, H_g)

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.0, 77.0, 69.3, 33.2, 26.2, 22.0, 13.5.

Synthesis of 4-ethoxy-1,3-dioxolan-2-one: C_5-Ethyl-Ether

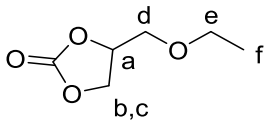


Figure II-3: Structure of C_5-Ethyl-Ether

C_5-Ethyl-Ether was synthesized from ethyl glycidyl ether (5.00 g, 48.96 mmol) and LiBr (0.21 g, 2.45 mmol). The pure product C_5-Ethyl-Ether was obtained quantitatively as an orange liquid with 93% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-3 and SI - Figure II-4).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.76 (*m*, 1H, H_a), 4.44 (*m*, 1H, H_b), 4.29 (*m*, 1H, H_c), 3.73 – 3.36 (*m*, 4H, H_{de}), 1.12 (*t*, 3H, *J* = 7.0 Hz, H_f).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.1, 75.2, 69.2, 67.2, 66.2, 14.8.

Synthesis of 4-phenoxy-1,3-dioxolan-2-one: C_5-Phenyl-Ether

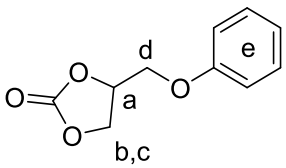


Figure II-4: Structure of C_5-Phenyl-Ether

C_5-Phenyl-Ether was synthesized from 1,2-epoxy-3-phenoxypropane (7.00 g, 46.61 mmol) and LiBr (0.20 g, 2.33 mmol). The pure product C_5-Phenyl-Ether was obtained quantitatively as an orange liquid with 92% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-5 and SI - Figure II-6).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.31 (*m*, 2H, H_e), 7.01 (*m*, 1H, H_e), 6.91 (*m*, 1H, H_e), 5.02 (*m*, 1H, H_a), 4.61 (*dd*, 1H *J* = 8.4, 8.4 Hz, H_b), 4.53 (*dd*, 1H, *J* = 8.5, 5.9 Hz, H_c), 4.18 (*m*, 1H, H_d).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.0, 155.0, 129.9, 122.2, 114.8, 74.4, 67.1, 66.4.

Synthesis of ethyl 2-oxo-1,3-dioxolane-4-carboxylate: C_5-Ethyl-Ester

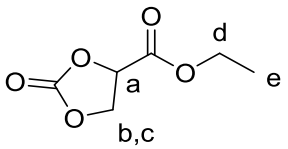


Figure II-5: Structure of C_5-Ethyl-Ester

C_5-Ethyl-Ester was synthesized from ethyl 2,3-epoxypropionate (5.00 g, 43.06 mmol) and LiBr (0.19 g, 2.15 mmol). The pure product C_5-Ethyl-Ester was obtained quantitatively as a brown liquid with 91% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-7 and SI - Figure II-8).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.08 (*dd*, 1H, *J* = 9.0, 5.4 Hz, H_a), 4.67 (*dd*, 1H *J* = 9.0, 9.0 Hz, H_b), 4.49 (*dd*, 1H *J* = 8.9, 5.4 Hz, H_c), 4.28 (*q*, 2H, *J* = 7.2 Hz, H_d), 1.29 (*t*, 4H *J* = 7.1 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.43, 153.98, 72.46, 66.95, 62.90, 13.99.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl acetate: C_5-Acetate

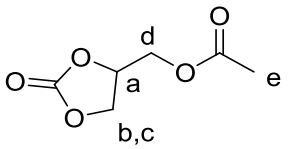


Figure II-6: Structure of C_5-Acetate

In a two-neck bottom-flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3 g, 25.40 mmol) and pyridine (2.21 g, 27.94 mmol) were dissolved in dry dichloromethane (15 mL). Acetic anhydride (2.85 g, 27.94 mmol) dissolved in dichloromethane (15 mL) were added dropwise to the mixture. The reaction was then allowed to stand at room temperature with continuous stirring for 12h. The crude mixture was washed twice with brine, dry over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C_5-Acetate was obtained quantitatively as a transparent liquid with 93% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-9 and SI - Figure II-10).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.87 (*m*, 1H, H_a), 4.48 (*dd*, 1H, *J* = 8.7, 8.7 Hz, H_b), 4.18 (*m*, 3H, H_{cd}), 1.98 (*s*, 3H, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 170.2, 154.5, 73.8, 65.8, 62.8, 20.2.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl benzoate: C_5-Benzoate

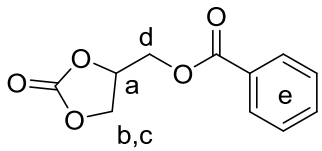


Figure II-7: Structure of C_5-Benzoate

In a two-neck round-bottom flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3.00 g, 25.40 mmol) and triethylamine (3.34 g, 33.02 mmol) were dissolved in dry dichloromethane (15mL). Benzoyl chloride (3.93 g, 27.94 mmol) dissolved in dry dichloromethane (15mL) was added dropwise to the stirring solution under 20 minutes at 0°C under nitrogen. The reaction was allowed to go back to room temperature then stirred during 12h. The ammonium salt was filtered off and the filtrate was washed twice with saturated $NaHCO_3$ aqueous solution then three times with deionized water, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product C_5-Benzoate was obtained quantitatively as a white solid with 93% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-11 andSI - Figure II-12).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (m, 2H, H_e), 7.59 (m, 1H, H_e), 7.45 (m, 2H, H_e), 5.06 (m, 1H, H_a), 4.72 – 4.46 (m, 3H, H_{bd}), 4.42 (dd, 1H, J = 8.8, 5.7 Hz, H_c).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 154.6, 133.8, 129.8, 128.8, 128.7, 74.0, 66.2, 63.8.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methanol: Protected TMP

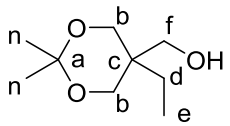


Figure II-8: Structure of Protected TMP

1,1,1-Tris(hydroxymethyl)propane (TMP) (100.00 g, 745.32 mmol) were dissolved in 700 mL of acetone in a round bottom-flask equipped with a condenser. When the mixture became homogeneous, paratoluene sulfonic acid (1.42 g, 7.45 mmol), was added. The medium was stirred at room temperature for 16 h. Potassium carbonate (1.03 g, 7.45 mmol) was subsequently added and left stirring at room temperature for 1h. After evaporation of acetone, the product was dissolved with 1000 mL of ethyl acetate and washed twice with deionized water. Organic layers were collected, dried over anhydrous magnesium sulfate and evaporated

under vacuum. The pure product Protected TMP was obtained quantitatively as colorless liquid with 98% of yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-13 andSI - Figure II-14).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.68 – 3.41 (*m*, 6H, H_{bf}), 3.22 (*s*, 1H, OH), 1.32 (*m*, 6H, H_g), 1.22 (*q*, 2H, *J* = 7.6 Hz, H_d), 0.75 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 98.1, 65.0, 62.1, 36.9, 27.1, 23.6, 20.3, 7.0.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate: Esterified Protected TMP 1 and a general procedure for esterified TMP-Protected

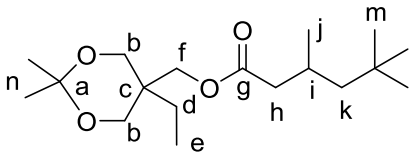


Figure II-9: Structure of Esterified Protected TMP 1

In a three-neck round-bottom flask (250 mL), Protected TMP (10.00 g, 57.39 mmol) and triethylamine (6.39 g, 63.13 mmol) were dissolved in 90 mL of dry dichloromethane. The mixture was immersed in an ice bath under nitrogen atmosphere. 3,5,5-Trimethylhexanoyl chloride (11.15 g, 63.13 mmol) was added dropwise to the solution, with continuous stirring for 20 minutes. The reaction was then placed at room temperature for 12 hours. At the end of reaction, the solution was filtered and the filtrate was washed twice with saturated $NaHCO_3$ aqueous solution then three times with deionized water, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product Esterified Protected TMP 1 was obtained quantitatively as colorless liquid with 71% of yield (^{1}H and 13C spectra, SI - Figure II-15 and SI - Figure II-16).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.10 (*m*, 2H, H_f), 3.57 (*m*, 4H, H_b), 2.25 (*m*, 1H, H_h), 2.06 (*dd*, 1H, *J* = 14.4, 8.2 Hz, H_h), 1.96 (*m*, 1H, H_i), 1.32 (*d*, 6H, *J* = 12.0 Hz, H_n), 1.25 (*m*, 2H, H_d), 1.10 (*m*, 2H, H_k), 0.90 (*d*, 3H, *J* = 6.6 Hz, H_j), 0.82 (*s*, 9H, H_m), 0.75 (*t*, 2H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.87, 98.08, 64.97, 63.62, 50.43, 43.90, 35.70, 30.93, 29.85, 27.00, 26.45, 23.89, 22.60, 20.76, 6.89.

Synthesis of (5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl)methyl benzoate: Esterified Protected TMP 2

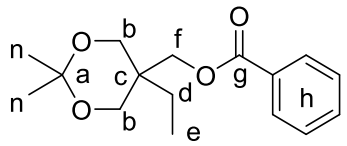


Figure II-10: Structure of Esterified Protected TMP 2

Esterified Protected TMP 2 was synthesized from Protected TMP (15.00 g, 86.09 mmol) and benzoyl chloride (18.15 g, 129.13 mmol). The crude Esterified Protected TMP 2 was obtained as yellow liquid with 98% yield. Remaining benzoyl chloride is visible on the ^{1}H and ^{13}C NMR spectra (^{1}H and ^{13}C NMR spectra, SI - Figure II-17and SI - Figure II-18).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (*m*, 2H, H_h), 7.51 (*m*, 1H, H_h), 7.40 (*m*, 2H, H_h), 4.44 (*s*, 2H, H_f), 3.73 (*m*, 4H, H_b), 1.52 – 1.27 (*m*, 8H, H_{dn}), 0.86 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.4, 133.2, 129.8, 128.4, 98.3, 65.2, 64.5, 36.2, 26.9, 24.2, 20.6, 7.1.

Synthesis of 2,2-bis(hydroxymethyl)butyl 3,5,5-trimethylhexanoate: Esterified TMP 1 and a general procedure for deproctection of Esterified Protected TMP

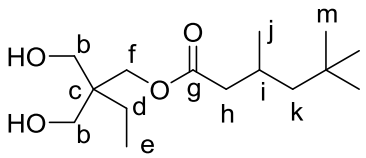


Figure II-11: Structure of Esterified TMP 1

In a round-bottom flask (100 mL) equipped with a refrigerating apparatus, Esterified Protected TMP 1 (8 g, 35.04 mmol), methanol (20 mL) and aqueous hydrochloric acid (1M) (4 mL) were introduced. The reaction proceeds at 40°C for 24h with continuous stirring. The methanol was removed under vacuum and the crude product was dissolved in ethyl acetate (100 mL) and washed with deionized water until pH=7. Organic layers were collected, dried over magnesium sulfate, and evaporated under vacuum. The pure product Esterified TMP 1 was obtained quantitatively as colorless liquid with 74% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-19 andSI - Figure II-20).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.06 (*m*, 2H, H_f), 3.50 (*s*, 4H, H_b), 2.30 (*dd*, 1H, *J* = 14.6, 5.7 Hz, H_h), 2.11 (*dd*, 1H, *J* = 14.6, 8.3 Hz, H_h), 1.98 (*m*, 1H, H_i), 1.27 (*q*, 2H, *J* = 7.6 Hz, H_d), 1.13 (*m*, 2H, H_k), 1.00 – 0.71 (*m*, 15H, H_{ejm}).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 174.1, 65.1, 63.9, 50.5, 43.9, 42.7, 31.0, 29.9, 29.9, 27.0, 22.6, 22.3, 7.3.

Synthesis of 2,2-bis(hydroxymethyl)butyl benzoate: Esterified TMP 2

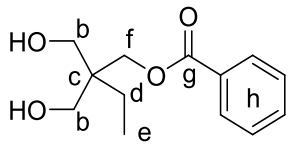


Figure II-12: Structure of Esterified of TMP 2

Esterified TMP 2 was synthesized from Esterified Protected TMP 2 (15.00 g, 54.08 mmol), 7.5 mL of HCl 1M and 37.5 mL of methanol. The pure product Esterified Protected TMP 2 was obtained quantitatively as yellow liquid with 88% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-21 and SI - Figure II-22).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.99 (*dd*, 2H *J* = 8.2, 1.1 Hz, H_h), 7.53 (*m*, 1H, H_h), 7.39 (*m*, 2H, H_h), 4.35 (*s*, 2H, H_f), 4.12 (*brs*, 2H, OH), 3.34 (*m*, 4H, H_b), 1.40 (*q*, 2H, *J* = 7.6 Hz, H_d), 0.89 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 167.2, 1332, 129.8, 129.6, 128.4, 65.0, 64.5, 43.0, 22.5, 7.4.

Synthesis of 5-((allyloxy)methyl)-5-ethyl-1,3-dioxan-2-one: C_6-Allyl-Ether and general procedure for carbonate ring formation

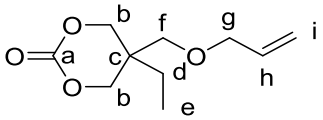


Figure II-13: Structure of C_6-Allyl-Ether

Ethyl chloroformate (6.22 g, 57.39 mmol) was added dropwise to a solution of trimethylolpropane allyl ether (TMPAE) (5.00 g, 28.70 mmol) and triethylamine (6.39 g, 63.13 mmol) in 200 mL of dried THF at 0°C over a period of 30 min. The reaction mixture was then stirred at room temperature for 2 h. The precipitated triethylamine hydrochloride was filtrated off, and the filtrate was concentrated under vacuum. Then, the crude was diluted

with ethyl acetate (300 mL) and washed two times with aqueous hydrochloric acid (1M) and two times with deionized water. Organic phase was dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography (eluent 20/80 ethyl acetate/cyclohexane). The pure product C_6-Allyl-Ether was obtained quantitatively as colorless liquid with 74% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-23 and SI - Figure II-24).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.76 (*m*, 1H, H_h), 5.13 (*m*, 2H, H_i), 4.14 (*m*, 4H, H_b), 3.88 (*m*, 2H, H_g), 3.31 (*s*, 2H, H_f), 1.44 (*q*, 2H, *J* = 7.6 Hz, H_d), 0.82 (*t*, 3H, *J* = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 148.4, 133.9, 117.1, 72.6, 72.1, 68.0, 35.2, 23.0, 7.1.

Synthesis of (5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl 3,5,5-trimethylhexanoate: C_6-Trimethylhexanoate

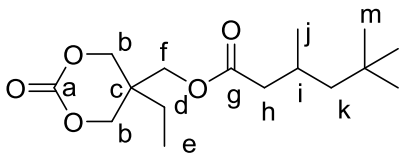


Figure II-14: Structure of C_6-Trimethylhexanoate

C_6-Trimethylhexanoate was synthesized from Esterified TMP 1 (5.00 g, 18.22 mmol), triethylamine (4.05 g, 40.08 mmol) and ethyl chloroformate (3.95 g, 36.44 mmol). The pure product C_6-Trimethylhexanoate was obtained quantitatively as yellow liquid with 76% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-25 and SI - Figure II-26).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.19 (*m*, 4H, H_b), 4.04 (*m*, 2H, H_f), 2.28 (*dd*, 1H, *J* = 14.8, 5.9 Hz, H_h), 2.10 (*dd*, 1H, *J* = 14.8, 8.2 Hz, H_h), 1.95 (*m*, 1H, H_i), 1.47 (*q*, 2H, *J* = 7.6 Hz, H_d), 1.11 (*m*, 2H, H_k), 0.95 – 0.74 (*m*, 15H, H_{ejm}).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 172.4, 147.9, 72.4, 72.39, 62.3, 50.3, 43.4, 34.4, 30.9, 29.8, 26.8, 23.2, 22.5, 7.1.

Synthesis of (5-ethyl-2-oxo-1,3-dioxan-5-yl)methyl benzoate: C_6-Benzoate

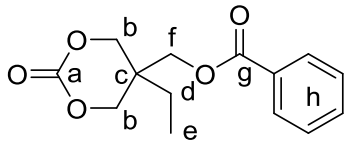


Figure II-15: Structure of C_6-Benzoate

C_6-Benzoate was synthesized from Esterified TMP 2 (5.00 g, 20.98 mmol), triethylamine (4.67 g, 46.16 mmol) and ethyl chloroformate (4.55 g, 41.97 mmol). The pure product C_6-Benzoate was obtained quantitatively as yellowish solid after recrystallization in cyclohexane with 33% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-27 and SI - Figure II-28).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.01 (*m*, 2H, H_h), 7.59 (*m*, 1H, H_h), 7.47 (*m*, 2H, H_h), 4.37 (*s*, 2H, H_f), 4.35 (*m*, 4H, H_b), 1.64 (*q*, 2H, J = 7.6 Hz, H_d), 1.00 (*t*, 3H, J = 7.6 Hz, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.0, 148.1, 133.6, 129.7, 129.2, 128.7, 72.6, 63.2, 35.1, 23.7, 7.5.

Synthesis of ethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate:C_6-Ethyl-Ester

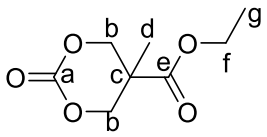


Figure II-16: Structure of C_6-Ethyl-Ester

2,2-bis(hydroxymethyl)propionic acid (Bis-MPA) (10.00 g, 74.55 mmol) was added at solution of ethanol (70 mL) and Amberlyst-15 (3 g). After 12 hours of reaction at 80°C, the solution was filtered and the filtrate was evaporated. Dichloromethane (200 mL) was added to the resulting viscous liquid and the solution was washed 3 times with brine to remove the unreacted reagents and byproducts. The solution was then dried over anhydrous magnesium sulfate and concentrated under vacuum The crude was added at solution of dried THF (80 mL) and trimethylamine (2.2 equivalent) at 0°C. Ethyl chloroformate (2.0 equivalents) dissolved in dried THF was added dropwise. After 4 hours of reaction at 0°C, the mixture was filtered and the filtrate was concentrated under reduced pressure. Then, the crude was diluted with ethyl acetate and washed two times with aqueous hydrochloric acid (1M) and two times with deionized water. Organic phase was dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash column chromatography (eluent 20/80 ethyl acetate/cyclohexane). The pure product C_6-Ethyl-Ester was obtained

quantitatively as colorless liquid with 69% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-29 and SI - Figure II-30).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.66-4.19 (*m*, 4H, H_b), 4.21 (*q*, 2H, H_f), 2.28 (*dd*, 1H, *J* = 14.8, 5.9 Hz, H_h), 2.10 (*dd*, 1H, *J* = 14.8, 8.2 Hz, H_h), 1.95 (*m*, 1H, H_i), 1.27 (s, 3H, H_d), 1.25 (*t*, 3H, H_g).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 171.3, 147.8, 73.2, 62.4, 40.2, 17.6, 14.1.

Synthesis of 5-(ethoxymethyl)-1,3-oxathiolane-2-thione: C_s-Ethyl-Ether

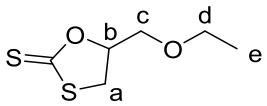


Figure II-17: Structure of C_s-Ethyl-Ether

In a two-neck round-bottom flask (50 mL), ethyl glycidyl ether (5.00 g, 48.96 mmol) and carbon disulfide (4.1 g, 53.85 mmol) were introduced at 0°C with a catalytic amount of LiBr (0.21 g, 2.45 mmol) in THF (9 mL). After 20 min, the reaction was allowed to proceed at room temperature for 24 h. The mixture was then poured in ethyl acetate and washed three times with deionized water. The organic phase was dried over magnesium sulfate prior to the evaporation of the solvent under vacuum to obtain the pure product as yellowish liquid with 85% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-31 and SI - Figure II-32).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.14 (*m*, 1H, H_b), 3.77 – 3.31 (*m*, 6H, H_{acd}), 1.08 (*t*, 3H, *J* = 8.4, H_e).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 212.0, 89.4, 68.7, 66.8, 35.6, 14.6.

Synthesis of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one): Bis-C_5-Ether

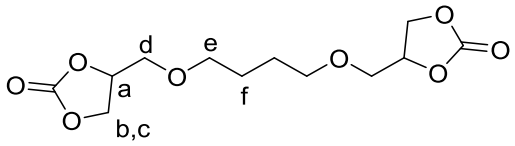


Figure II-18: Structure of Bis-C_5-Ether

Bis-C_5-Ether was synthesized according to the general procedure for epoxy carbonation, 1,4-butanediol diglycidyl ether (20.00 g, 98.89 mmol) and LiBr (0.43 g, 4.94 mmol). The pure

product Bis-C_5-Ether was obtained quantitatively as a white waxy solid with 95% yield (^{1}H and ^{13}C NMR spectra, SI - Figure II-33 and SI - Figure II-34).

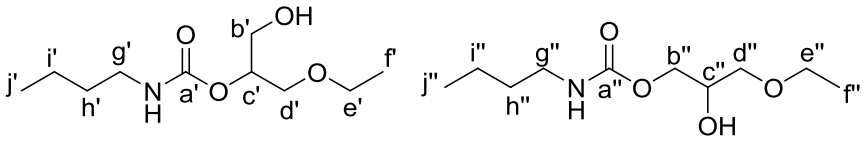
^{1}H NMR (DMSO-d_6, 400 MHz) δ (ppm) = 4.91 (*m*, 2H, H_a), 4.52(*t*, 2H, *J*=8.4 Hz, H_b), 4.25 (*dd,* 2H, *J*=8.3 Hz, *J*=5.9 Hz, H_c), 3.59 (*m*, 4H, H_d), 3.46 (*m*, 4H, H_e), 1.54 (*m*, 4H, H_f)

^{13}C NMR (DMSO-d_6, 100 MHz): δ (ppm) = 155.0, 75.5, 70.5, 69.5, 66.11, 25.6.

Standard procedure for kinetic experiments

The kinetic studies were performed directly in a NMR tube at 1 mol.L^{-1} in deuterated solvent at 25°C and with a stoichiometric ratio between cyclic carbonate and EDR-148. EDR-148 were previously dried under CaO, distilled and stocked under inert gas. Around 0.5 mL of dried deuterated solvent and around 10 mg of benzophenone were added at mixture as internal reference and the latter was homogenized. EDR-148 was then added just before putting the tube in NMR spectrometer. The reaction was monitored by acquisition of ^{1}H NMR spectra every 15 minutes during 6 hours and by follow of disappearance of the cyclic carbonate protons. In order to keep agitation of NMR tube in spectrometer during kinetic experiment, a succession of ^{1}H NMR spectra of 13 and 2 minutes of acquisition were recorded. Nevertheless, only the ^{1}H NMR of 2 minutes of acquisition were used to draw the kinetics curves.

Synthesis of hydroxyurethane compound models



Hydroxyurethane 1 Hydroxyurethane 2

Figure II-19: Structure of hydroxyurethane compound models

In a round-bottom flask (10 mL), C_5-Ethyl-Ether (0.300 g, 2.00 mmol, 1.00 eq), benzophenone (0.010 g) and butylamine (0.146 g, 2.00 mmol, 1.00 eq) were stirred in 2 mL of chloroform or methanol during 24 hours at room temperature (25°C) (^{1}H and ^{13}C NMR spectra, Figure II-32 and Figure II-33).

^{1}H NMR (400 MHz, *CDCl$_3$*) δ (ppm) = 4.73 (*m*, 1H, $H_{b'}$), 4-10 – 3.90 (*m*, 2H, $H_{b''}$), 3.84 (*m*, 1H, $H_{c''}$), 3.62 (*m*, 2H, $H_{b''}$), 3.57 – 3.22 (*m*, 8H, $H_{e',e'',d',d''}$), 3.02 (td, 4H, $H_{g',g''}$), 1.43 – 1.14 (*m,* 8H, $H_{h', h'', i'}$), 1.06 (*m*, 6H, $H_{f', f''}$), 0.78 (*t*, 6H, $H_{j', j''}$).

^{13}C NMR (100 MHz, *CDCl$_3$*) δ (ppm) = 156.4, 156.0, 73.3, 70.9, 68.9, 68.5, 66.3, 65.7, 61.6, 40.2, 31.4, 19.3, 14.5, 13.3.

Titration of the carbonate equivalent weight by ^{1}H NMR

The carbonate equivalent weight (CEW) is the amount of substance (in grams) containing one gram-equivalent of carbonate functions. It was determined by ^{1}H NMR spectroscopy. First, a solution of DMSO-*d$_6$* containing toluene as internal standard was prepared (c = 52.9 mmol.L^{-1}). Then a known amount of Bis-C$_5$-Ether (around 90 mg) and the toluene containing deuterated solution (around 800 mg) were weighed and transferred into an NMR tube. Three characteristic cyclic carbonate peaks at 4.94 ppm, 4.53 ppm and 4.26 ppm were chosen. The CEW is calculated with Equation II-1 by comparing the integral ($\int H_{toluene}$) of the CH_3 protons of toluene with the integral ($\int H_{cyclic\ carbonate}$) of the three cyclic carbonate protons.

Equation II-1
$$CEW = \left(\frac{\int H_{toluene}}{\int H_{cyclic\ carbonate}}\right)\left(\frac{m_{cyclic\ carbonate}}{m_{toluene}}\right)(M_{toluene})$$

General procedure to synthesize poly(hydroxyurethane)s

Step growth polymerization of Bis-C$_5$-Ether (CEW=149 g.eq^{-1}, 1.500 g, 1.00 eq) was performed with EDR-148 (AEW=74 g.eq^{-1}, 0.744 g, 1.00 eq.) with a molar ratio of 1:1 in 5 mL of chloroform or in mixture 3.3/1.6 mL of chloroform/methanol at room temperature. The concentration of 1 mol.L^{-1} in Bis-C$_5$-Ether was respected. No catalysts were added for the polymerization reactions. Conversions (p), degree of polymerization ($\overline{DP}n$) and molar masses ($\overline{M}n$) were determined by ^{1}H NMR spectroscopy after 1, 2, 3, 4 ,5, 17, 24, 31, 48, 72 and 144 h of reaction.

IV. Results and Discussion

This article is divided in two parts. The first part is dedicated to the kinetics study of the aminolysis reaction of cyclic carbonate models with various structures and substituents. This preliminary study aims to identify the best precursors and conditions in order to synthesize, in the second part of this article, poly(hydroxyurethane)s (PHU) at room temperature with improved conversion.

IV.1 Kinetic study of aminolysis reaction of cyclic carbonates

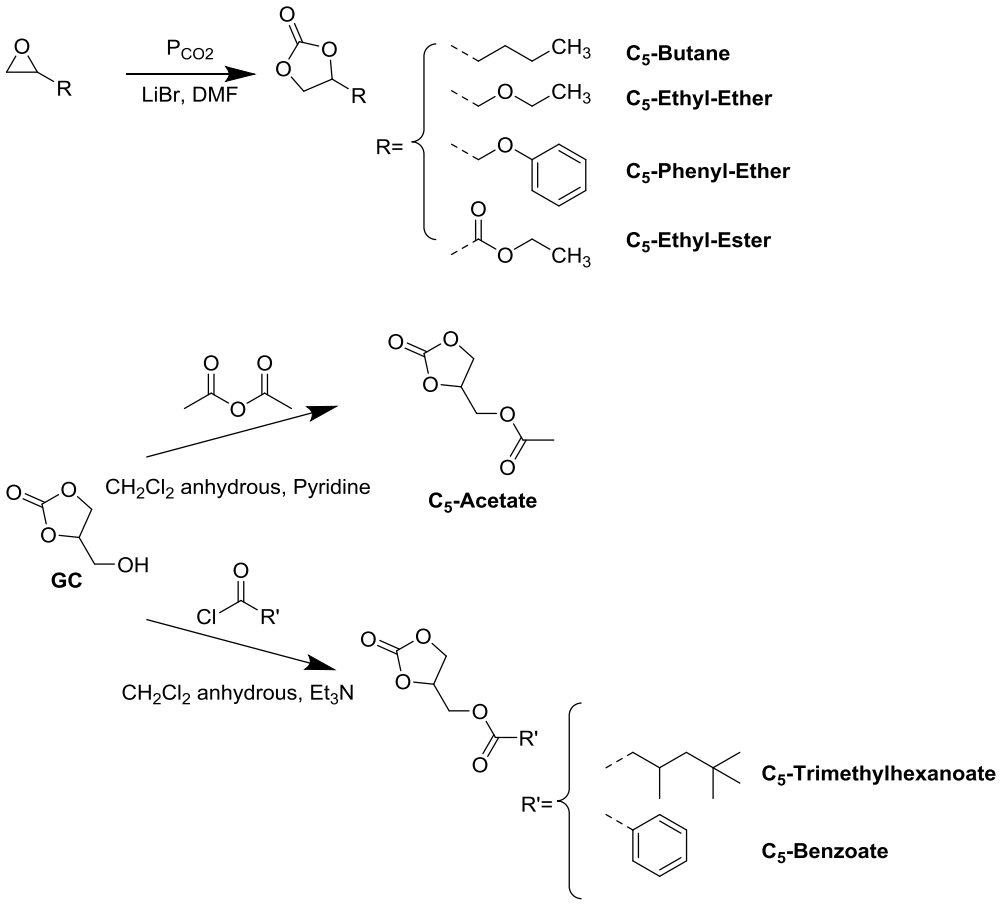
Currently, numerous works studied the parameters that influence the reactivity of the aminolysis of cyclic, such as the structure of cyclic carbonates [34, 38, 48, 49] and amines [55, 56], the nature of substituents attached to the carbonate [35, 47, 57], the catalysis of reaction [52, 53] and the solvent [57]. However, reported works were sometimes much debated, therefore our work intend to propose a wider reactivity study on various C_5 and C_6, in order to determine both the influence of substituents attached to cyclic carbonate and to compare the reactivity of C_5 and C_6 with exactly same substituents. Moreover, we completed this study with new structures with promising reactivity such as C_5 and C_6 with Ethyl-Ester or trimethylhexanoate substituents that never were studied in literature. Hence, a range of cyclic carbonate models with different structure, 5-, 6-membered cyclic carbonate (C_5, C_6) or 5-membered-dithio-cyclic carbonate (C_s), was synthesized.

IV.1.1 Synthesis of cyclic carbonate models

IV.1.1.1 Synthesis of five-membered cyclic carbonate models

Seven 5-membered cyclic carbonates (C_5-Butane, C_5-Ethyl-Ether, C_5-Phenyl-Ether, C_5-Ethyl-Ester, C_5-Acetate, C_5-Trimethylhexanoate and C_5-Benzoate), were synthesized according to two pathways depending on type of substituent attached to cyclic carbonate (Scheme II-1). The first pathway, described by Brocas *et al.* [58], consists to the carbonation of 1,2-epoxyhexane, ethyl glycidyl ether, 1,2-epoxyphenoxypropane or ethyl 2,3-epoxypropionate in presence of LiBr and DMF around 15 bars of CO_2 to obtain respectively C_5-Butane, C_5-Ethyl-Ether, C_5-Phenyl-Ether and C_5-Ethyl-Ester. After 12 hours of reaction at 80°C, the ^{1}H NMR spectra of carbonated monomers (SI - Figure II-35) show a total disappearance of all peaks corresponding to protons a, b and c of epoxide ring, and the appearance of peaks corresponding to carbonate protons a, b and c. The pure products are obtained with quantitative yield after distillation and extraction of DMF and LiBr.

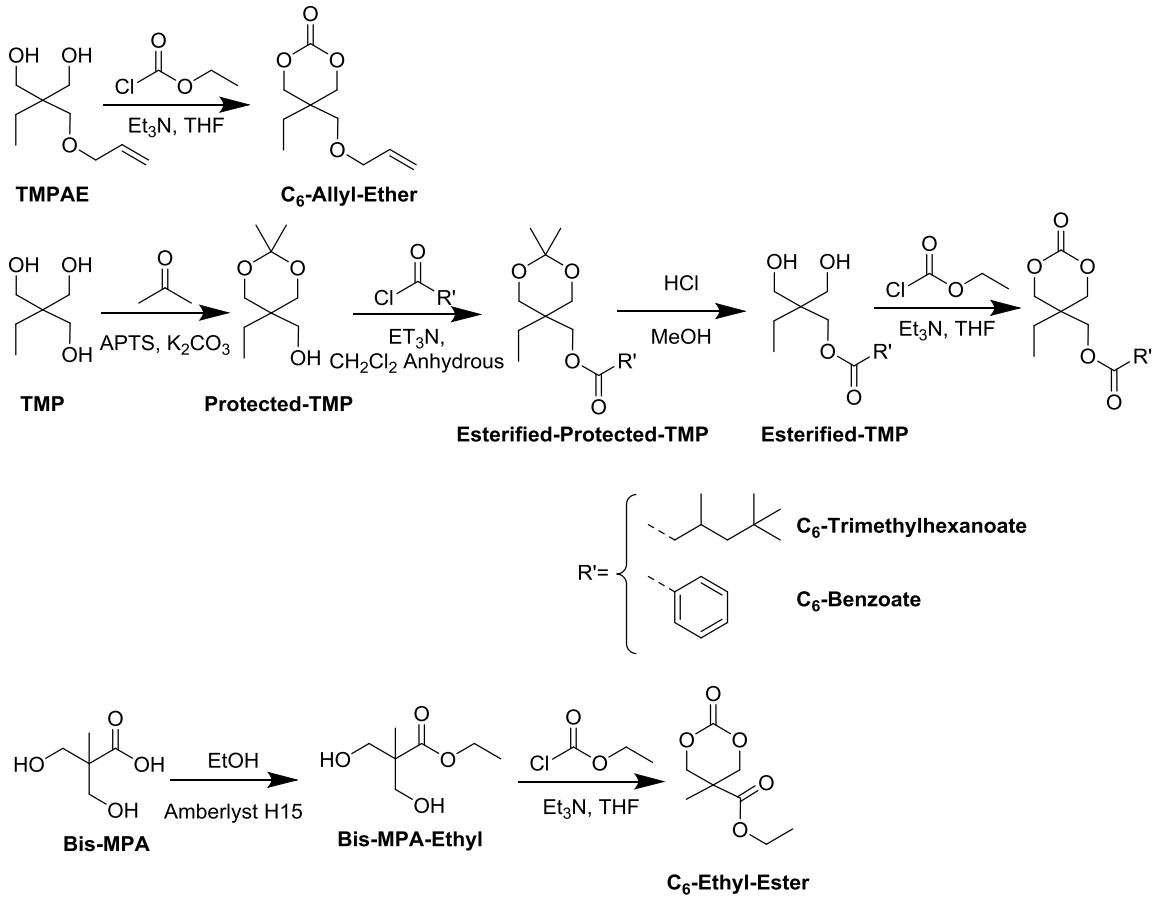
The second pathway corresponds to the transesterification and esterification of glycerin carbonate (GC) with anhydride acetic, 3,5,5-trimethylhexanoyl chloride or benzoyl chloride to obtain C_5-Acetate, C_5-Trimethylhexanoate and C_5-Ester-Phenyl, respectively. These reactions do not need any thermal activation and they were stopped after the total disappearance of the characteristic signals of protons CH_2 at α position of OH of the glycerin carbonate (^{1}H NMR spectra,SI - Figure II-36). Pure products were easily recovered with high yield.



Scheme II-1: Synthesis of 5-membered cyclic carbonate models

IV.1.1.2 Synthesis of six-membered cyclic carbonates models

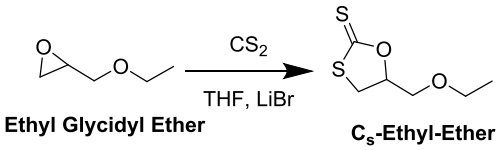
Four 6-membered cyclic carbonate (C_6) models were synthesized from 1,1,1-tris(hydroxymethyl)propane (TMP), trimethylolpropane allyl ether (TMPAE) or 2,2-Bis(hydroxymethyl)propionic acid (Bis-MPA). To synthesize C_6 with ether substituent (C_6-Ethyl-Allyl), TMPAE was reacted with ethyl chloroformate to give the corresponding 6-membered cyclic carbonate. For C_6 with ester substituent (C_6-Trimethylhexanoate and C_6-Benzoate), a first step of protection of TMP with acetone to obtain Protected-TMP was performed. In a second step, an ester group was attached by esterification with 3,5,5-trimethylhexanoyl chloride or benzyl chloride. Then, in a third step, a deprotection of Esterified-Protected-TMP with hydrochloric acid 1M at 30°C was performed. Finally, TMP-esterified was used as reactant with ethyl chloroformate to produce the 6-membered corresponding cyclic carbonates: C_6-Trimethylhexanoate and C_6-Benzoate. Finally, C_6-Ethyl-Ester was synthesized with ethylchloroformate and Bis-MPA previously esterified with ethanol (Bis-MPA-Ethyl). Scheme II-2 summarizes all synthesis routes to produce C_6 cyclic carbonate.



Scheme II-2: Syntheses of 6-membered cyclic carbonate models

IV.1.1.3 Synthesis of 5-membered cyclic dithiocarbonate model

Finally, five-membered cyclic dithiocarbonate (Cs-Ethyl-Ether) was synthesized by reaction of the corresponding epoxide precursor with carbon disulfide in presence of LiBr (Scheme II-3) [59]. This reaction was monitored by ^{1}H NMR (SI - Figure II-37) and stopped when the characteristic signals of epoxide ring had totally disappeared. Cs-Ethyl-Ether was purified by water extraction.

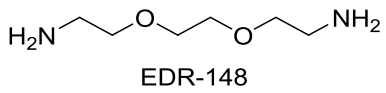


Scheme II-3: Synthesis of Cs-Ethyl-Ether

IV.1.2 Reactivity of aminolysis of model cyclic carbonates

Webster *et al.* [56] and Diakoumakos *et al.* [55] showed that primary aliphatic amines are the most reactive amines for aminolysis of cyclic carbonate, therefore we used in our study the, 2,2'-ethane-1,2-diylbis(oxy))bis(ethan-1-amine) noted EDR-148 (Figure II-20). This diamine

was previously distilled and stored under inert atmosphere, in order to prevent amine carbonation phenomenon described by Blain *et al.* [60]. We monitored the aminolysis reaction of various cyclic carbonates with EDR-148 *in situ* by ^{1}H NMR spectroscopy. Kinetic experiments were carried out at 25°C in $CDCl_3$ solvent at an initial concentration around 1 mol.L^{-1} and the reactions were monitored by acquisition of ^{1}H NMR spectra every 15 minutes during 6 hours. Cyclic carbonates conversions were recorded by ^{1}H NMR with benzophenone as reference.



EDR-148

Figure II-20: Structure of EDR-148

As demonstrated in previous studies, the conversion of cyclic carbonates follows generally a second-order kinetic [35, 38, 61-63]. Therefore, the reaction rate constant (k) is estimated by Equation II-2 where [Cyclic Carbonate] and [Amine] are the respective concentrations of cyclic carbonate and amine groups. The integrations of Equation II-2 gives Equation II-3 supposing that [Cyclic Carbonate] = [Amine]. $[Cyclic\ Carbonate]_0$ is the initial concentration of cyclic carbonate groups. Nevertheless, the kinetics of the reaction slowed down and the conversion ultimately reached a plateau. Therefore, k corresponds to the slope of the linear part of the $1/[Cyclic\ Carbonate]-1/[Cyclic\ Carbonate]_0 = f(t)$ curve.

Equation II-2
$$-\frac{d[Cyclic\ carbonate]}{dt} = k[Cyclic\ Carbonate][Amine]$$

Equation II-3
$$\frac{1}{[Cyclic\ Carbonate]} - \frac{1}{[Cyclic\ Carbonate]_0} = kt$$

The reactivity and the reaction rate constants (k) were determined for each cyclic carbonate according to its structure (C_5, C_6 and C_s) and substituent (aliphatic carbon chain, aliphatic/aromatic ether or ester).

IV.1.2.1 Influence of ring structure

The reactivity of cyclic carbonates was studied according to their ring structure: 5-, 6-membered or dithio-cyclic carbonate. Despite reactivity results in numerous papers [34, 38, 49, 62], our study is the first, to the best of our knowledge, to compare C_5, C_6 and C_S with same substituents to thoroughly determine the influence of ring structure on reactivity (Figure II-21). From this graph, Cs-Ethyl-Ether reacts with di-amine faster than analogous 5- and 6-membered cyclic carbonate. Indeed, after 2h of reaction, the conversion of di-thiocyclic

carbonate reaches 54%, while it only reaches 20% for C_6-Ether-and 11% for C_5-Ethyl-Ether (Table II-1). The difference of reactivity between C_5 and C_6 with analogous substituent is confirmed by reaction rate constant values: $k_{C6\text{-}Allyl\text{-}Ether}$ is 3.2 times higher than $k_{C5\text{-}Ethyl\text{-}Ether}$. This difference of reactivity can be based on the ring strain of 6-membered cyclic carbonates being larger than of 5-membered ones: ring strain energy difference is 2.86 kcal.mol^{-1} [64]. The difference of reactivity between thiocarbonyl and carbonyl groups during the aminolysis reaction is explained by the difference of spatial geometry of 2p and 3p-orbitals of C-S bond compare to 2p and 2p-orbitals of C-O bond. The necessary overlap of the carbon 2*p*-orbitals and sulfur 3*p*-orbitals is less efficient than the 2*p*-2*p* overlap of the C-O bond [65]. Therefore, the C-S bond is less stable than the C-O bond and the aminolysis reaction is promoted in the case of dithio-cyclic carbonate compared to classic cyclic carbonates.

According to these results, the most reactive cyclic carbonate are dithio-cyclic carbonates or 6-membered cyclic carbonates. Nevertheless, their synthesis requires harmful substances such as CS_2, phosgene or derivatives (ethylchloroformate). Therefore, in the purpose of the substitution of toxic substances in the synthesis of polyurethane, C_s and C_6 are not the best precursors compared to C_5 which can be synthesized by easy and safe carbonation of epoxide monomers or (trans)esterification of glycerol carbonate.

The rest of the article aims to improve the reactivity of 5-membered cyclic carbonates. In this purpose, several C_5 carbonates with different substituents were synthesized and studied.

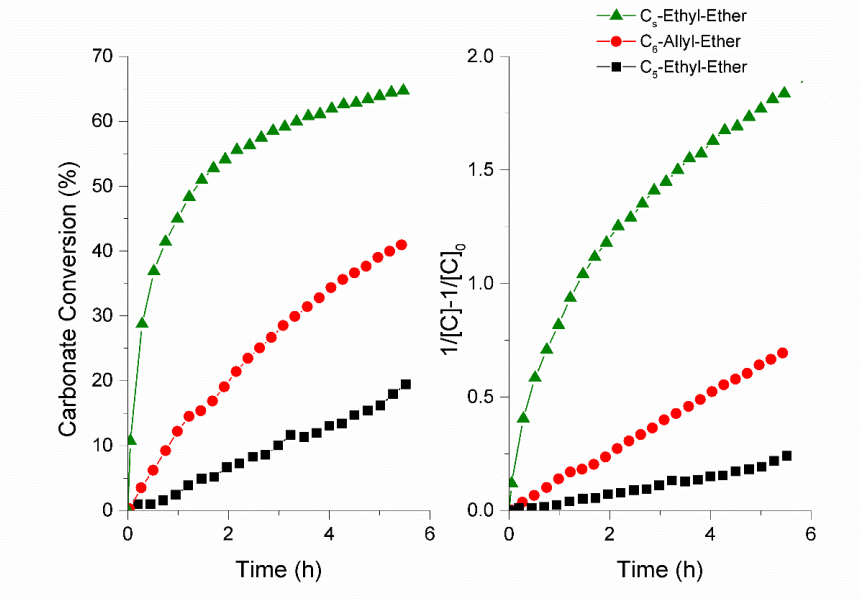


Figure II-21: Time-conversion curves (left) and Time-1/[C]-1/[C]$_0$ (right) relationships in the reaction of C_5-Ethyl-Ether (black), C_6-Allyl-Ether (red) and Cs-Ethyl-Ether (green) with EDR-148 in $CDCl_3$ (initial cyclic carbonate concentration 1 M) at 25°C

IV.1.2.2 Reactivity of cyclic carbonates – influence of substituents

The same kinetic experiments were performed in order to compare the reactivity of C_5 cyclic carbonates with various substituents: alkyl chain (C_5-Butane); aliphatic/aromatic ether; ester with aliphatic (C_5-Alkyl-Ether or C5-Acetate) or aromatic groups (C_5-Phenyl-Ether or C_5-Benzoate). The reactivity order of these 5-membered cyclic carbonate is C_5-Ethyl-Ester > C_5-Acetate > C_5-Trimethylhexanoate > C_5-Benzoate ≈ C_5-Ethyl-Ether > C_5-Phenyl-Ether > C_5-Butane (Figure II-22). This is confirmed by the rate-reaction constant calculated and given in Table II-1. These results show that the presence of ether (C_5-Ether), or ester groups (C_5-Ester) activate the cyclic carbonate compared to alkyl substituent (C_5-Butane). In addition, the position of ester function modifies the reactivity of cyclic carbonate. Indeed, C_5-Ester-Ethyl is far more reactive than C_5-Acetate.

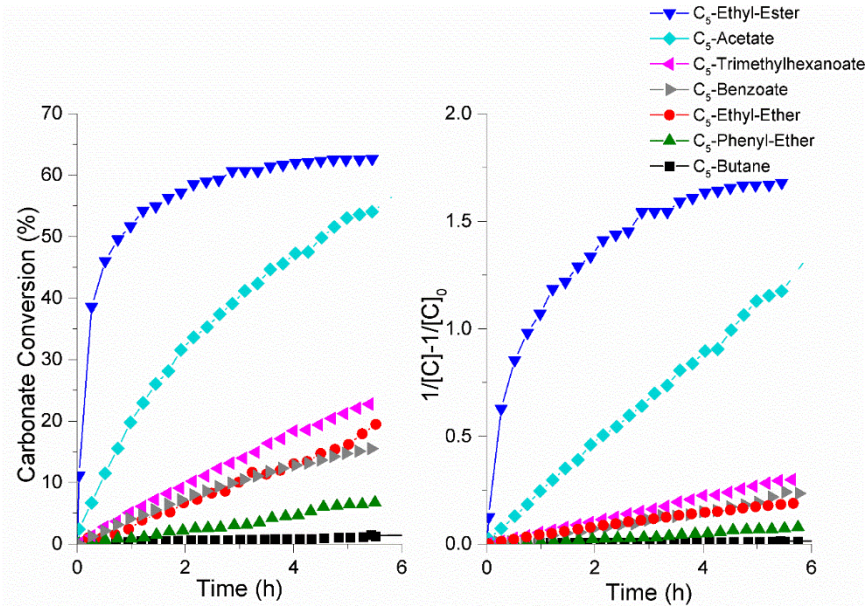


Figure II-22: Time-conversion curves (left) of five-membered cyclic carbonate and Time-1/[C]-1/[C]$_0$ (right) relationships in the reaction of C_5 with EDR-148 in $CDCl_3$ (initial cyclic carbonate concentration 1 M) at 25°C

The influence of the substituent on the reactivity of 5-membered cyclic carbonates has already been studied in the literature [25, 34, 37, 40-43, 46, 66] and attributed to electronic effect of substituents. Indeed, Garipov *et al.* [57] and Lamarzelle *et al.* [47] reported that the electron-withdrawing substituents –I (ether groups) and –M (ester groups) increase the electrophilicity of carbonyl and, therefore, activate nucleophilic attack of the amine. Nevertheless, it seems surprising that the electronic effect could only explain such differences of reactivity, when substituents are attached 4 to 5 carbons far from cyclic carbonate. In fact, it is well known that the electronic effect decrease with the distance between groups.

Therefore, we assume that another phenomenon explain the influence of substituents on the reactivity of cyclic carbonates. Hence, Cupples *et al.*[67] reports the effect of hydrogen bonds on the reactivity of epoxide monomers with amine. Indeed, oxygen atoms of ether or ester groups allow the creation of hydrogen bonds with amine that put amine in a favorable position to open the epoxide ring and increase the reactivity of these cyclic carbonates. This process could also be adapted to aminolysis of cyclic carbonates with ether or ester groups. In addition, the negative mesomeric effect of ester group allows to create a stronger hydrogen interaction with amine than ether group with negative inductive effect. This difference of electronic effect could also explain the higher reactivity of C_5-Ester compared to C_5-Ether and C_5-Butane (Figure II-23).

Finally, steric hindrance of substituents could also have an influence on reactivity of 5-membered cyclic carbonate. Indeed, from kinetics profile, C_5-Ethyl-Ether and C_5-Acetate are more reactive than C_5-Phenyl-Ether and C_5-Benzoate respectively since the phenyl group exhibit more steric hindrance than alkyl groups and therefore disfavors the nucleophilic attack of amine.

As a conclusion, the reactivity of cyclic carbonates is influenced by three correlated parameters: firstly, electronic effects of substituents; secondly, the steric hindrance of substituent; and finally the capacity to create hydrogen bonds between amine and oxygen of substituent allowing a favorable position for the attack of amine which could be a parameter of great influence.

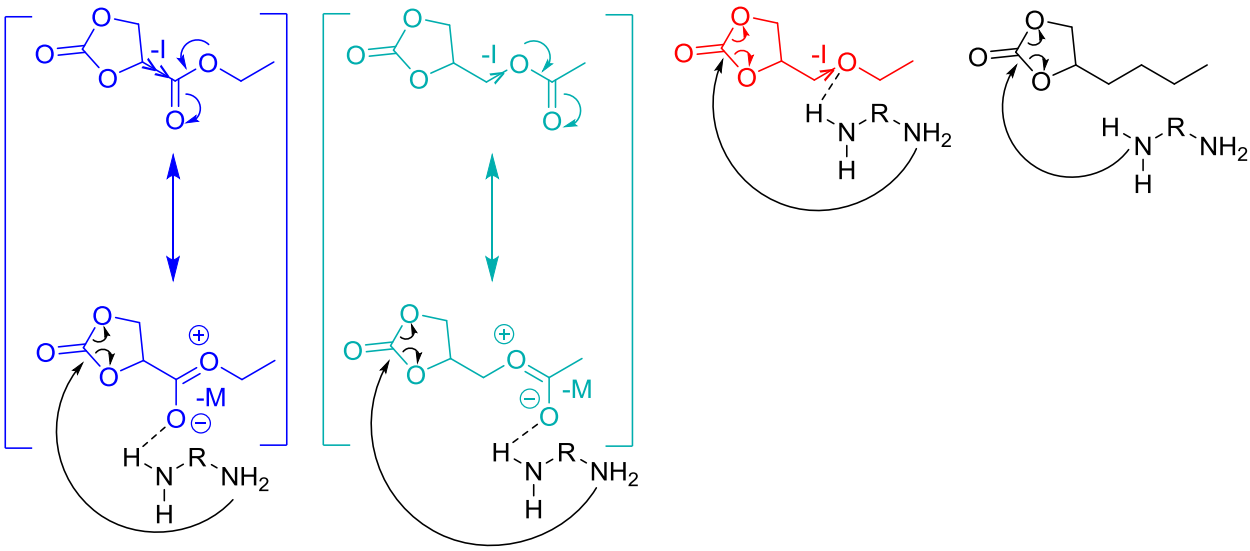


Figure II-23: Electronic effects and amine approach for opening cyclic carbonate

In order to check these hypotheses, the same study was also performed on C_6 carbonates with the same type substituent than for C_5. The kinetic profiles (Figure II-24) and the reaction rate constants (Table II-1) show a similar kinetic results and confirm the influence of substituents on the reactivity of cyclic carbonates.

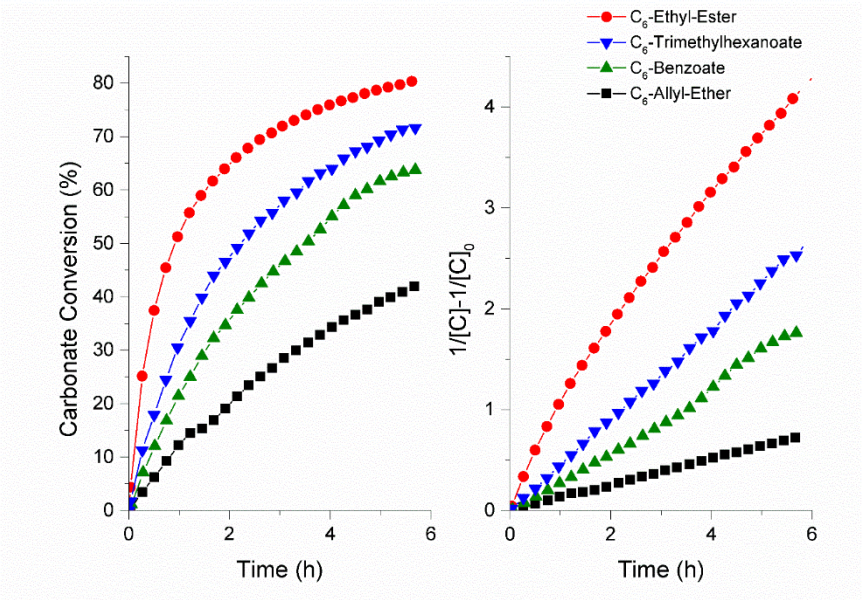


Figure II-24: Time-conversion curves (left) of six-membered cyclic carbonate and Time-1/[C]-1/[C]$_0$ relationships (time) in the reaction of C_6 with EDR-148 in $CDCl_3$ (initial cyclic carbonate concentration 1 M) at 25°C

Table II-1: Carbonate conversion and reaction rate constant (k) obtained for the different model reaction between cyclic carbonates and EDR-148

Entry	Cyclic Carbonate	Ratio Carbonate/Amine	Solvent	Carbonate Conversion t=2h (%)	k (L.mol^{-1}.h^{-1})
1	C_5-Butane	1/1	$CDCl_3$	0.6	0.002[a]
2	C_5-Ethyl-Ether	1/1	$CDCl_3$	6	0.04[a]
3	C_5-Ethyl-Ether	1/1	THF-d_8	2	0.01[a]
4	C_5-Ethyl-Ether	1/1	DMF-d_7	7	0.05[a]
5	C_5-Ethyl-Ether	1/1	Methanol-d_4	63	1.88[b]-0.46[c]
6	C_5-Phenyl-Ether	1/1	$CDCl_3$	2	0.01[a]
7	C_5-Ethyl-Ester	1/1	$CDCl_3$	58	1.31[d]
8	C_5-Acetate	1/1	$CDCl_3$	33	0.22[a]
9	C_5-Acetate	1/.5	$CDCl_3$	43	0.41[a]
10	C_5-Acetate	1/2	$CDCl_3$	59	0.82[e]
11	C_5-Trimethylhexanoate	1/1	$CDCl_3$	10	0.05[a]
12	C_5-Benzoate	1/1	$CDCl_3$	7	0.04[a]
13	C_6-Allyl-Ether	1/1	$CDCl_3$	19	0.13[a]
14	C_6-Ethyl-Ester	1/1	$CDCl_3$	64	0.70[a]
15	C_6-Trimethylhexanoate	1/1	$CDCl_3$	47	0.45[a]
16	C_6-Benzoate	1/1	$CDCl_3$	35	0.32[a]
17	Cs-Ethyl-Ether	1/1	$CDCl_3$	54	0.83[f]

[a]: Value calculated between 0 and 6 h of reaction using a second order kinetic law (Equation II-3), [b]: Value calculated between 0 and 0.5h, [c]: Value calculated between 0.5 and 6h of reaction, [d]: Value calculated between 0 and 3h [e]: Value calculated between 0 and 1h of reaction, [f]: Value calculated between 0 and 3h or reaction

Hence, even if ester substituents enhance the reactivity of cyclic carbonate, at room temperature, all the kinetic curves reach a plateau of conversion between 60 and 80% for the most reactive cyclic carbonates. This phenomenon was often reported in literature [47], but has

never been explained. If the limitation of diffusion of monomers during the polymerization due to the creation of the hydrogen bonds was envisaged, this never was demonstrated. In order to check this hypothesis, aminolysis reactions of 5-membered cyclic carbonate in different conditions (temperature, stoichiometry, solvent) were studied in the rest of this study.

IV.1.3 Limitation of conversion of cyclic carbonate aminolysis

Three experiments were performed in order to study the limitation of conversion of reaction model between C_5-Acetate and EDR-148.

In the first experiment, different ratios of cyclic carbonate / amine (1/1; 1/1.5 and 1/2) were introduced at t=0 and the carbonate conversion was monitored by ^{1}H NMR. From the kinetic curves (Figure II-25) and the values of k (Table II-1), both the reactivity and conversion after 6 hours of reaction increase with increasing content of amine. This could be due to a higher quantity of available amine functions for polymerization. However, with 1/1.5 ratio, the carbonate conversion is still limited at 76% after 8 hours of reaction while with 1/2 ratio the conversion reaches 94 %.

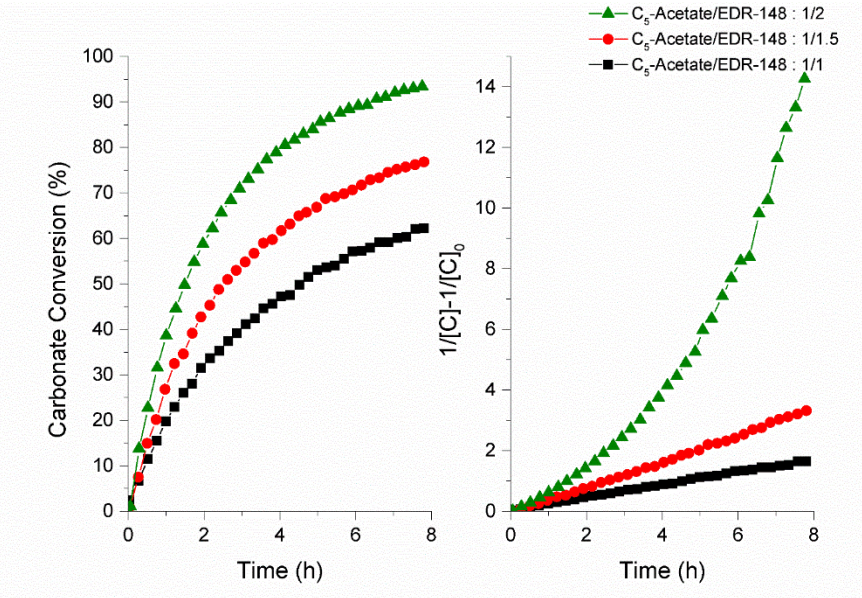


Figure II-25: Time-conversion curves (left) of five-membered cyclic carbonate and Time-1/[C]-1/[C]$_0$ relationships (time) in the reaction of C_5-Acetate with EDR-148 in different ratio in $CDCl_3$ (initial cyclic carbonate concentration 1 M) at 25°C

The second experiment consists to introduce an excess of amine after the blocking of cyclic carbonate / amine reaction. Hence, the reaction was performed in stoichiometry 1/1 ratio during 10 hours of the reaction - conversion reaches 65%; then after 10h of reaction, one

equivalent of EDR-148 is added in the NMR tube and the kinetics reaction was continued during 14h. Figure II-26 shows the obtained result. The carbonate conversion increases again after the amine addition to reach a quantitative conversion. This experiment confirms that the conversion is blocked by amine diffusion, probably due to hydrogen bonds created during polymerization.

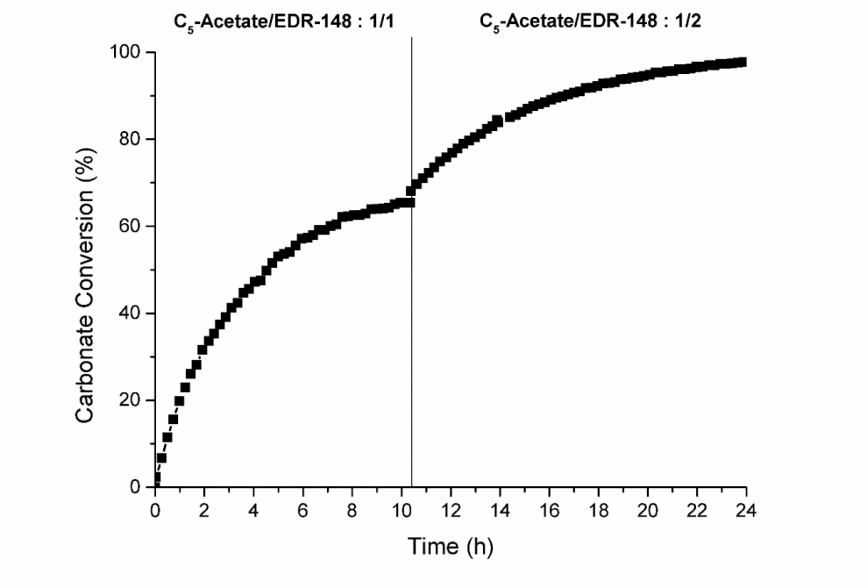


Figure II-26: Effect of addition of diamine after 10h in aminolysis reaction of C_5-Acetate with EDR-148

A third experiment shows the influence of a temperature increase after the blocking of reaction at room temperature. Indeed, conversion is blocked at 76% after 13.5h of reaction at 25°C, and after an increase of temperature at 40°C, reaction continues and conversion reaches 90% Figure II-27. This can be explained by an increased energy and mobility conferred to polymer chains at higher temperature that allow continuation of reaction.

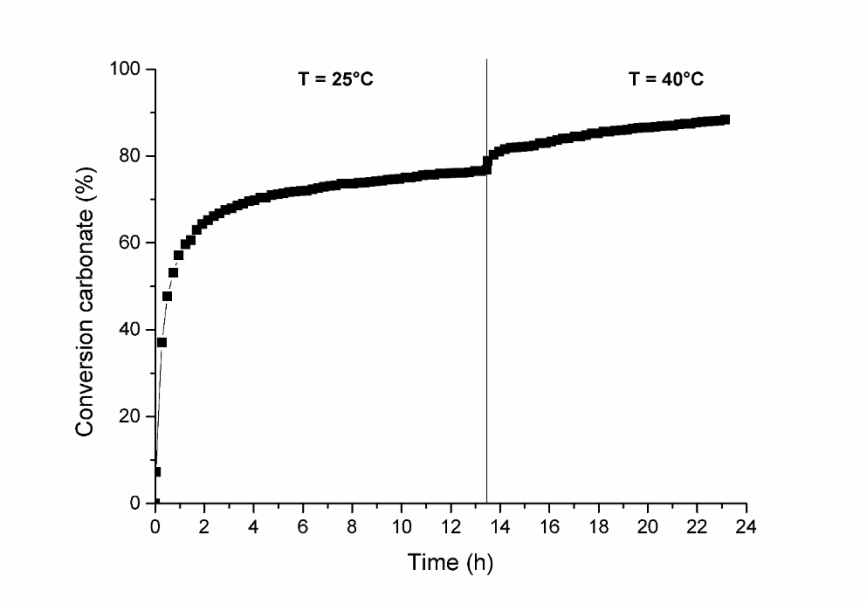


Figure II-27: Temperature effect on aminolysis reaction of C_5-Acetate with EDR-148 after blocking of reaction at room temperature

Hence, these experiments prove, for the first time, that the limitation of aminolysis reaction of cyclic carbonates, and thus the limitation of molar masses is due to the limited diffusion of reactants at room temperature. This diffusion is limited by the creation of a high amount of hydrogen bonds between carbamate and hydroxyl functions and amines. In order to increase the conversion of aminolysis of cyclic carbonates, the reaction needs thermal activation of an excess of amine. However, Besse *et al.* [68] and Lamarzelle *et al.* [47] proved by ^{1}H and ^{13}C NMR that side-reaction such as urea formation or dehydration could occur during aminolysis of 5-membered cyclic carbonates with ester functions (Figure II-28), which could modify the stoichiometry of reactants and limit also the molar masses. On the ^{13}C NMR spectrum of hydroxyurethane produced after 6h of reaction between C_5-Acetate and EDR-148 in stoichiometric proportion at room temperature, we identify products from amidification side-reactions. Nevertheless, we do not identify any urea or side-products from dehydration reaction. This was confirmed with the comparison of ^{13}C NMR spectra of 1,3-dibutlurea; N-methylacetamide and synthesized hydroxyurethane (SI - Figure II-38).

Therefore, the C_5-Ether seems be the best cyclic carbonate to synthesize PHUs without side-products despite a lower reactivity than ester carbonates. The rest of this study will be devoted to the activation of aminolysis reaction of C_5-Ether at room temperature.

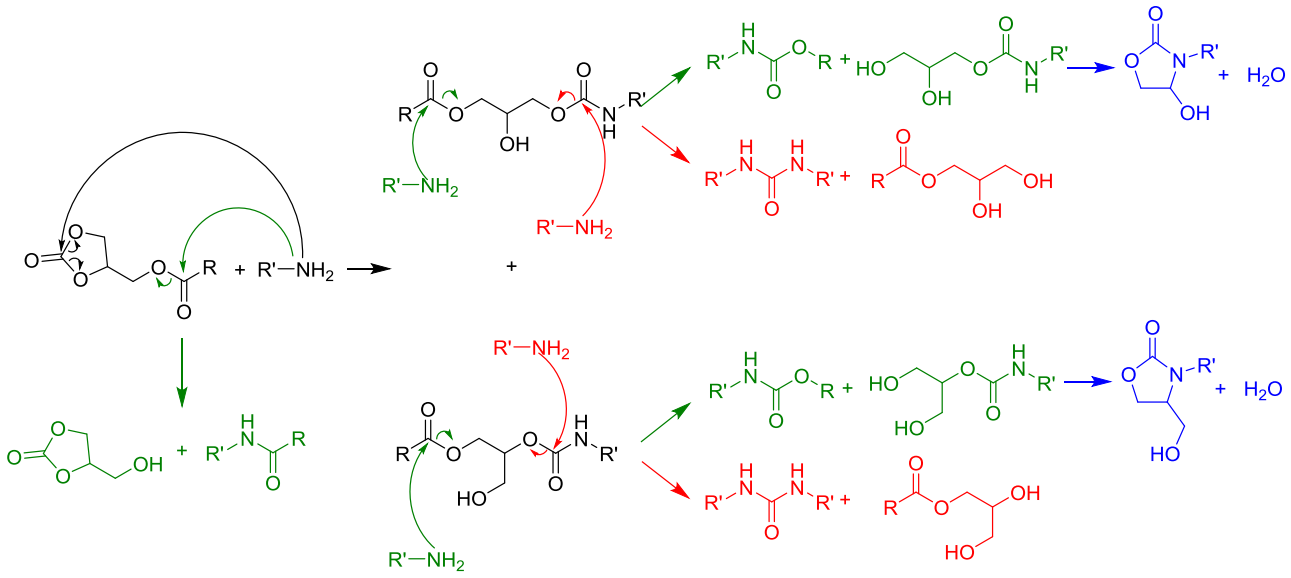


Figure II-28: Possible reactions between C_5 with ester groups and amine: (black) aminolysis, (green) amidification, (red) urea formation and (blue) dehydratation.

IV.1.4 Activation of aminolysis reaction on ether-C_5 carbonate with protic solvent

Garipov *et al.* [57] (Figure II-29) reported the influence of the solvent on the reactivity of 5-membered cyclic carbonates. The authors proposed a mechanism on ring opening of cyclic carbonates by amines in three steps (Figure II-29). In a first step, a tetrahedral intermediate is created by nucleophile attack of the amine on the carbonyl of cyclic carbonate. In a second step, a second amine deprotonates the tetrahedral intermediate. And in a third step, the electron density initiates the rupture of the carbon-oxygen bond, leading to hydroxyurethane with primary or secondary alcohol. The secondary alcohol opening is favored since it is more thermodynamically stable[41]. The first step of this mechanism is the limiting step in an aprotic solvent. However, in a protic solvent, hydrogen bonds are created between solvent and heteroatoms of carbonate which increases the positive charge of the carbon of carbonyl (Figure II-30), promoting the nucleophile attack of the amine. Therefore, in that case, the limiting step is the second step which corresponds to the deprotonation of tetrahedral intermediate. Nevertheless, only protic solvents (butanol, hexanol and octanol) were tested by Garipov on the aminolysis reaction who didn't use any aprotic solvent for comparison. This feature constitutes the limits of his study.

In order to confirm this interesting hypothesis and complete the study of Garipov *et al.* [57], a kinetic study with C_5-Ethyl-Ether and EDR-148 was performed in different aprotic ($CDCl_3$,

DMF-d_6 and THF-d_7) and protic (Methanol-d_4) deuterated solvents. The Figure II-31 shows for the first time, the reactivity of C_5-Ethyl-Ether according to protic and aprotic solvents (Figure II-31). These kinetic profiles highlight the effectiveness of protic solvent, methanol-d_4, compared to $CDCl_3$, DMF-d_7 and THF-d_8. In fact, methanol allows to increase significantly the reactivity ($k_{0\text{-}0.5h}$=1.88 $L.mol^{-1}.h^{-1}$, $k_{0.5\text{-}6h}$=0.46 $L.mol^{-1}.h^{-1}$) of cyclic carbonate / amine reaction compared to DMF-d_7 (k=0.05 $L.mol^{-1}.h^{-1}$), $CDCl_3$ (k=0.04 $L.mol^{-1}.h^{-1}$) or THF-d_8 (k=0.01 $L.mol^{-1}.h^{-1}$). Two linear curves can be observed in the kinetic profile of the reaction performed in methanol, explaining the two values of k. Interactions between solvent and the carbonyl of carbonate disturb the second order of reaction.

The conversion of C_5-Ethyl-Ether reaches 80% after 6 hours of reaction in Methanol-d_4 whereas it is around 25% in $CDCl_3$ and DMF-d_7 and only 3% in THF-d_8. This can be explained by interactions between solvent and polyhydroxyurethane that reduce the inter- and intra-molecular hydrogen bonding between PHU chains, increasing the mobility of the polymer chains (Figure II-34). In order to prove that the C_5-Ethyl-Ether does not undergo a transcarbonatation reaction with deuterated methanol and that the increasing of conversion is only due to of aminolysis, C_5-Ethyl-Ether was stirred during 48 hours in deuterated methanol. The ^1H NMR of C_5-Ethyl-Ether after 48 hours in Methanol-d_4 (SI - Figure II-39) doesn't show any side-products issued from any side-reaction between deuterated methanol and cyclic carbonate.

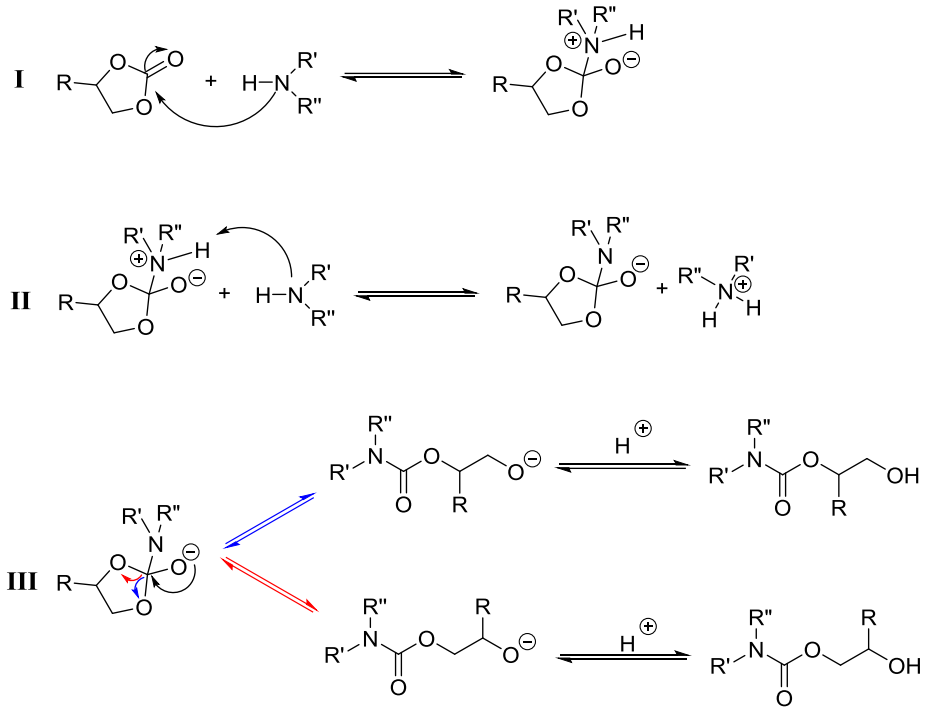


Figure II-29: Mechanism of cyclic carbonate / amine reaction

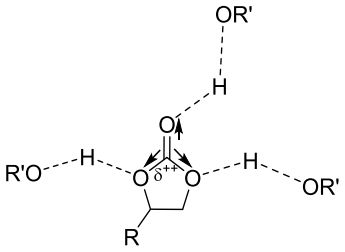


Figure II-30: Increasing of the electrophilicity of cyclic carbonate in presence protic solvent

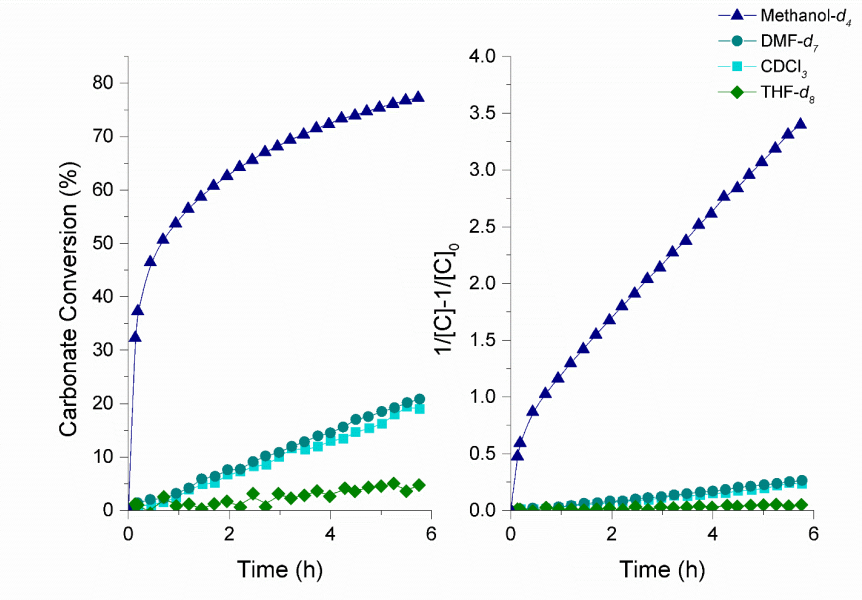


Figure II-31: Time-conversion curves (left) of five-membered cyclic carbonate and Time-1/[C]-1/[C]$_0$ relationships (time) in the reaction of C_5-Ether-Methyl with EDR-148 in different deuterated solvents (initial cyclic carbonate concentration 1 M) at 25°C

In order to validate this study and verify the absence of side-reactions during the polymerization in protic solvent, hydroxyurethanes were synthesized in methanol and analyzed by ^{1}H (Figure II-32-b) and ^{13}C (Figure II-33-b) NMR. These spectra were compared to those of hydroxyurethanes synthesized in chloroform (Figure II-32-a Figure II-33-a).

The model hydroxyurethanes were synthesized by reaction between C_5-Ethyl-Ether and butylamine in chloroform (1 M) or methanol (1 M). The butylamine was chosen instead of EDR-148 in order to simplify the identification of characteristic peak in NMR. Reactions were performed at room temperature (25°C) without catalyst during 24 hours. These reactions were monitored by ^{1}H and ^{13}C NMR (Figure II-32 and Figure II-33). In order to quantify the cyclic carbonate conversion and alcohol I / II ratio. An internal reference (Benzophenone) was used.

After 24 hours of reaction, the ^{1}H NMR spectrum (Figure II-32) of synthesized products shows the appearance of peak at 3.01 ppm corresponding to protons CH_2 at α position of carbamate group (g' and g''). In addition, the production of carbamate group is confirmed by ^{13}C spectrum (Figure II-33). Indeed, characteristic carbon signal of carbamate group is identified at 156.22 ppm.

The form of the characteristic peaks of g' and g'' protons in ^{1}H NMR changes according to spectra. Indeed, in the spectrum b) of the Figure II-32, the peak is a doublet of triplet whereas

in the spectrum c), this signal is a broad triplet. Boutevin *et al.* [69] showed that the behavior of carbamate compounds in NMR is influenced by the concentration. In fact, in concentrated solution, CH_2 protons at α position of N-H appear as of broad triplet. When the carbamate concentration decreases, CH_2 at α position of carbamate correlates with the N-H proton, leading to a doublet of triplet.

According to the opening direction of the carbonate group with butylamine, two hydroxyurethane compounds with primary (Hydroxyurethane 1) or secondary (Hydroxyurethane 2) alcohol are created. The peaks at 3.62, 3.83, between 3.88 and 4.08, and 4.73 ppm characteristic of b', c'', b'' and c' prove the formation of these two hydroxyurethane compounds. In addition the ^{13}C NMR spectrum shows the split into two peaks between 156 and 157 ppm characteristic of a' and a'' carbons of carbamate group.

Nevertheless, a difference of conversion of synthesis of hydroxyurethane compounds in chloroform and methanol is observed after 24 hours of reaction. Indeed, in chloroform, characteristic peaks of b and c protons of C_5-Ethyl-Ether and of h proton of butylamine are identified in the ^1H NMR spectrum (Figure II-32-b). Moreover, in the ^{13}C NMR spectrum (Figure II-33-b), we observe the corresponding signals of h carbon of butylamine and a, b, c, and e carbons of C_5-Ethyl-Ether, highlighting the partial conversion of precursors at room temperature. The conversion is blocked at 85% after 24h and did not increase after 7 days of reaction (SI - Figure II-40). However, in methanol, total conversion of precursors has been reached after 24 hours of reaction. Indeed, the signals of protons and carbons (Figure II-32-c and Figure II-33-c) of C_5-Ethyl-Ether and butylamine disappeared respectively in ^1H and ^{13}C spectra of hydroxyurethane without the appearance of any side-product. This result confirms the effectiveness of methanol solvent for the synthesis hydroxyurethane products. The ratio between primary and secondary alcohols is 35:65 which is perfectly in accordance with literature [38, 41, 52].

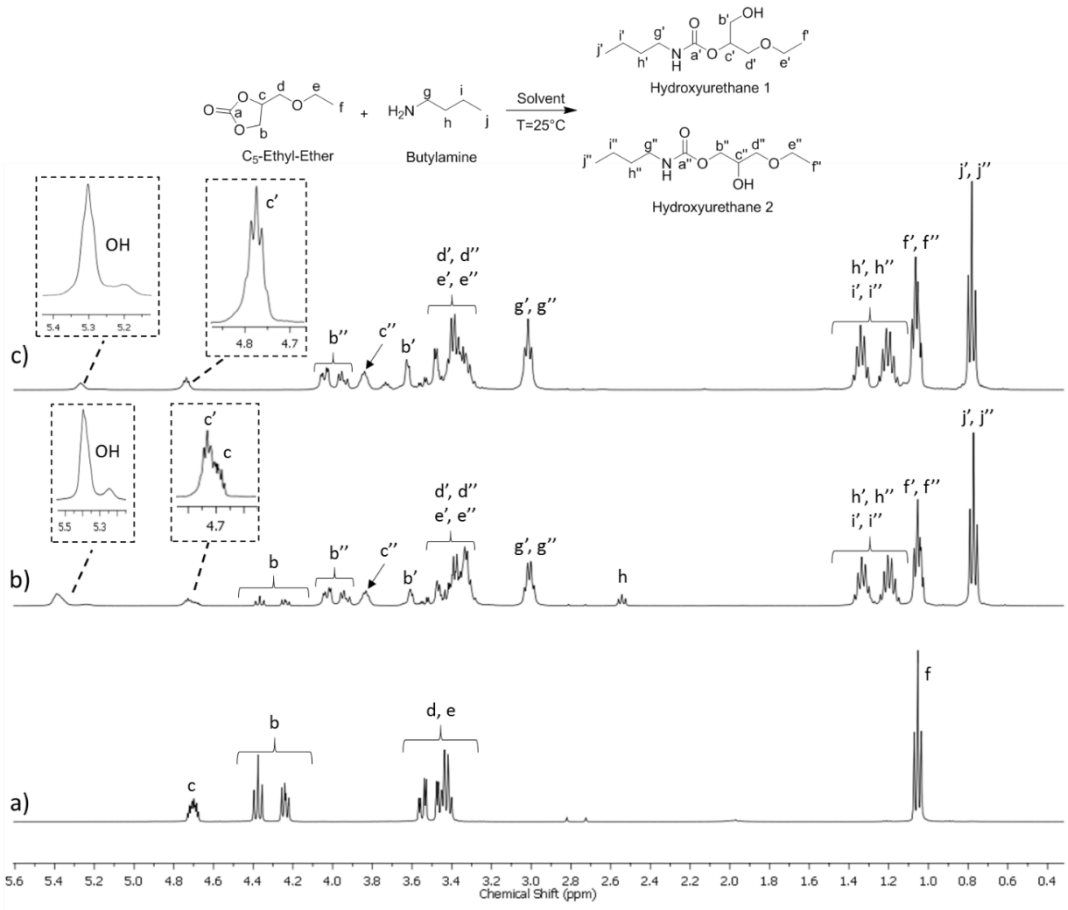


Figure II-32: Stacked ^{1}H NMR spectra in $CDCl_3$ of C_5-Ethyl-Ether (a) and hydroxyurethane synthesized with butylamine in chloroform (b) and methanol (c) at 25°C after 24 hours of reaction

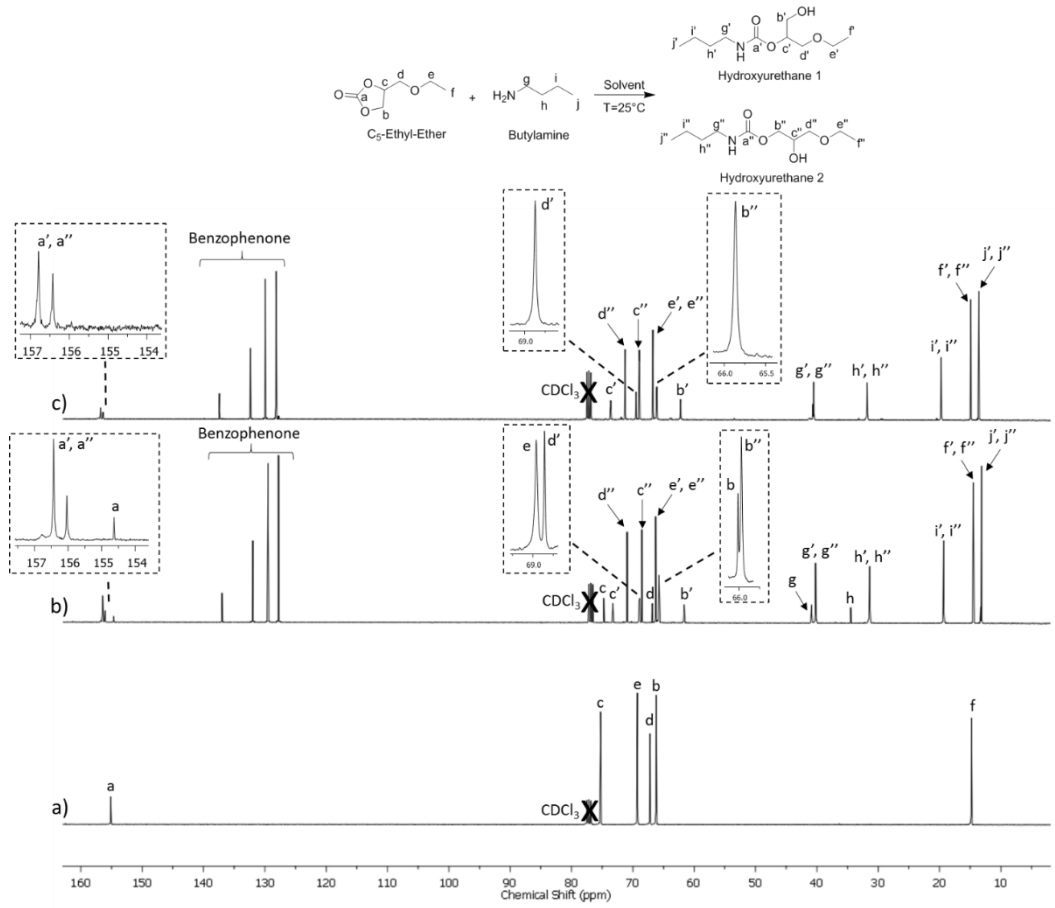


Figure II-33: Stacked ^{13}C NMR spectra in $CDCl_3$ of C_5-Ethyl-Ether (a) and hydroxyurethane synthesizedwith butylamine in chloroform (b) and methanol (c) at 25°C after 24 hours of reaction

As a conclusion, even if the reactivity of C_5-Ethyl-Ether is lower than 5-membered cyclic carbonate with ester groups, it could be activated in protic solvents. The hydrogen bonds created between oxygens of cyclic carbonate and protic solvent allows to increase the positive charge of carbonyl which favors the nucleophile attack of amine on cyclic carbonate (Figure II-30). Moreover, the protic solvent has positive effect on the conversion of cyclic carbonate during aminolysis. Since protic solvent has an effect on both reactivity and conversion of cyclic carbonate, it is interesting to study its effect on the molar masse of synthesized of PHUs at room temperature.

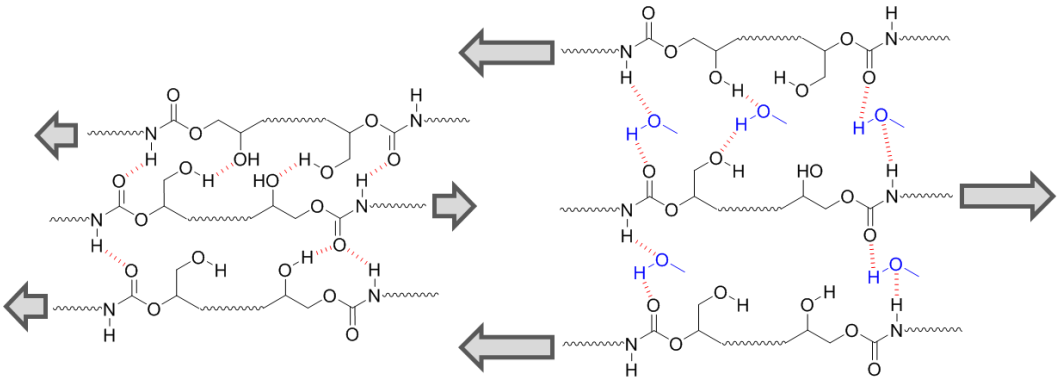


Figure II-34: Methanol effect on PHU hydrogen bonds

IV.2 Synthesis and characterization of polyhydroxyurethane in protic and aprotic solvents

Due to the performance of methanol on the model study, protic solvent was tested on PHU synthesis by reaction between Bis-C_5-Ether and EDR-148 in stoichiometric proportions (1:1) at room temperature. Since Bis-C_5-Ether is partially soluble in methanol at room temperature, a mixture chloroform/methanol (0.66/0.33) was used. Difunctionality of both monomers was confirmed by ^{1}NMR (Figure II-36). In order to compare the effectiveness of protic solvent, the degree of advancement of reaction (p), the polymerization degree ($\overline{DP}n$) and the molar mass ($\overline{M}n$) calculated from ^{1}H NMR at different time of reaction were compared for synthesized PHU synthesized in both protic and aprotic solvents (Chloroform) (SI - Figure II-41 and SI - Figure II-42). The PHU ^{1}H NMR at 144 hours of reaction in mixture chloroform/methanol is presented in Figure II-36. Peaks were attributed by 2D COSY (SI - Figure II-43), HSQC (SI - Figure II-44) and HMBC (SI - Figure II-45) NMR. Prior the determination of p, $\overline{DP}n$ and $\overline{M}n$, the stoichiometric proportion was checked for each analyzed sample by comparing integration values of the characteristic signals corresponding to CH_2 and CH of cyclic carbonate and CH_2 at α position of amine. The degree of advancement of reaction, p, is calculated from $\int H_g$, corresponding to the CH_2 at α position to the carbamate of the PHU and $\int H_a$, $\int H_b$ corresponding to the CH and CH_2 respectively to the cyclic carbonate (Equation II-4). $\overline{DP}n$ is calculated from the Carothers' equation (Equation II-5) in the case of polyaddition in stoichiometric proportion. Finally, $\overline{M}n$ is calculated from $\overline{DP}n$ (Equation II-6) where 438 corresponds to the molar masses of repeating unit of PHU.

Equation II-4
$$p = \frac{\frac{\int H_g'}{2}}{\frac{\int a + \int b}{3} + \frac{\int H_g'}{2}}$$

Equation II-5
$$\overline{DP}n = \frac{1}{1-p}$$

Equation II-6
$$\overline{M}n = \overline{DP}n \times 438$$

Figure II-35 shows the evolution of p and $\overline{M}n$ of PHUs synthesized in chloroform or methanol and brings to light the positive influence of protic solvents (methanol) on cyclic carbonate conversion and, therefore, on molar masses of PHUs. Indeed, p increases more rapidly in methanol than in chloroform to reach 0.93 (0.85 in chloroform) after 336 hours of reaction.

The polymerization degree of polymers synthesized by polyaddition is controlled by Carothers' equation, which shows that, for high values of p, a small increase of conversion of monomers has a dramatic effect on the increase of $\overline{DP}n$ and $\overline{M}n$ (SI - Figure II-46). Therefore, for the polymerization in chloroform/methanol mixture, $\overline{M}n$ increases significantly between 48 and 336 h of reaction. In addition, as for model study, we didn't observe any side-product that and may modify the stoichiometry of reaction. The values of p, $\overline{DP}n$ and $\overline{M}n$ are summarized in Table II-2.

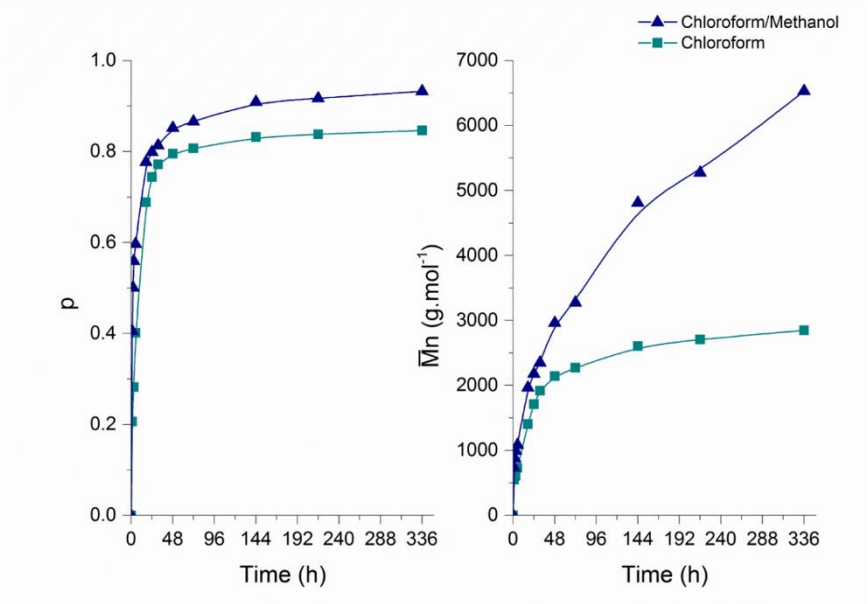


Figure II-35: Evolution of degree of advancement of the reaction (p) between Bis-C_5-Ether and EDR-148 (left) and evolution of molar masses (right) of PHU according to solvent (chloroform or mixture chloroform/methanol)

Table II-2: Degree of advancement (p) of the reaction between Bis-C_5-Ether (1 mol.L^{-1}) and EDR-148 at room temperature in chloroform (Chlor.) and chloroform/methanol mixture (Chlor./Meth. 0.66/0.33), polymerization degree ($\overline{DP}n$) and molar masses ($\overline{M}n$) of PHU determined by ^{1}H NMR

Time (h)	p		$\overline{DP}n$		$\overline{M}n$ (g.mol^{-1})	
	Chlor.	Chlor./Meth.	Chlor.	Chlor./Meth.	Chlor.	Chlor./Meth.
1	0.21	0.41	1.3	1.7	550	750
2	-	0.50	-	2.0	-	900
3	0.28	0.56	1.4	2.3	600	1000
5	0.40	0.60	1.7	2.5	750	1100
17	0.69	0.78	3.2	4.5	1400	2000
24	0.74	0.80	3.9	5.0	1700	2200
31	0.77	0.81	4.4	5.4	1900	2350
48	0.80	0.85	4.9	6.8	2150	3000
72	0.81	0.87	5.2	7.5	2300	3300
144	0.83	0.91	5.9	11.0	2600	4800
216	0.84	0.92	6.2	12.0	2700	5300
336	0.85	0.93	6.5	14.9	2800	6600

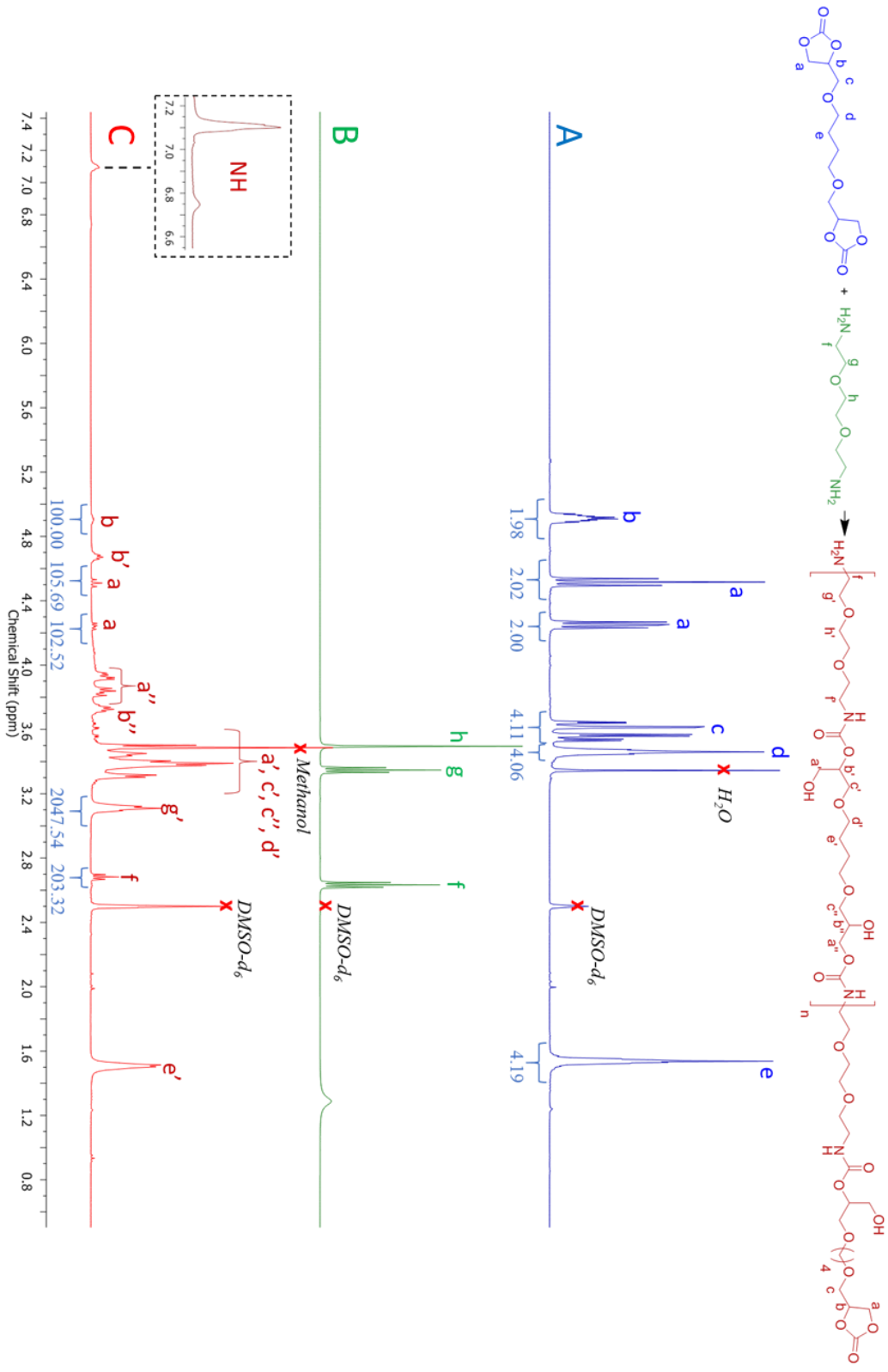


Figure II-36: Stacked of ^{1}H NMR of Bis-C_5-Ether (A), EDR-148 (B) and PHU (C) obtained at room temperature in mixture Chloroform/Methanol at t=144h

V. Conclusion

In this study, we have studied the influence of cyclic carbonates structures and solvents on aminolysis reaction in order to improve the synthesis of poly(hydroxyurethane)s at room temperature. Therefore we have performed a complete kinetic study on aminolysis reaction of various cyclic carbonates in order to identify the parameters that influence their reactivity and to select the best precursors to synthesize PHU polymers.

Hence in this study, we synthesized and investigated reactivity of new structures that never were studied beforehand, namely C_5 and C_6 with Ethyl-Ester or trimethylhexanoate substituents and we compared for the first time C_5, C_6 and C_S carbonate with same substituents. Thus, we demonstrated the influence of substituents on reactivity of C_5 and C_6 : Ethyl-Ester > Acetate > Trimethylhexanoate > Benzoate ≈ Ethyl-Ether > Phenyl-Ether > Butane.

Beyond the parameters already presented in literature, such as steric hindrance and electronic effect, we proposed the effect of hydrogen bonds between carbonate and amine that entail a favorable position of amine for its nucleophilic attack as the explanation of highest reactivity of ester-carbonates. Despite their high reactivity, these ester carbonate could undergo amidification side-reaction that modify stoichiometry, leading to a partial conversion.

Therefore we studied the activation of ether-carbonates, especially C_5, that are easily synthesized by direct carbonation of epoxides, and that didn't undergo side-reaction. Hence they seem the best monomers for PHU synthesis.

This study has also demonstrated the blocking of the aminolysis reaction by creation of inter- and intra-molecular hydrogen bonds. In order to increase the reactivity of ether-C_5 and reduce hydrogen bonding, the solvent effect was also studied. We showed that protic solvents have a positive influence both on the reactivity and conversion of cyclic carbonates.

Hence, in a last part, the use of protic solvent has been considered for the synthesis of PHU polymers from Bis-C_5-Ether and EDR-148 at room temperature and allowed a quasi-quantitative conversion.

VI. Acknowledgement

The Association Nationale de la Recherche et de la Technologie (ANRT) and the Agence Nationale de la Recherche (ANR) are deeply acknowledged for their financial support. The authors thank Huntsman for supplying EDR-148. Finally, the authors thank Cédric Totée for his help and fruitful discussions.

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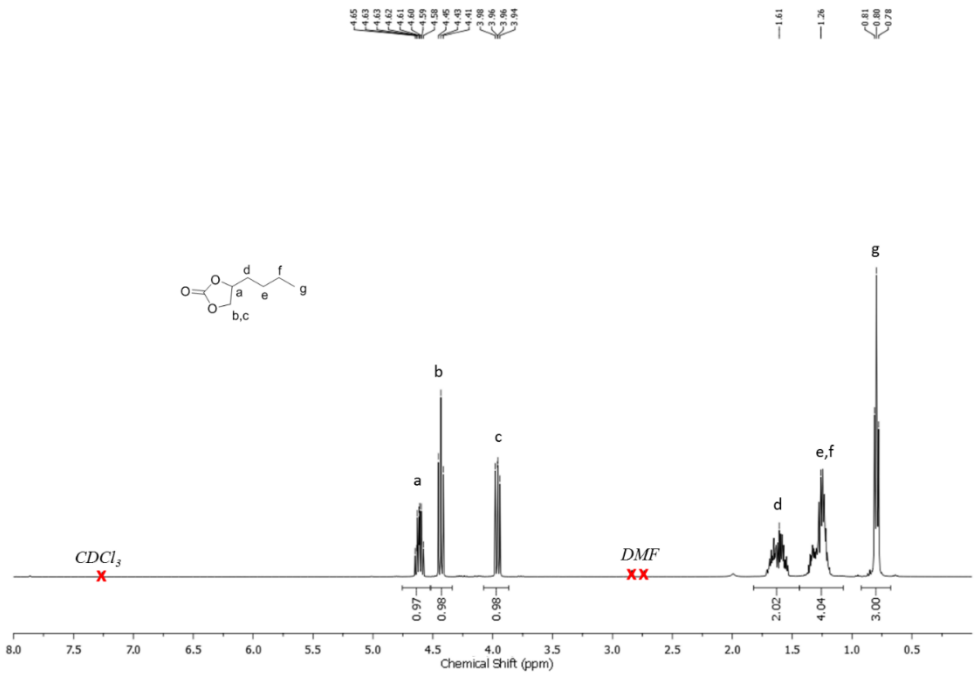
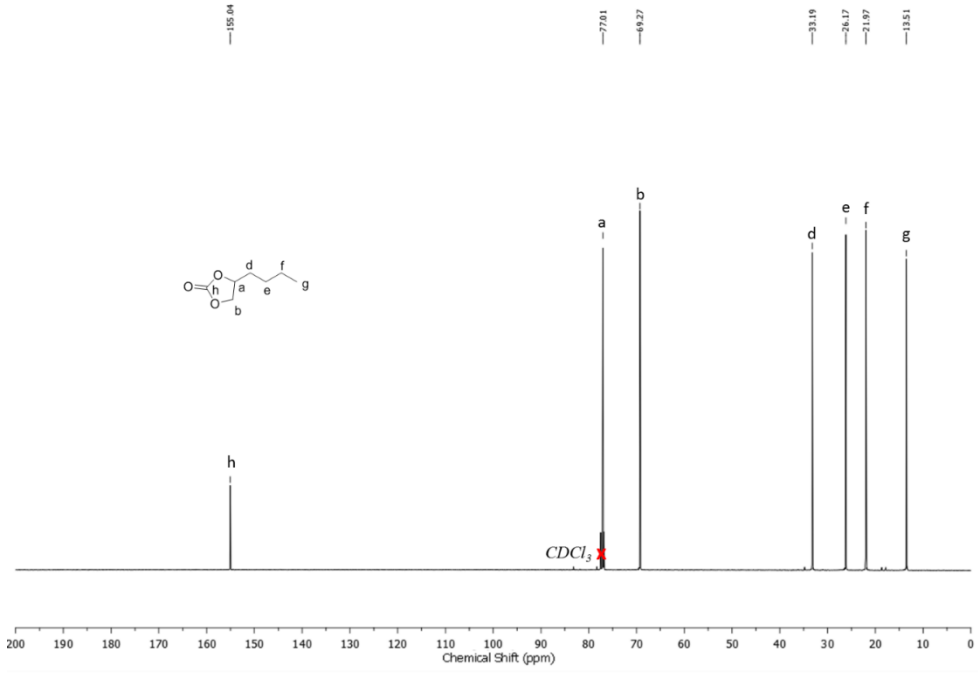
VIII. Supporting Informations

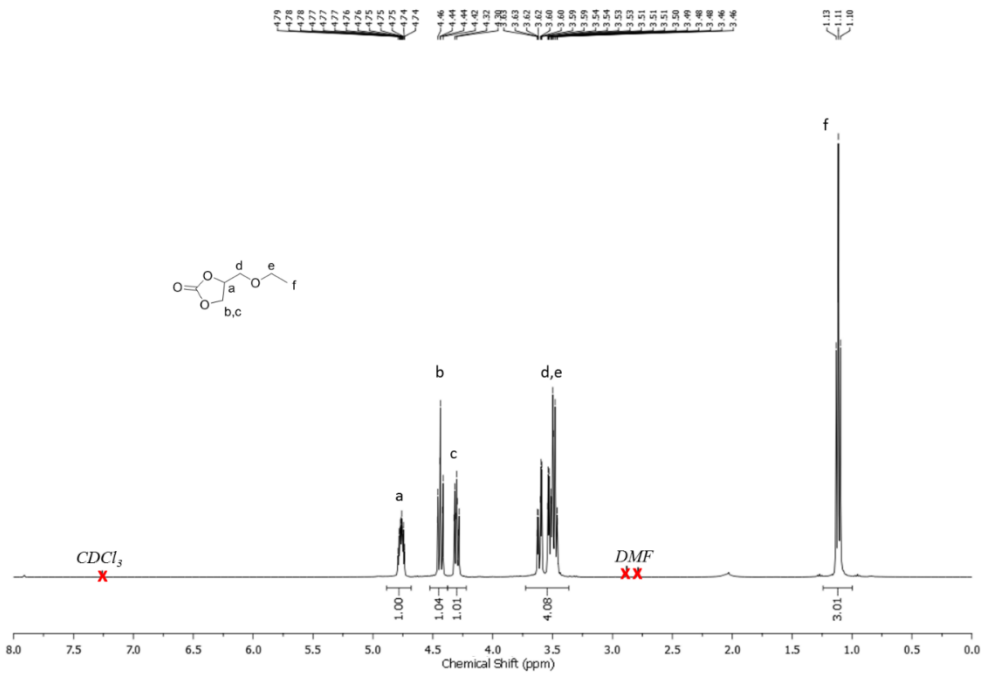
VIII.1 Graphical data of mono-cyclic carbonates and bis-cyclic carbonates



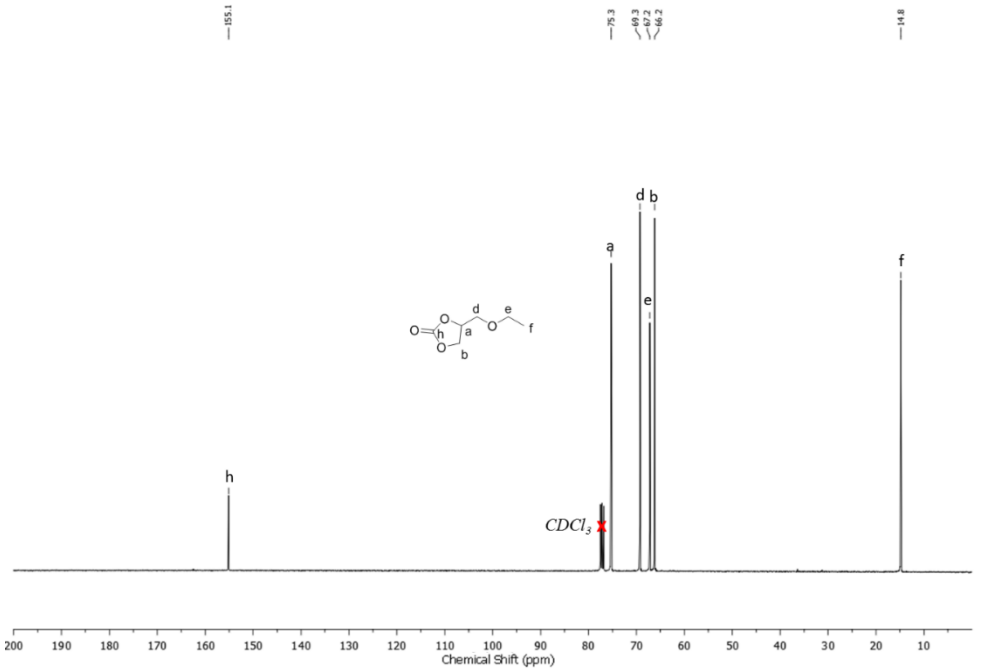
SI - Figure II-1: ^{1}H NMR spectrum of C_5-Butane in CDCl3



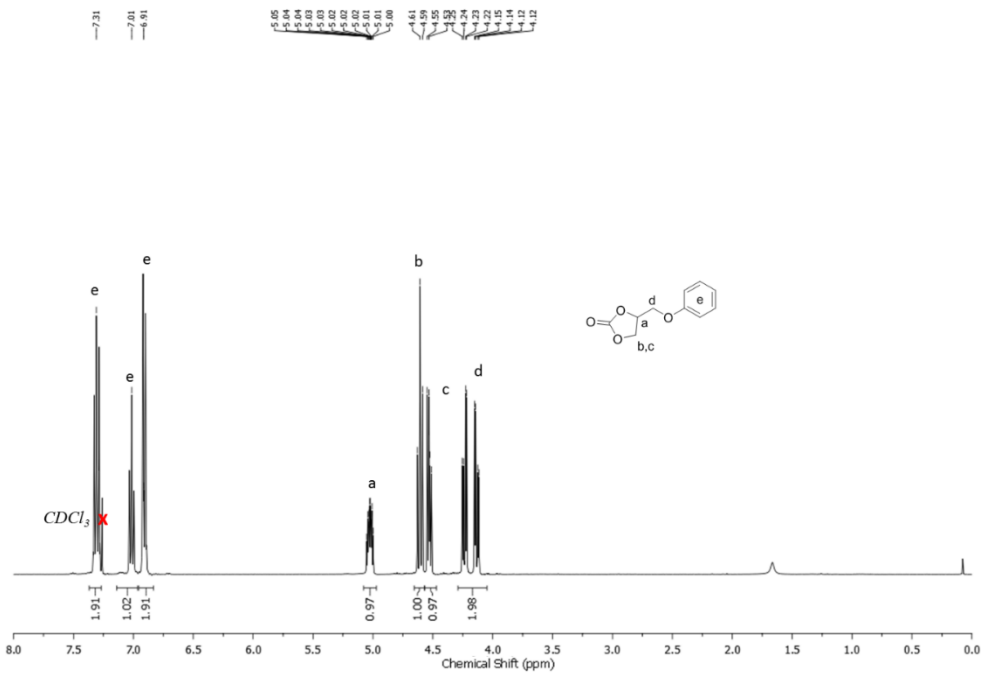
SI - Figure II-2 : ^{13}C NMR spectrum of C5-Butane in CDCl3



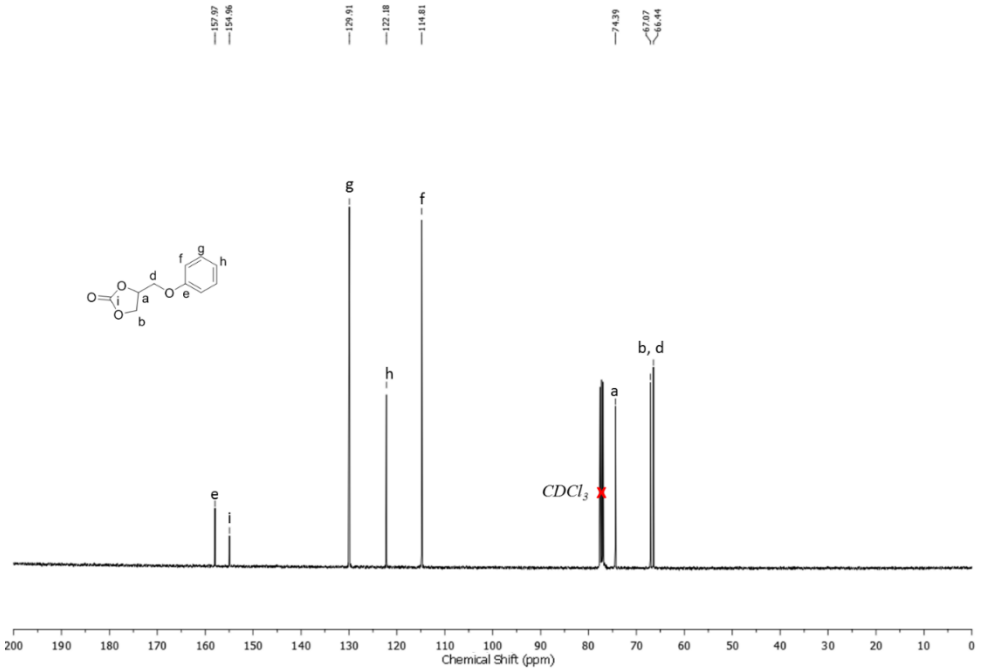
SI - Figure II-3 : ^{1}H NMR spectrum of C_5-Ethyl-Ether in $CDCl_3$



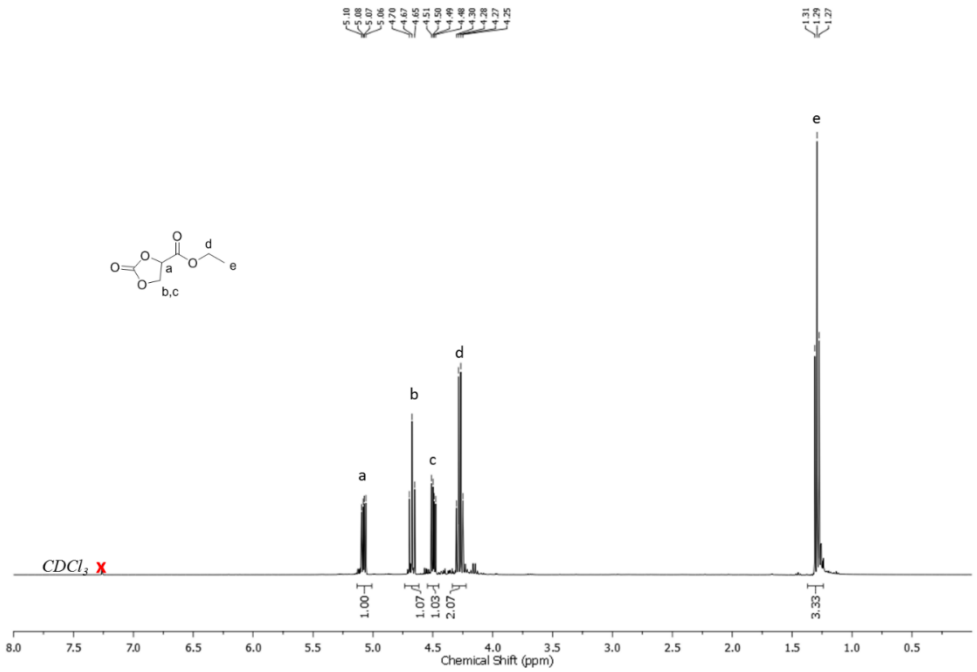
SI - Figure II-4 : ^{13}C NMR spectrum of C_5-Ethyl-Ether in $CDCl_3$



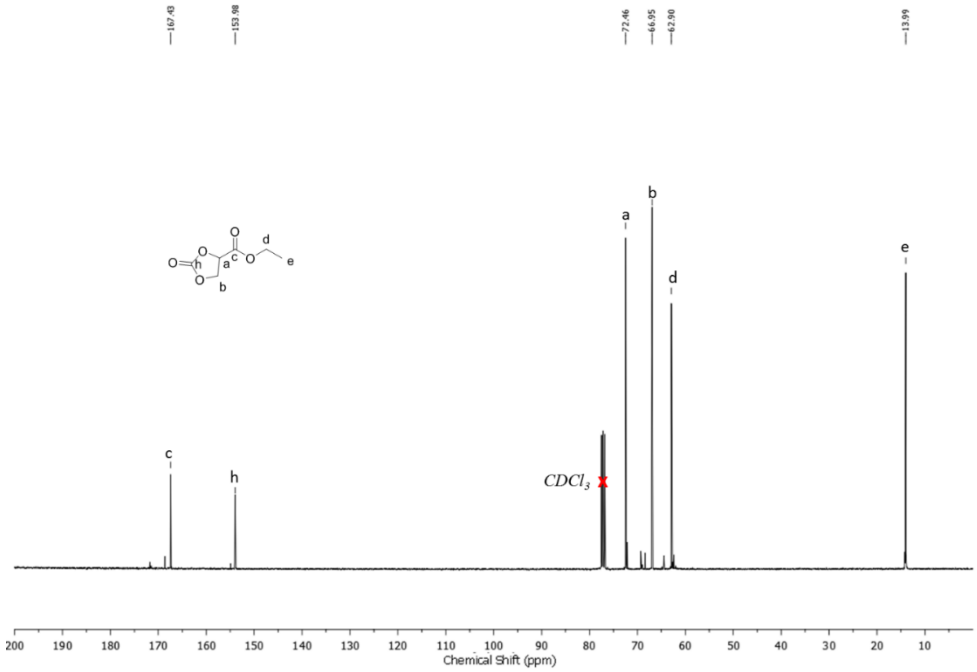
SI - Figure II-5 : ^{1}H NMR spectrum of C_5-Phenyl-Ether



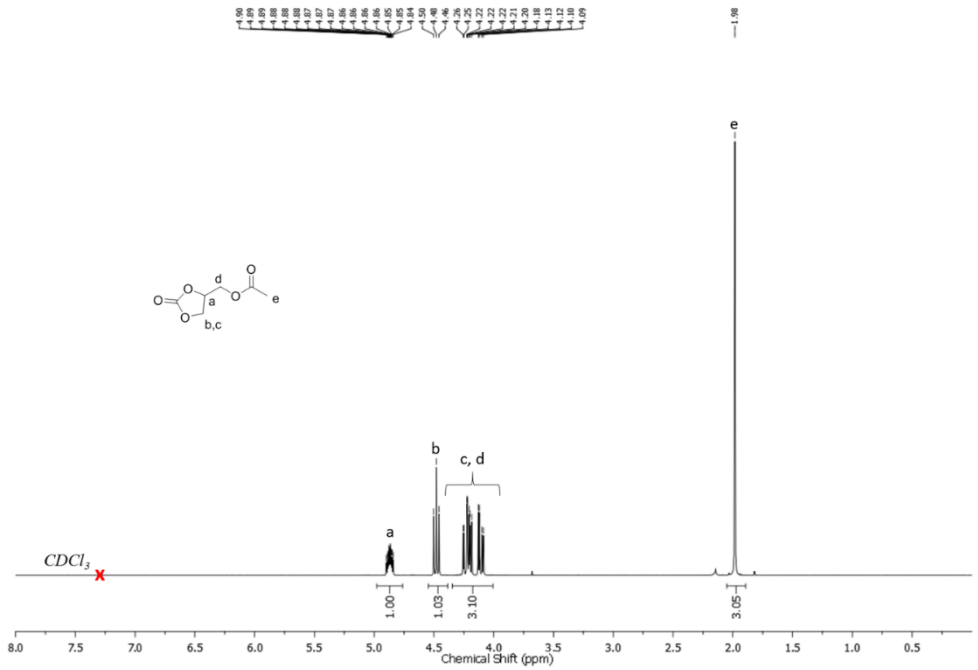
SI - Figure II-6: ^{13}C NMR spectrum of C_5-Phenyl-Ether in $CDCl_3$



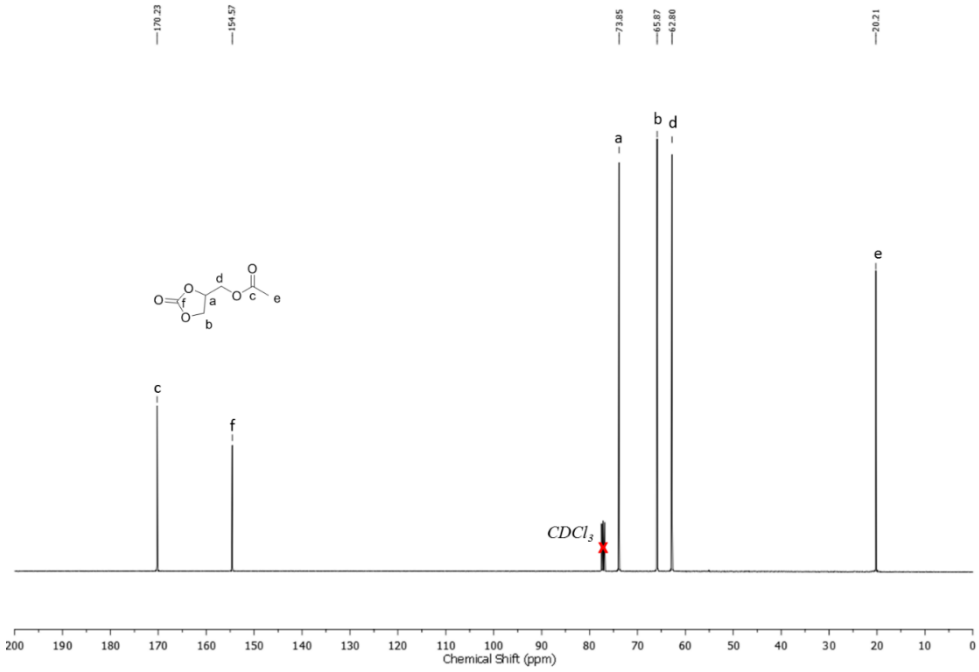
SI - Figure II-7: ^{1}H NMR spectrum of C5-Ethyl-Ester in CDCl3



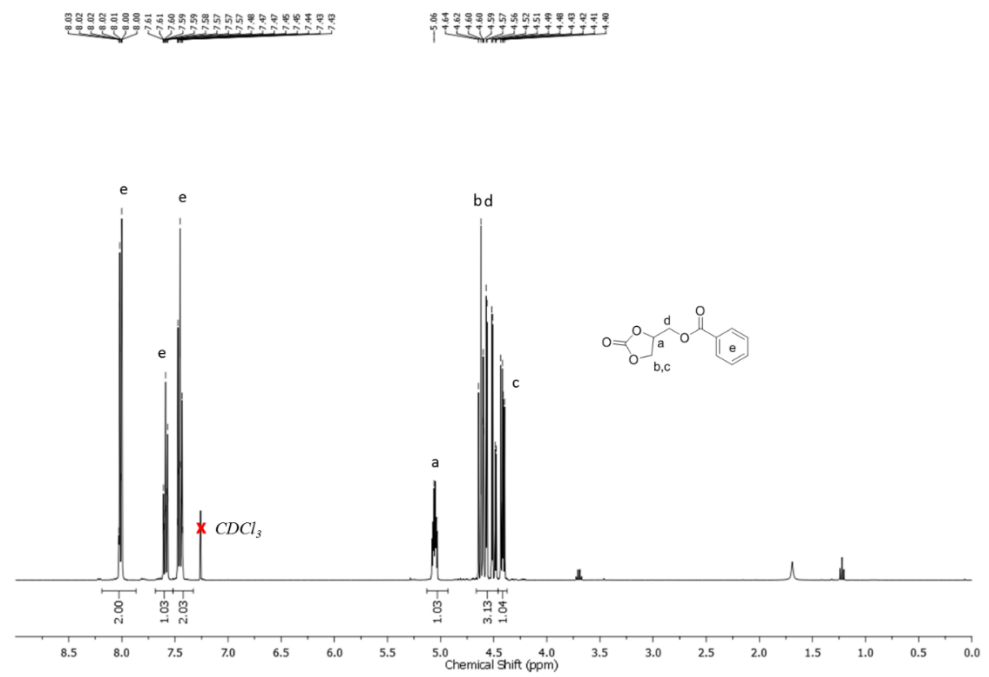
SI - Figure II-8: ^{13}C NMR spectrum of C_5-Ethyl-Ester in $CDCl_3$



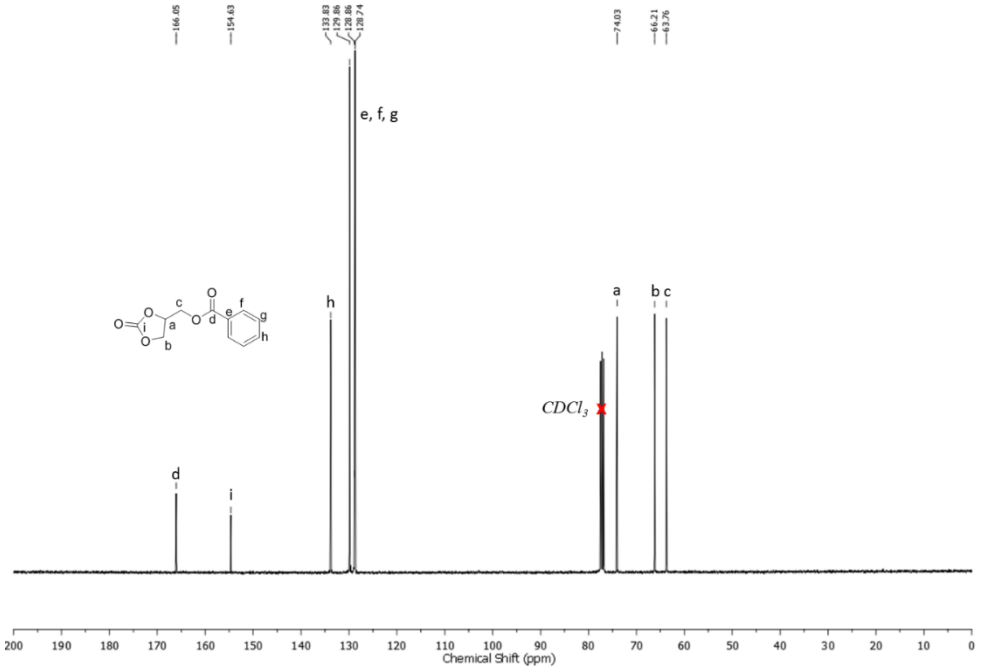
SI - Figure II-9: ^{1}H NMR spectrum of C_5-Acetate in $CDCl_3$



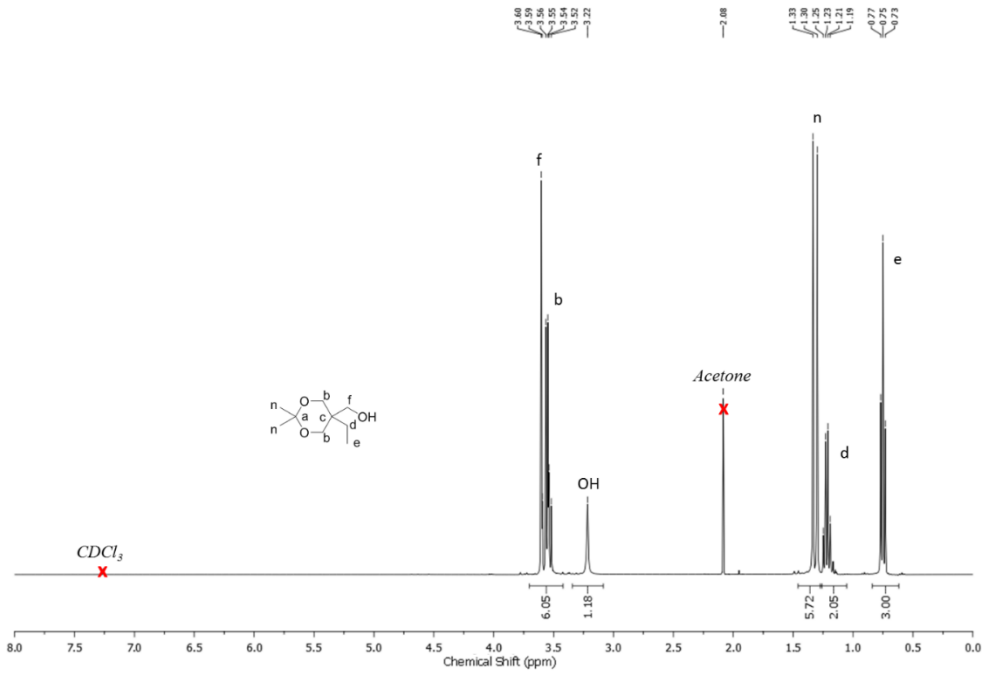
SI - Figure II-10: ^{13}C NMR spectrum of C_5-Acetate in $CDCl_3$



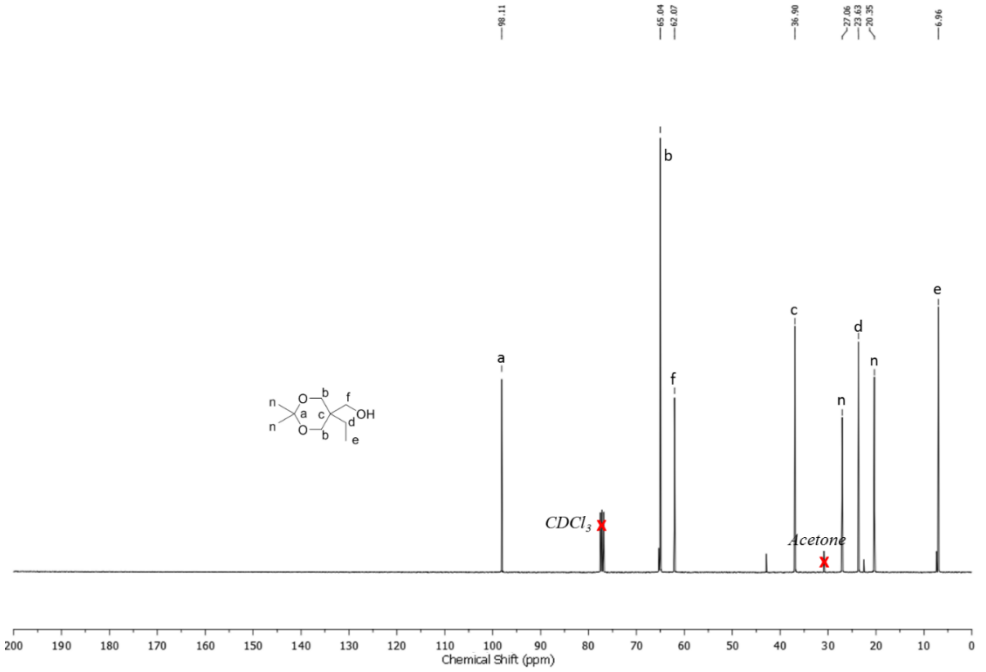
SI - Figure II-11: ^{1}H NMR spectrum of C_5-Benzoate in $CDCl_3$



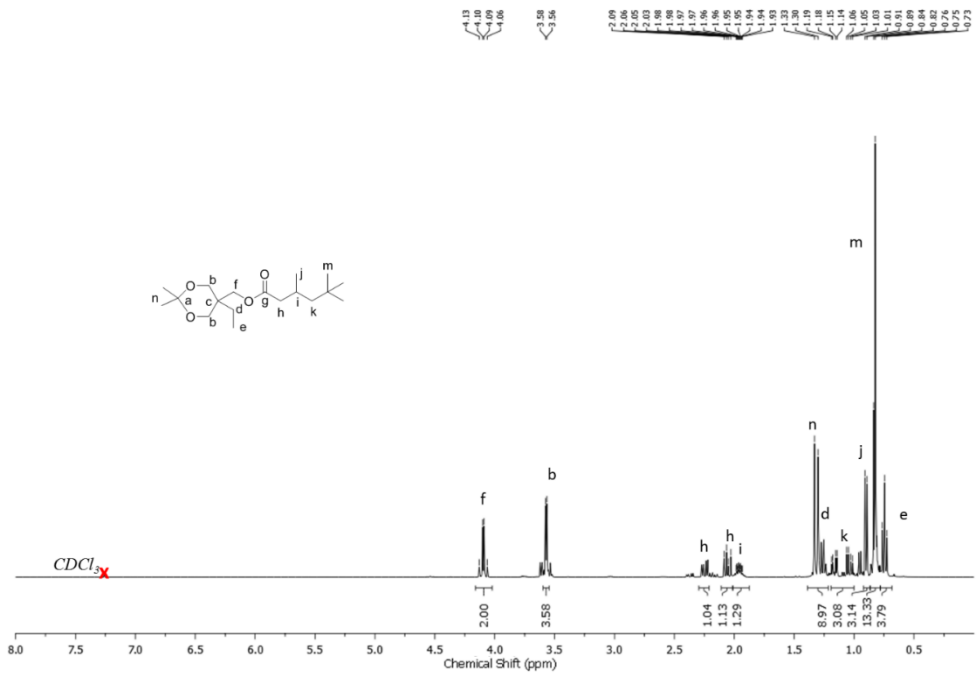
SI - Figure II-12: ^{13}C NMR spectrum of C_5-Benzoate in $CDCl_3$



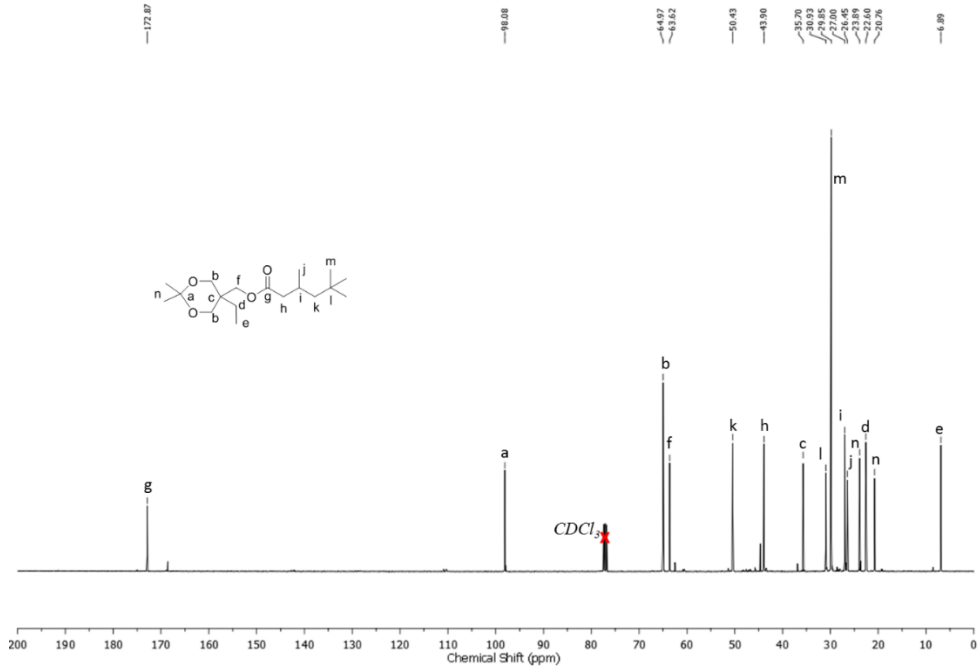
SI - Figure II-13: ^{1}NMR spectrum of Protected TMP in $CDCl_3$



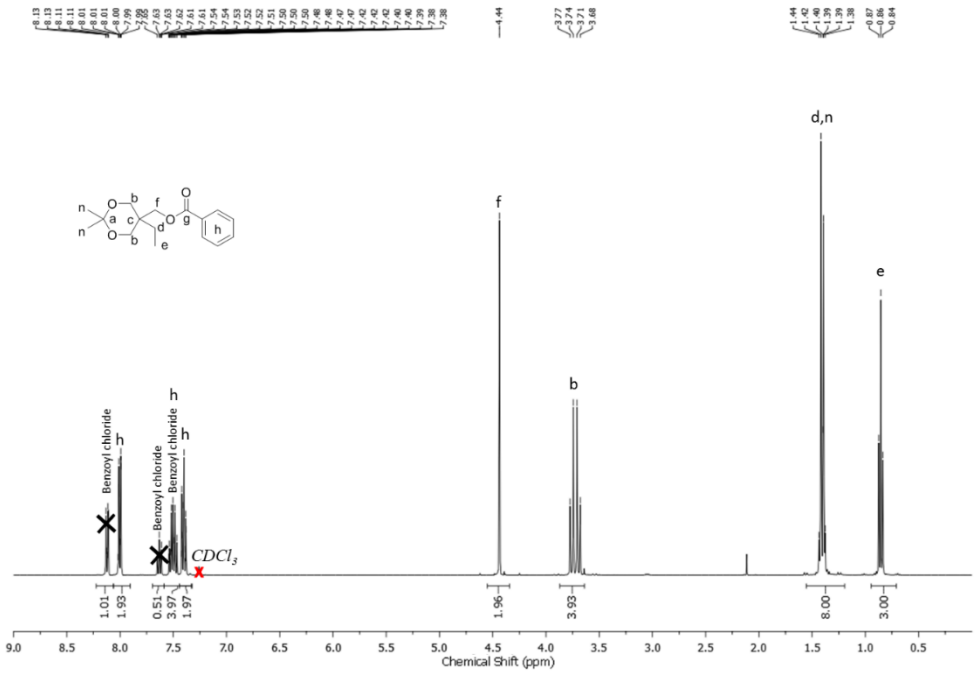
SI - Figure II-14: ^{13}C NMR spectrum of Protected TMP in $CDCl_3$



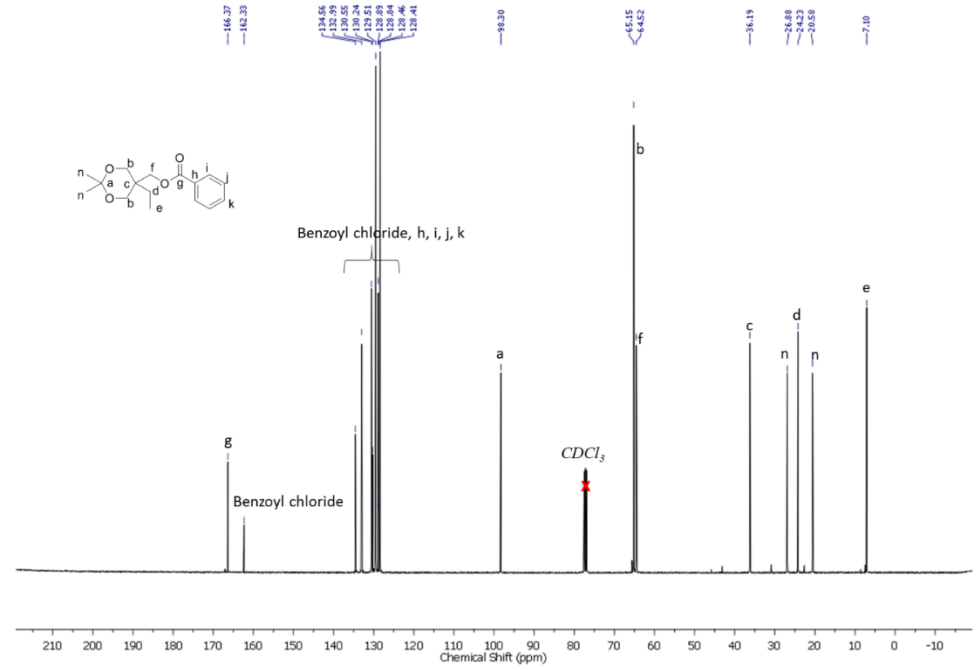
SI - Figure II-15: ^{1}H NMR spectrum of Esterified Protected TMP 1 in $CDCl_3$



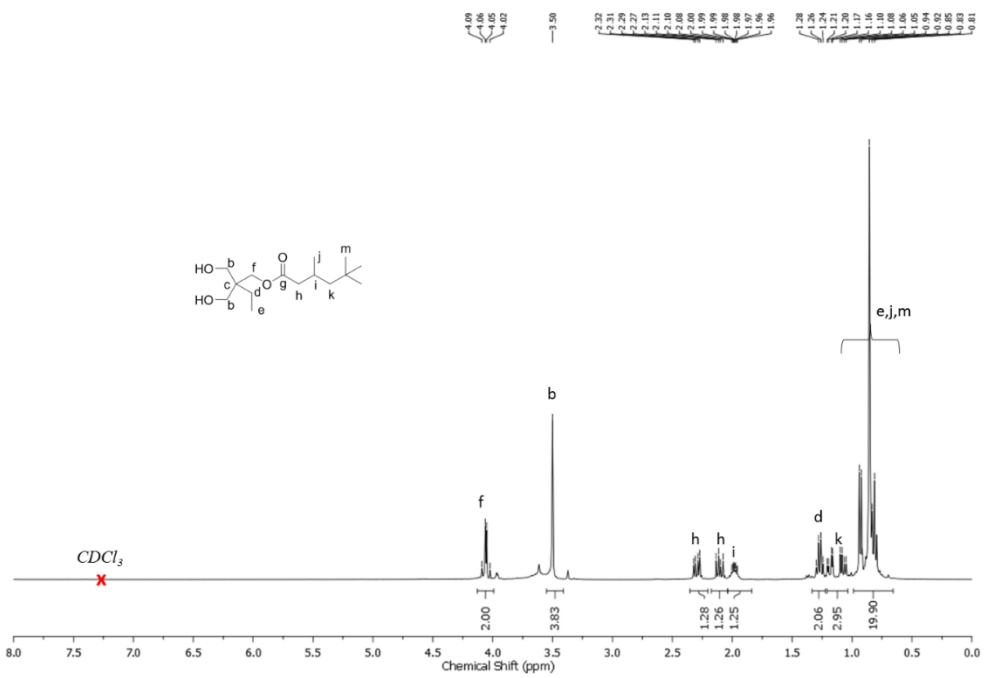
SI - Figure II-16: ^{13}C NMR spectrum of Esterified Protected TMP 1 in $CDCl_3$



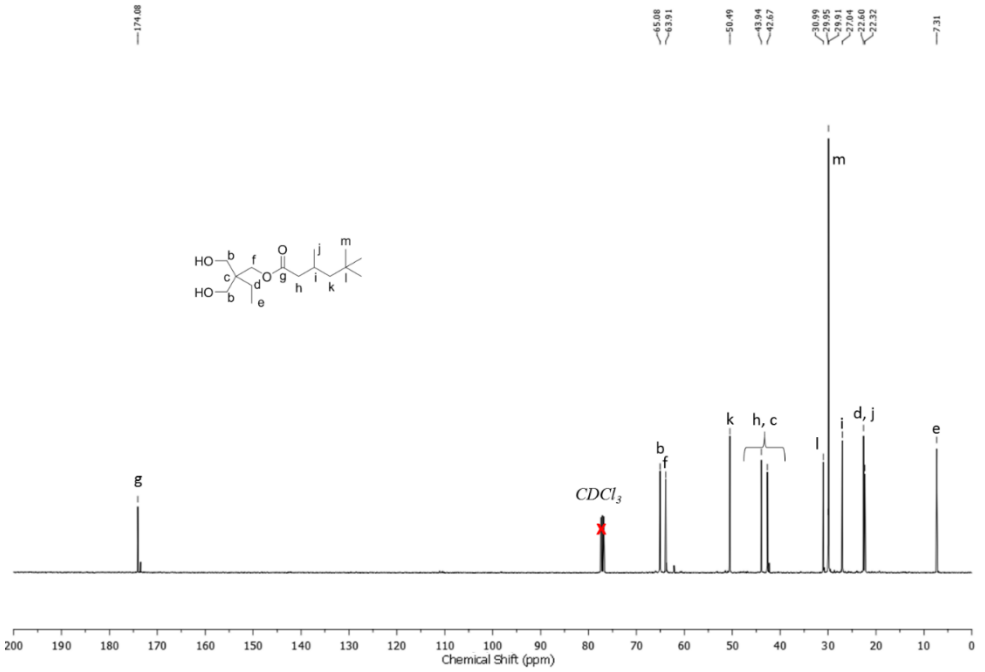
SI - Figure II-17: ^{1}H NMR spectrum of Esterified Protected TMP 2 in $CDCl_3$



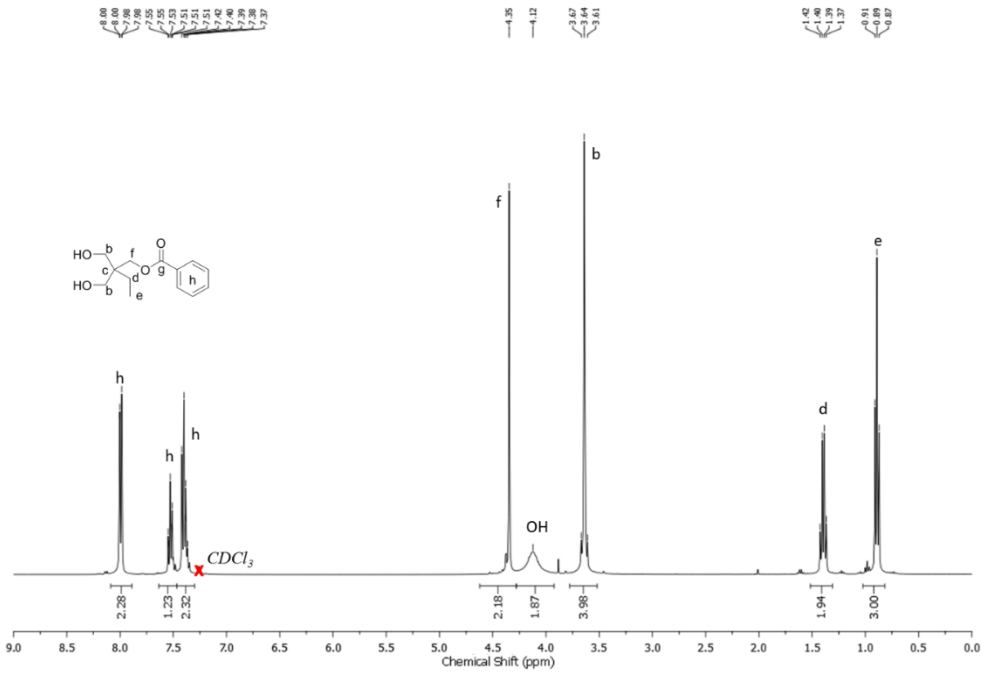
SI - Figure II-18: ^{13}C NMR spectrum of Esterified Protected TMP 2 in $CDCl_3$



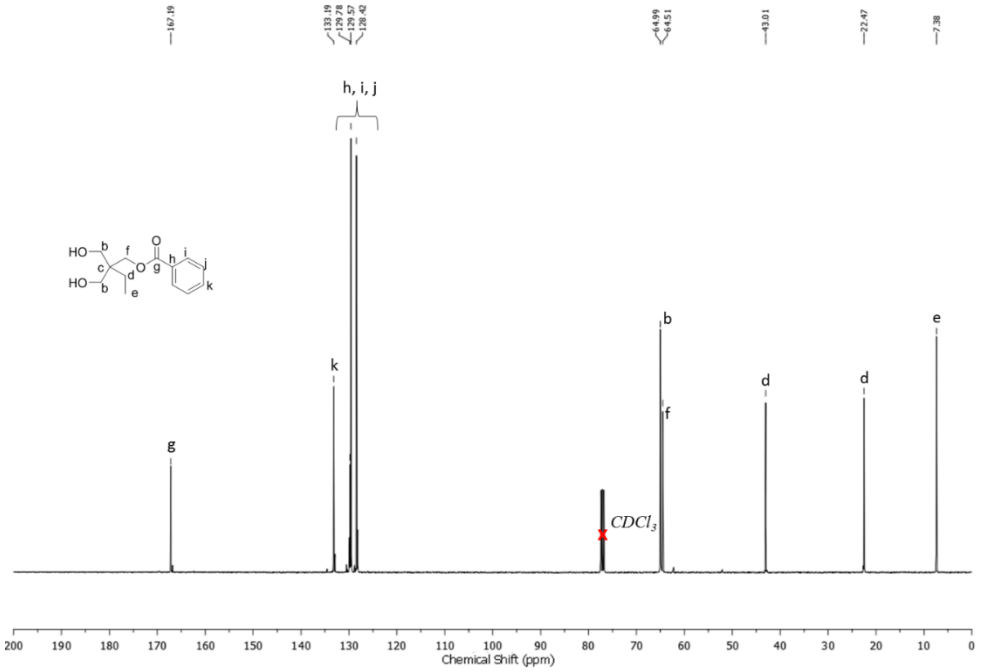
SI - Figure II-19: ^{1}H NMR spectrum of Esterified TMP 1 in $CDCl_3$



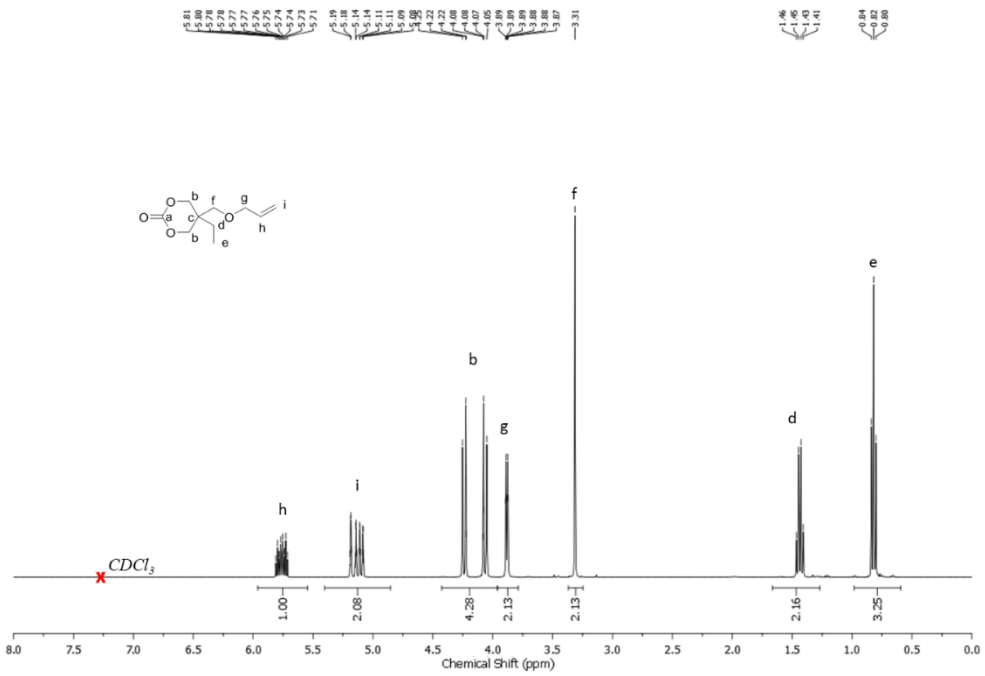
SI - Figure II-20: ^{13}C NMR spectrum of Esterified TMP 1 in $CDCl_3$



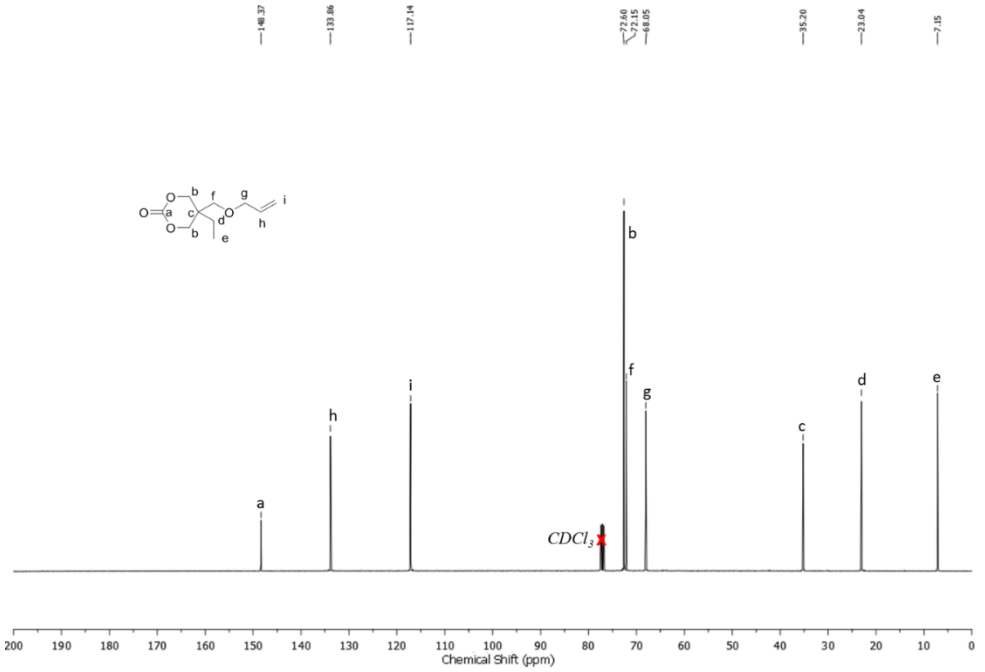
SI - Figure II-21: ^{1}H NMR spectrum of Esterified TMP 2 in $CDCl_3$



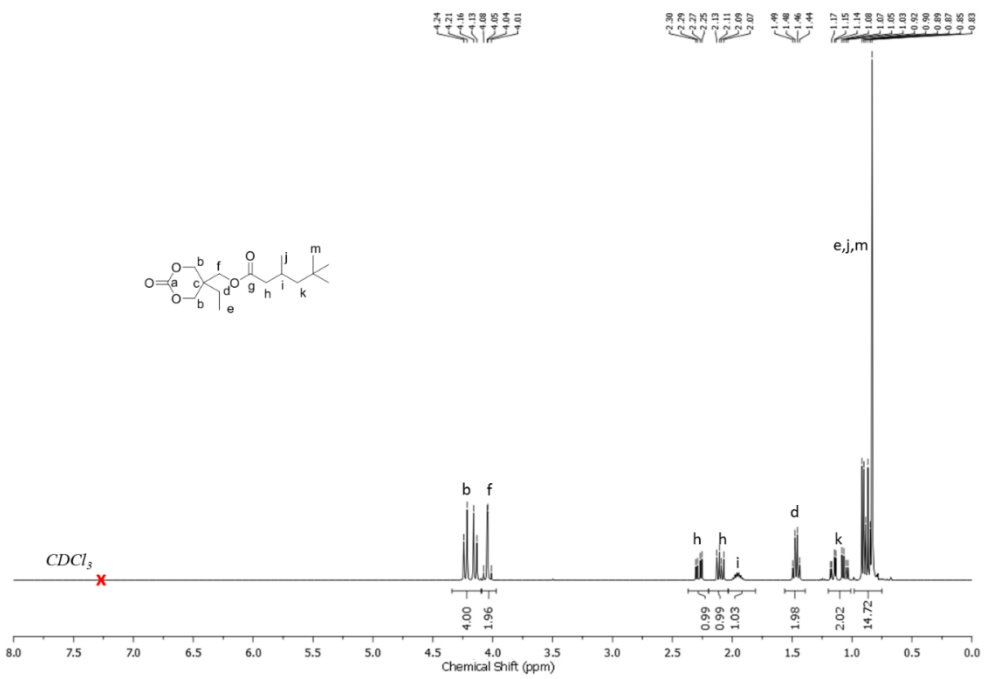
SI - Figure II-22: ^{13}C NMR spectrum of Esterified TMP 2 in $CDCl_3$



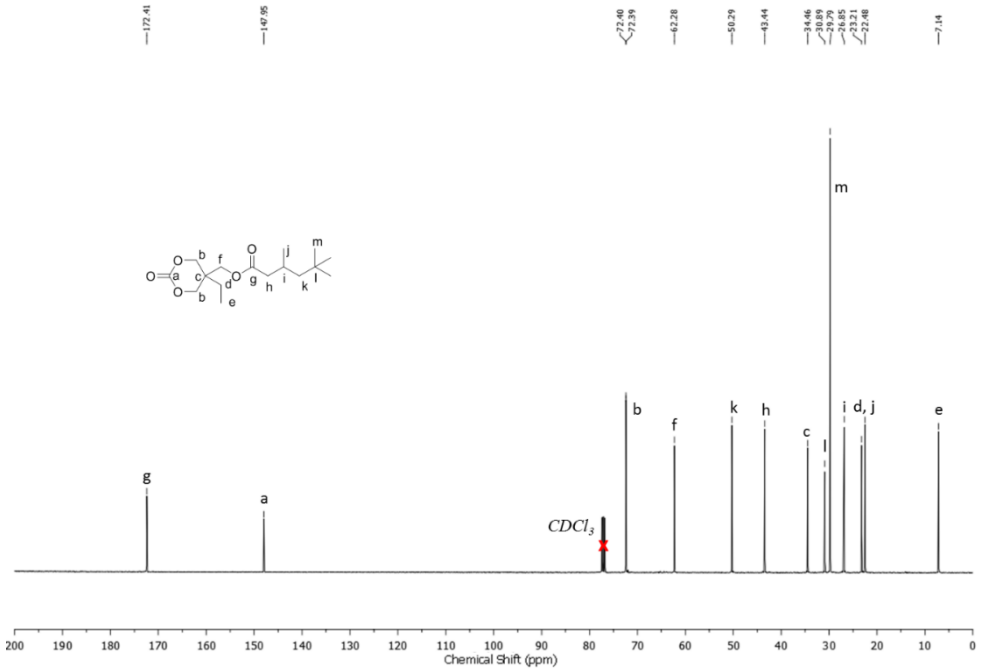
SI - Figure II-23: ^{1}H NMR spectrum of C_6-Allyl-Ether in $CDCl_3$



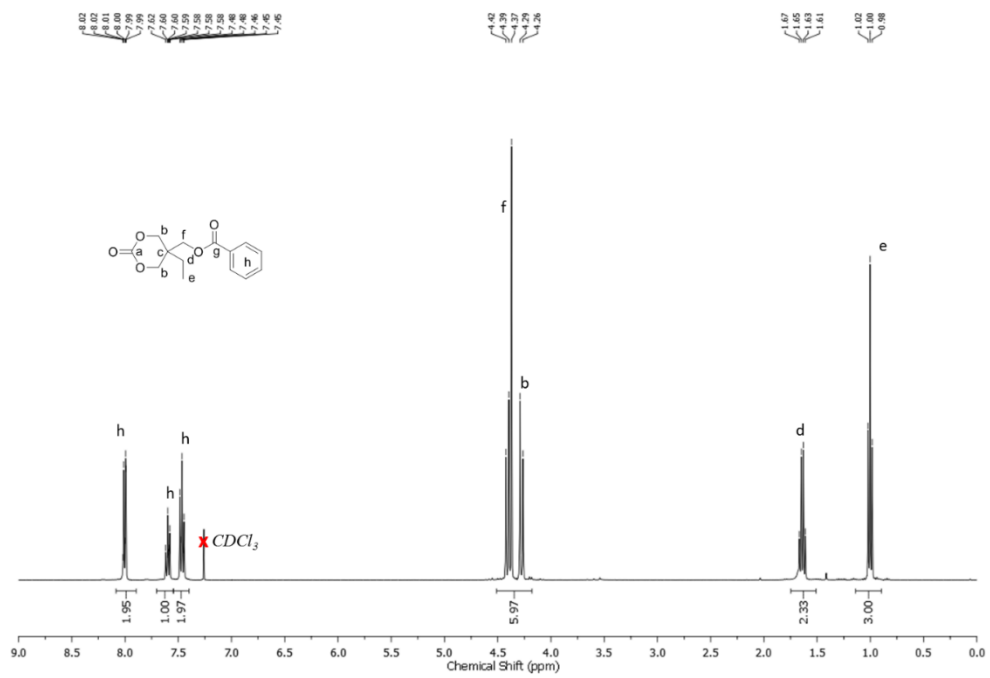
SI - Figure II-24: ^{13}C NMR spectrum of C_6-Allyl-Ether in $CDCl_3$



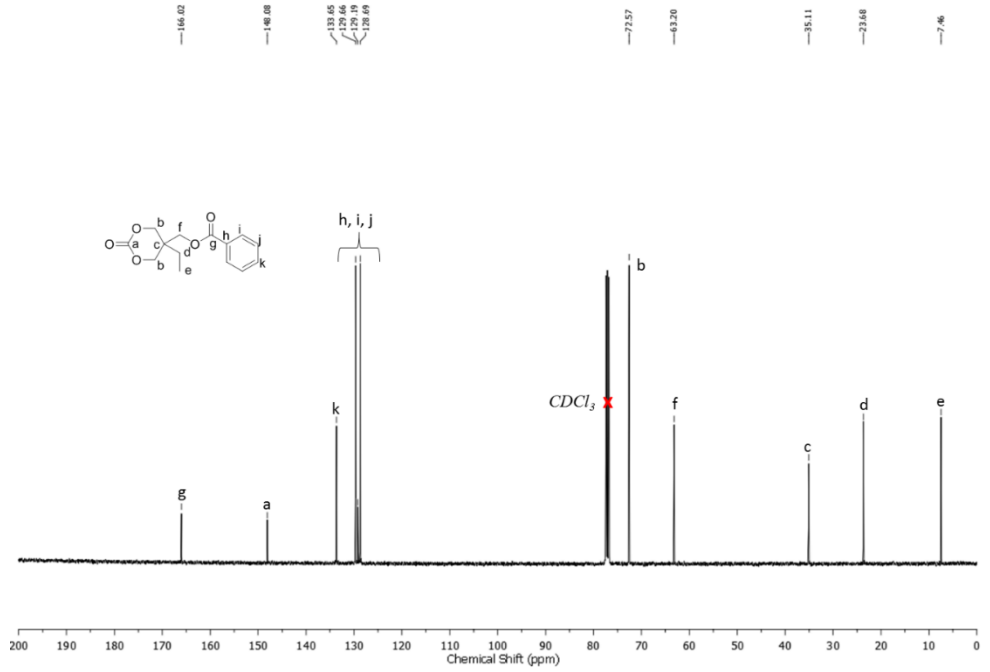
SI - Figure II-25: ^{1}H NMR spectrum of C6-Trimethylhexanoate in CDCl3



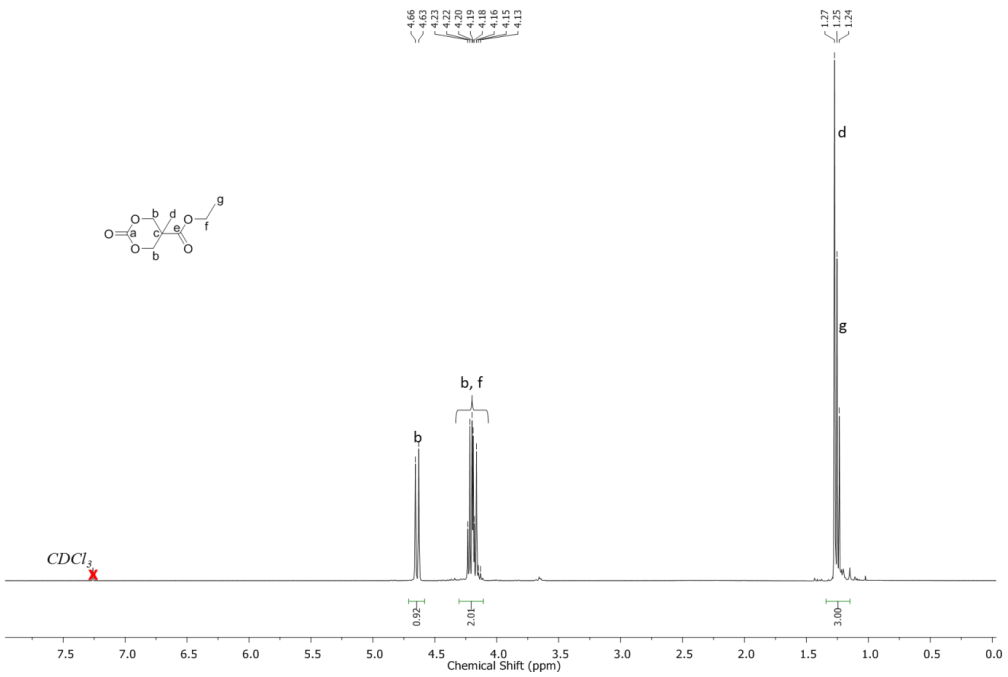
SI - Figure II-26: ^{13}C NMR spectrum of C_6-Trimethylhexanoate in $CDCl_3$



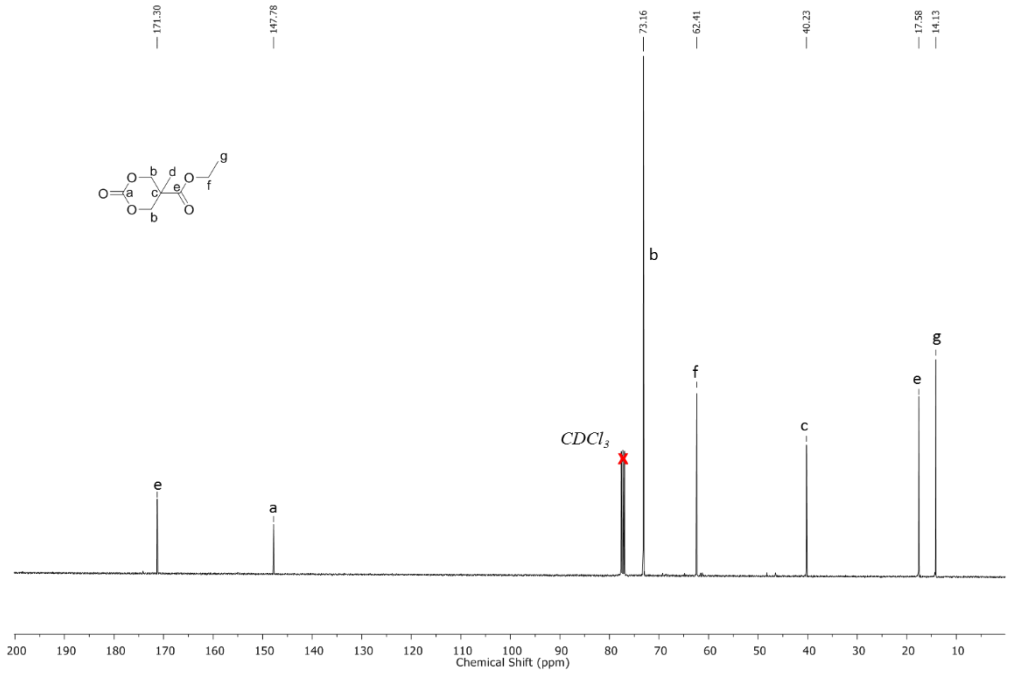
SI - Figure II-27: ^{1}H NMR spectrum of C_6-Benzoate in $CDCl_3$



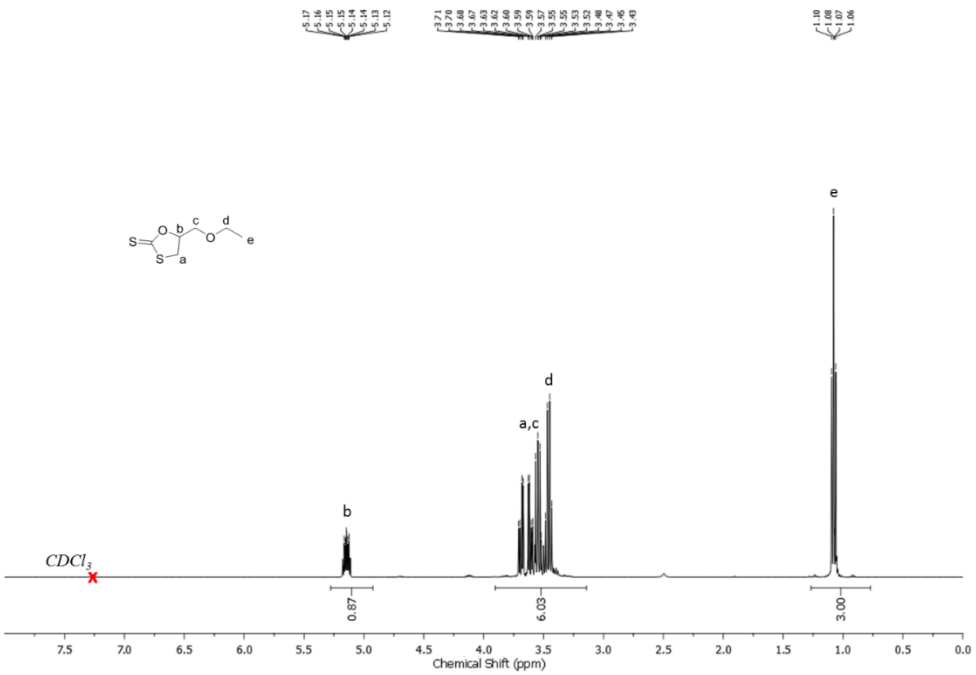
SI - Figure II-28: ^{13}C NMR spectrum of C6-Benzoate in $CDCl_3$



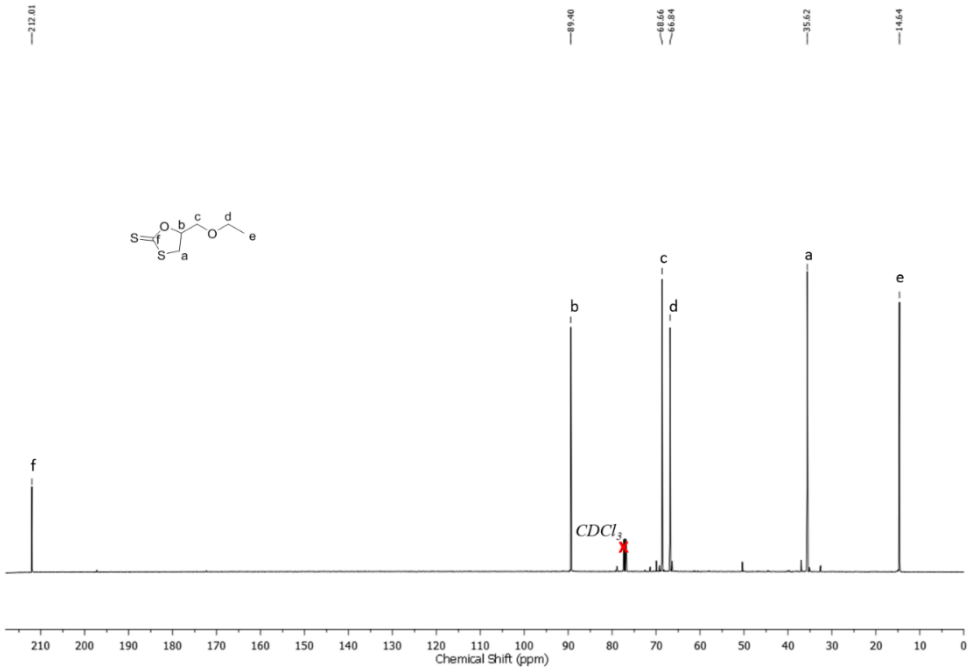
SI - Figure II-29: ^{1}NMR spectrum of C_6-Ethyl-Ester in $CDCl_3$



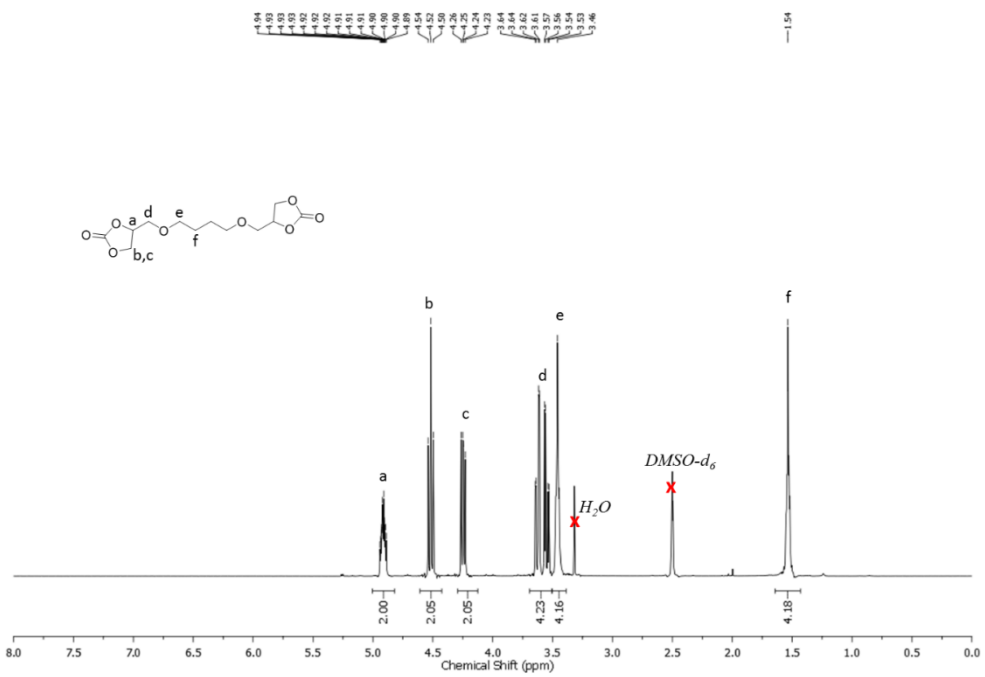
SI - Figure II-30: ^{13}C NMR spectrum of C_6-Ethyl-Ester in $CDCl_3$



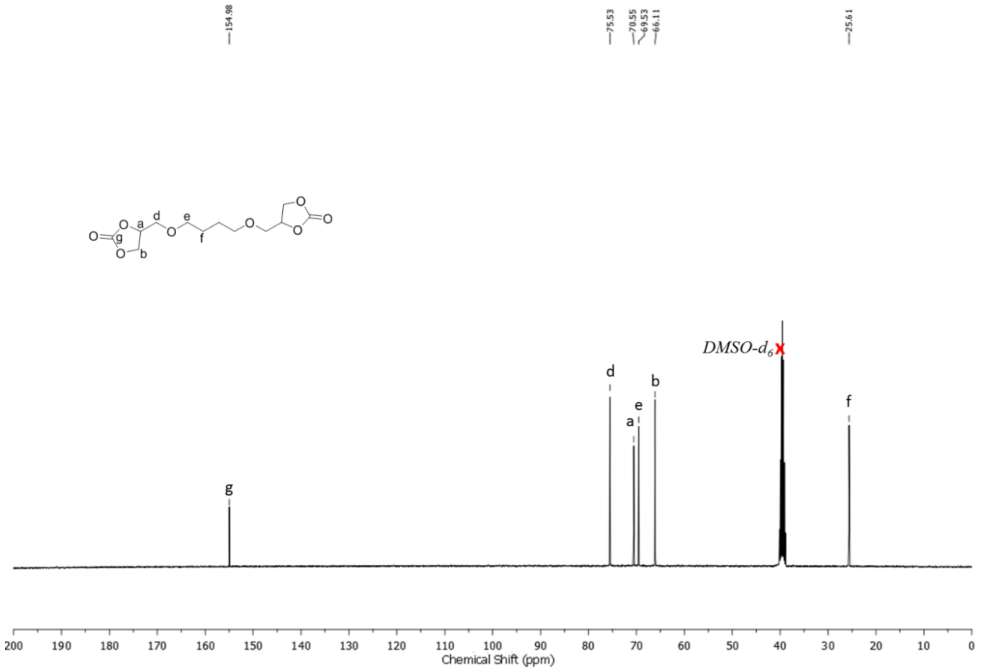
SI - Figure II-31: ^{1}H NMR spectrum of C_s-Ethyl-Ether in $CDCl_3$



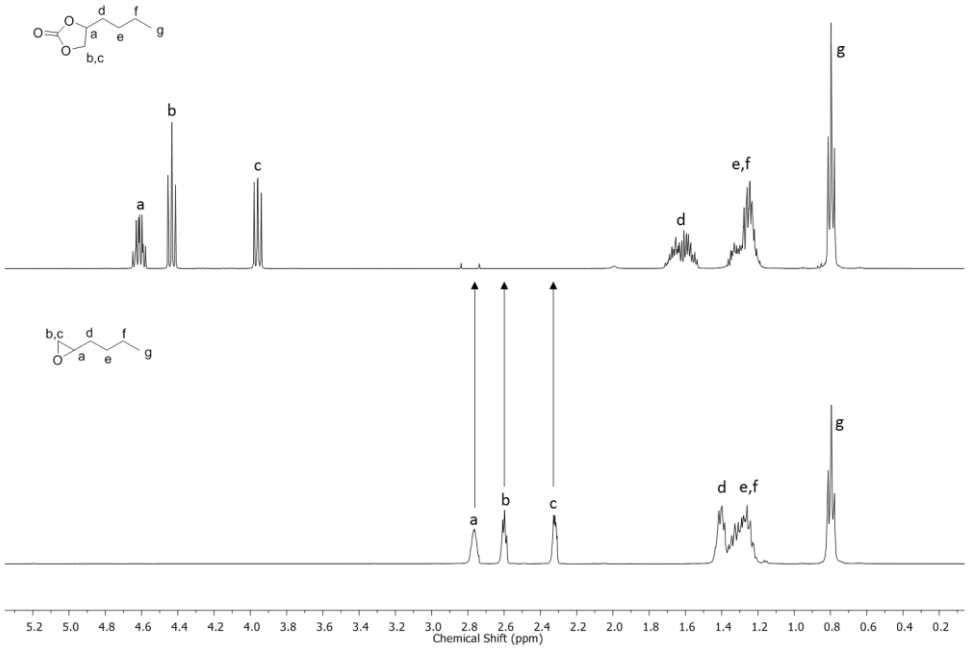
SI - Figure II-32: ^{13}C NMR spectrum of C_s-Ethyl-Ether in $CDCl_3$



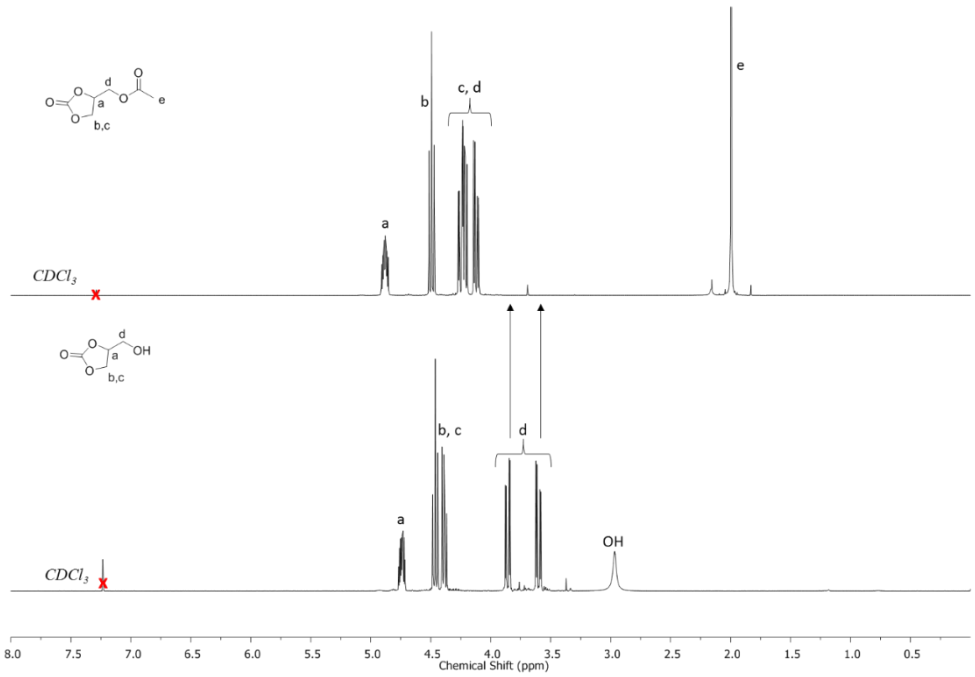
SI - Figure II-33: ^{1}H NMR spectrum of Bis-C_5-Ether in DMSO-d_6



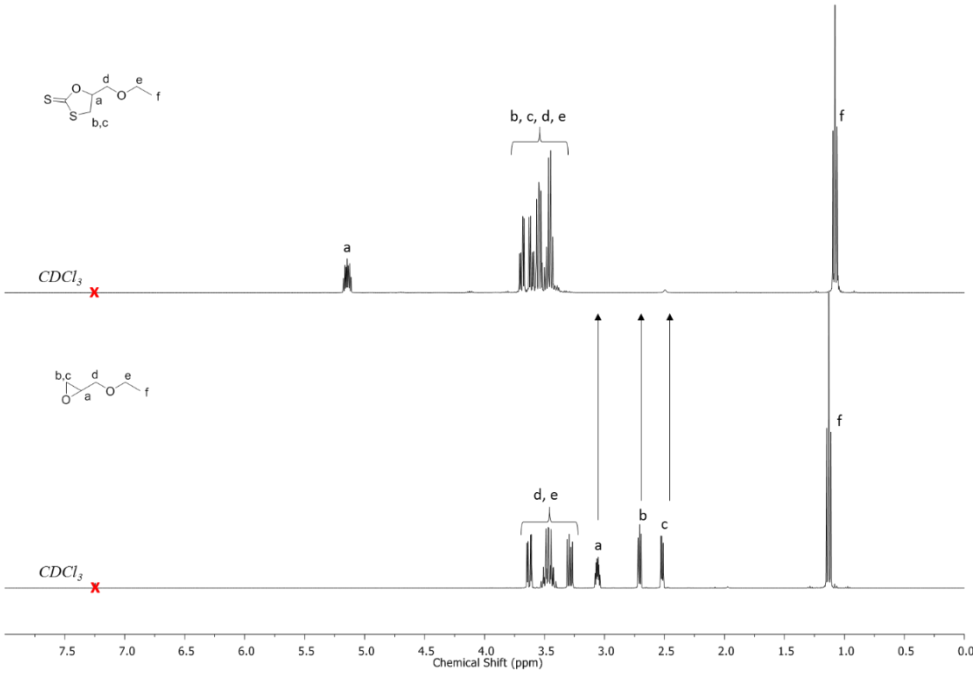
SI - Figure II-34: ^{13}C NMR spectrum of Bis-C_5-Ether in $CDCl_3$



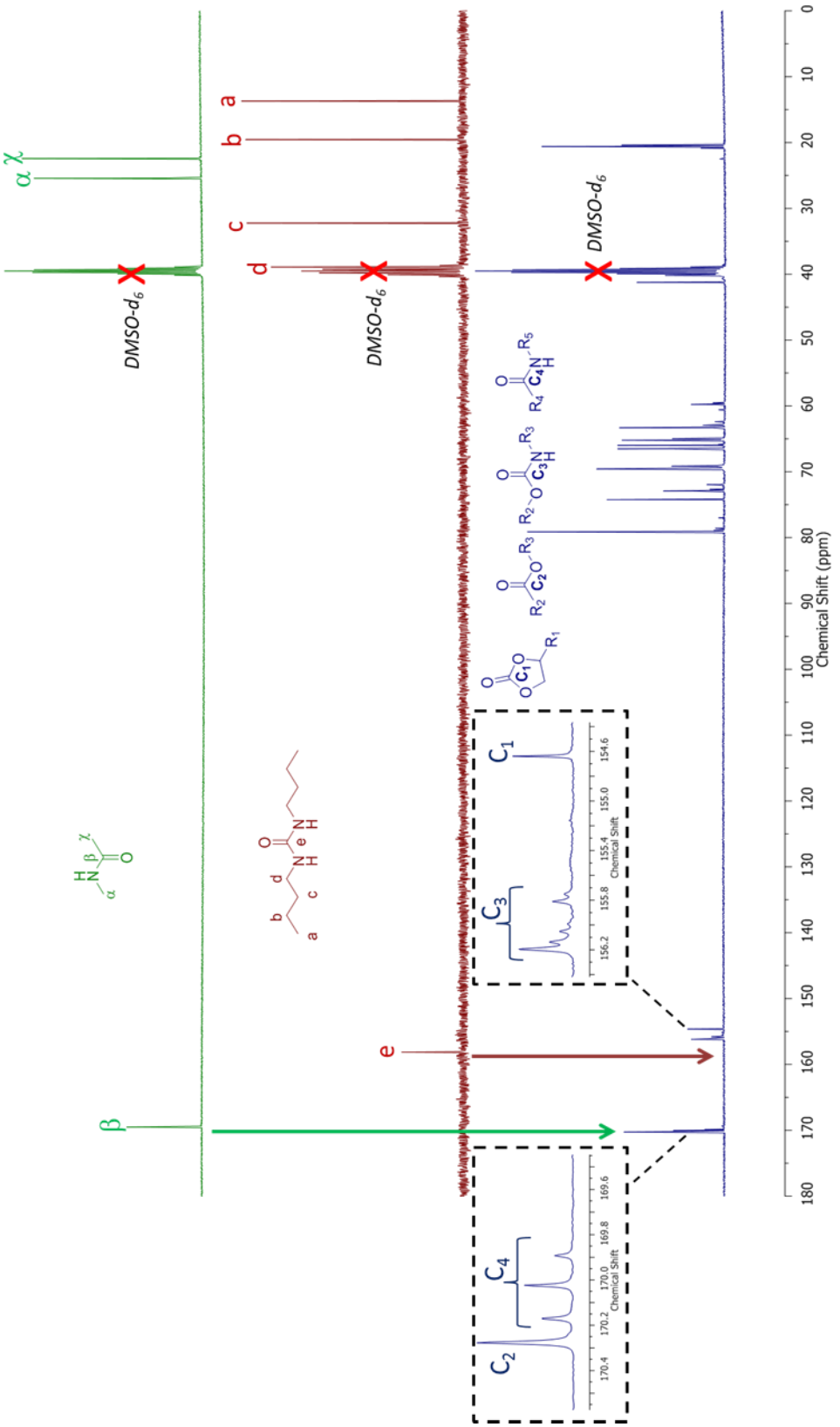
SI - Figure II-35: Stacked ^{1}H NMR spectra of 1,2-epoxyhexane and C_5-Butane in $CDCl_3$



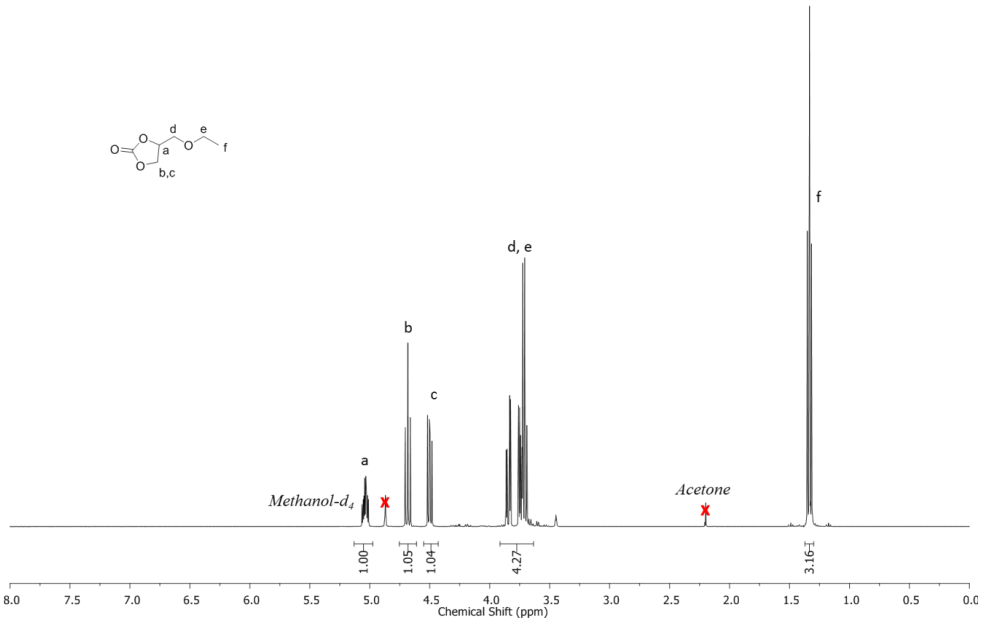
SI - Figure II-36: Stacked ^{1}H NMR spectra of glycerin carbonate and C_5-Acetate in $CDCl_3$



SI - Figure II-37: Stacked ^1H NMR spectra of ethyl glycidyl ether and C_s-Ethyl-Ether in $CDCl_3$

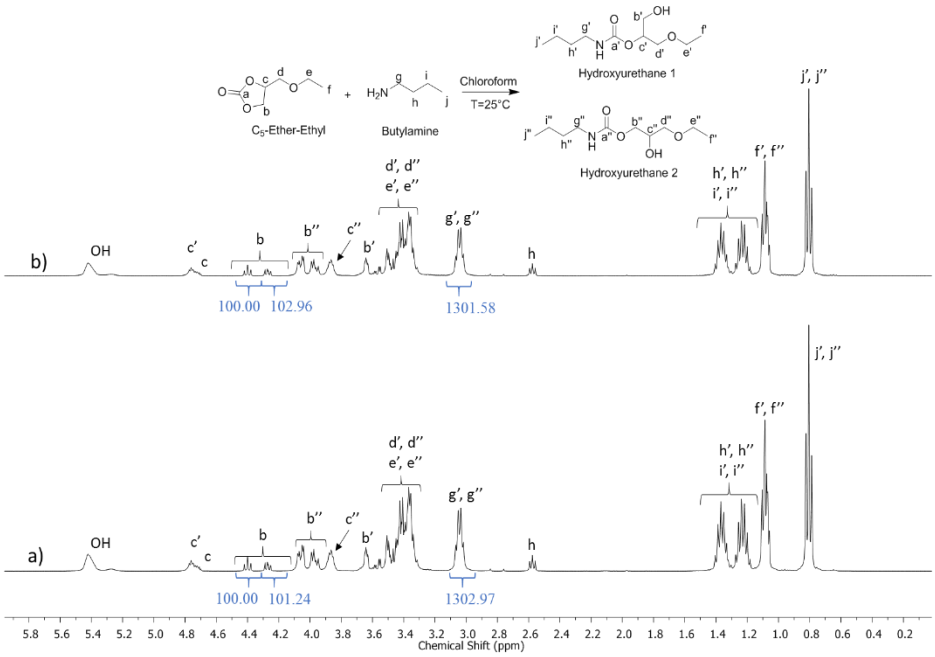


SI - Figure II-38: Stacked ^{13}C NMR spectra of N-dimethylacetamide (green spectrum), 1,3-dibutylurea (red spectrum) and hydroxyurethane compounds synthesized from reaction between C5-Acetate and EDR-148 (blue spectrum)

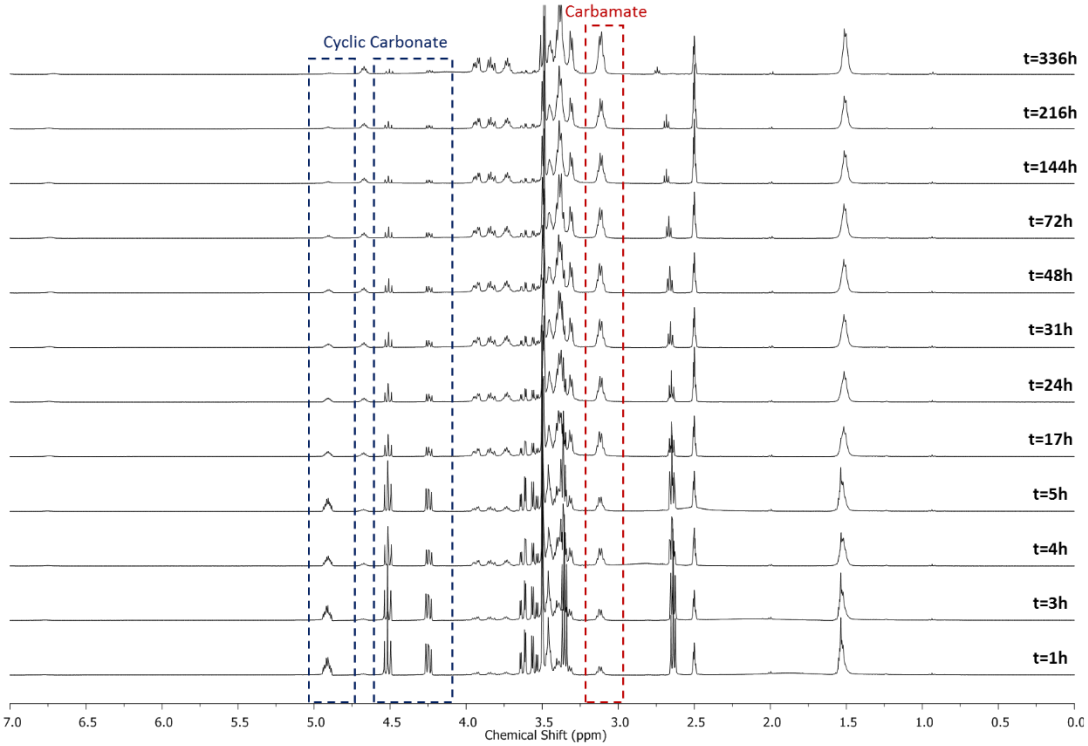


SI - Figure II-39: ^{1}H NMR spectrum of C_5-Ethyl-Ether in Methanol-d_4 after 48 h

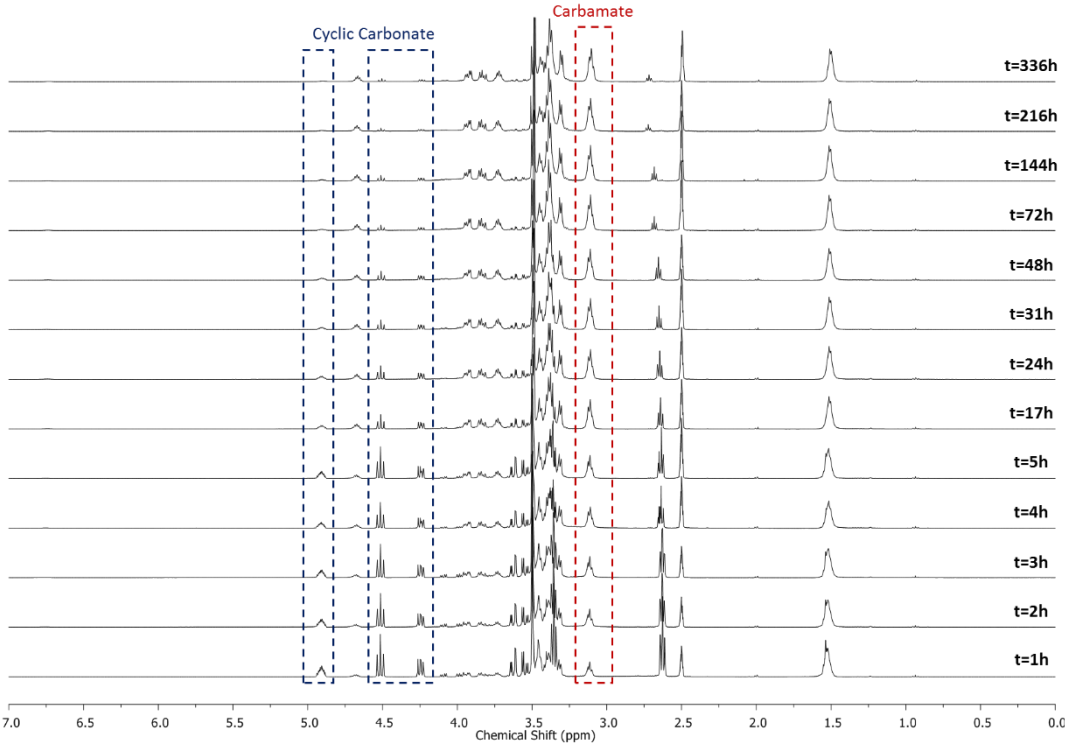
VIII.2 Graphical data of kinectic measurements



SI - Figure II-40: Stacked ^{1}H NMR spectra of hydroxyurethane compounds in $CDCl_3$ synthesized in chloroform from C_5-Ethyl-Ether and butylamine at a) 24h and b) 7 days of reaction

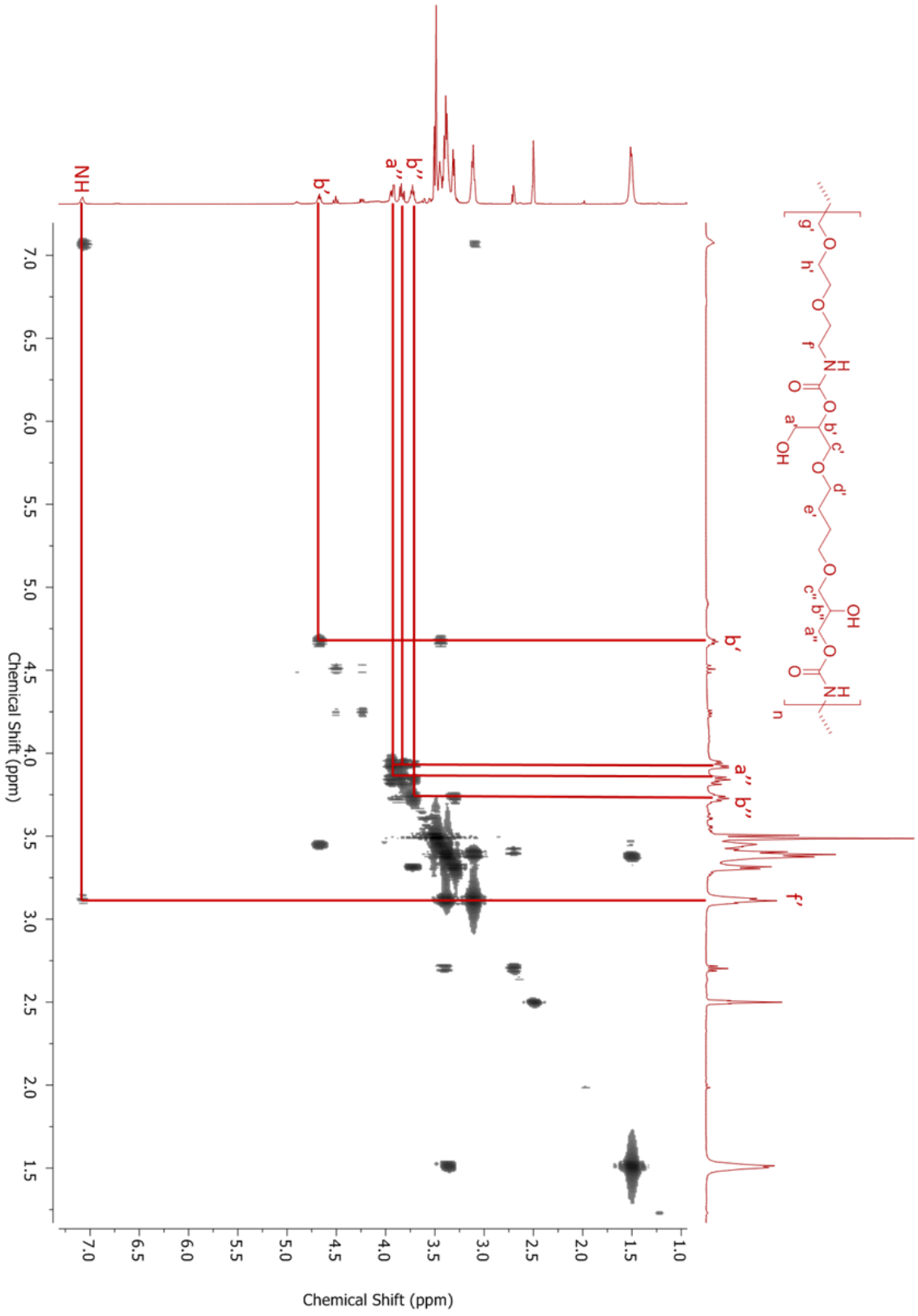


SI - Figure II-41: Stacked ^{1}H NMR spectra in DMSO-d_6 monitoring of the reaction between Bis-C_5-Ether and EDR-148 with a ratio 1:1, at 25°C in chloroform

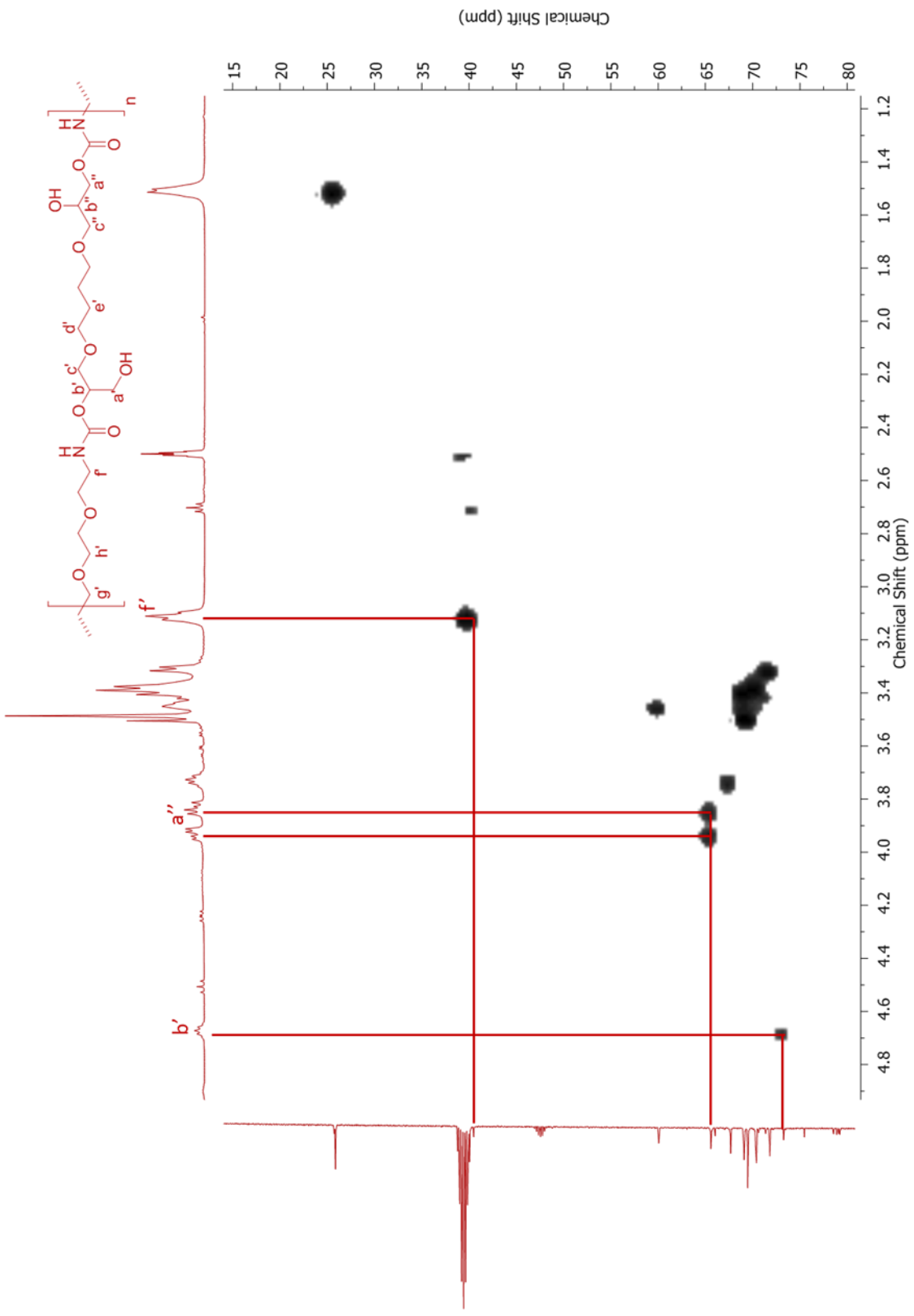


SI - Figure II-42: Stacked ^{1}H NMR spectra in DMSO-d_6 monitoring of the reaction between Bis-C_5-Ether and EDR-148 with a ratio 1:1, at 25°C in methanol

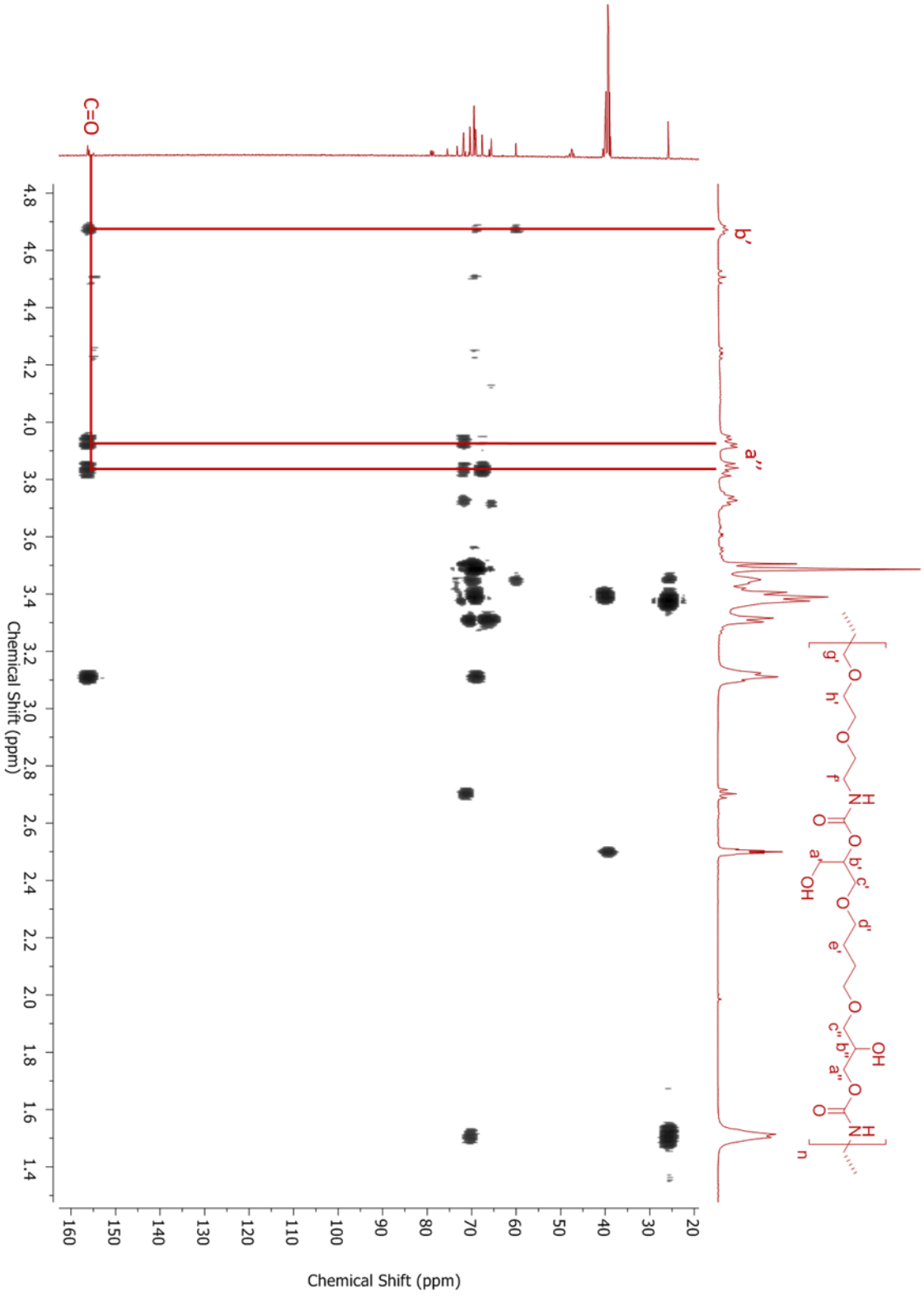
VIII.3 Graphical data of polyhydroxyurethane



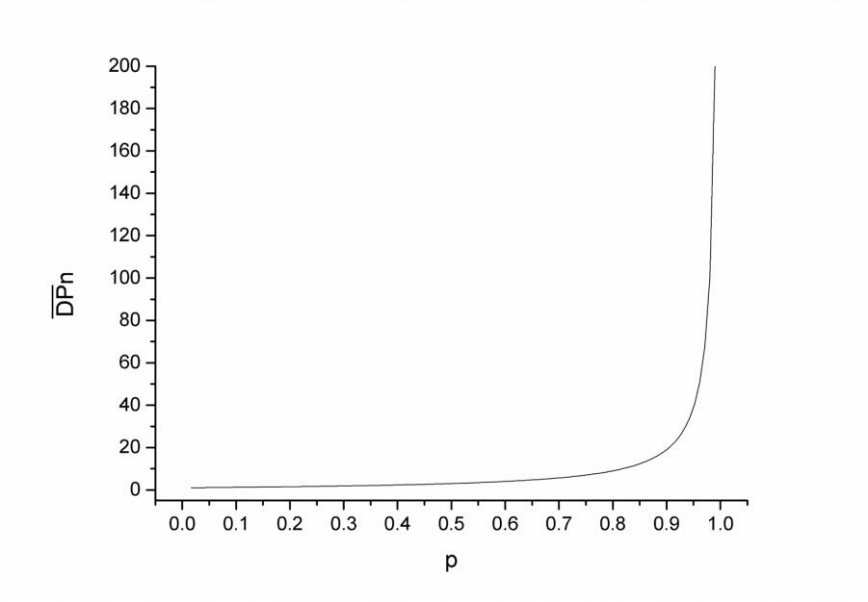
SI - Figure II-43: 2D COSY NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI - Figure II-44: 2D HSQC NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI - Figure II-45: 2D HMBC NMR spectra in DMSO-d_6 of PHU obtained from the reaction of Bis-C_5-Ether with EDR-148 in mixture chloroform/methanol



SI - Figure II-46: Theoretical evolution of the degree of polymerization ($\overline{DP}n$) according to advancement of reaction (p) during polyaddition of monomers in stoichiometric proportion

Conclusion Partie 1

La première partie de ce chapitre a montré une grande influence de la structure et de la nature des substituants des carbonates cycliques sur leur réactivité. Ces paramètres ont été évalués à l'aide de composés modèles monofonctionnels.

D'après les résultats obtenus, les meilleurs précurseurs carbonates cycliques pour synthétiser des PHUs à température ambiante sans avoir recours à des produits dangereux sont les carbonates cycliques à 5 membres porteurs de substituants éthers. De plus, ces précurseurs permettent d'accéder à des polymères PHUs sans la formation de sous-produits.

Il a également été démontré que le solvant permet une activation du carbonyle du carbonate en le rendant plus électrophile et donc plus favorable à une attaque nucléophile de l'amine.

Enfin, cette étude s'est focalisée sur les faibles conversions des carbonates cycliques à température ambiante lors de leur aminolyse, pouvant être à l'origine des faibles masses molaires des PHUs. Il a été démontré que le blocage de la réaction est principalement dû à la création de liaisons hydrogène inter- et intra-chaines limitant la diffusion des espèces lors de leur polymérisation. L'utilisation d'un solvant protique permet d'augmenter la conversion en limitant ces interactions et permet d'accéder à des polymères PHUs de plus hauts degrés de polymérisation.

Partie 2 - Evaluation de la réactivité des carbonates cyclique lors de leur aminolyse à partir de composés polyfonctionnels

Cette partie découle directement des résultats précédents. En effet la partie 1 a été consacrée à l'étude de la réactivité sur des molécules monofonctionnelles. Afin d'enrichir et de compléter ces résultats, une seconde étude a été menée sur la polymérisation de précurseurs polyfonctionnels. Dans cette seconde étude, la polymérisation carbonate cyclique / amine est caractérisée par DSC et RMN. Ces travaux sont présentés sous forme de publication scientifique soumise dans *Journal of Applied Polymer Science.*

Hydrogen bonds prevent obtaining high molar masse PHUs

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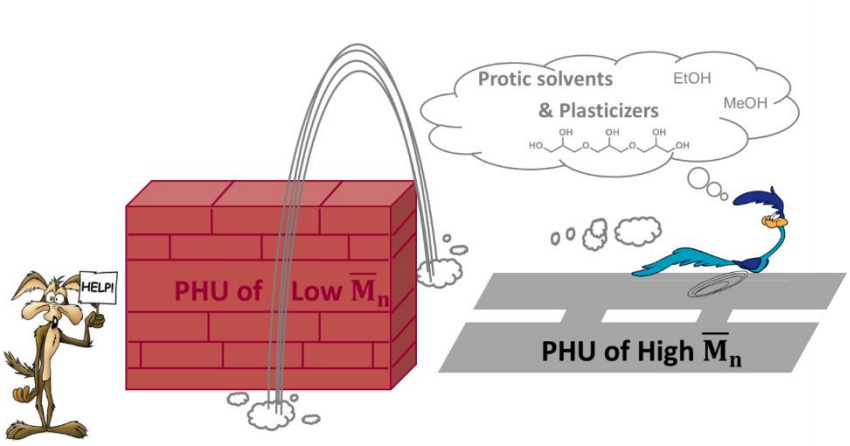
I. Abstract

Poly(hydroxyurethane)s (PHUs) are desired to replace PolyUrethanes (PUs) which are synthesized using harmful isocyanates. Nevertheless, the synthesis of PHUs starting from cyclic carbonates and amines displays two major drawbacks: the low reactivity observed during the opening of (poly)cyclic carbonates by (poly)amines and the low molar masses of polymers obtained. Currently, intensive work is carried out in order to increase the efficiency of the aminolysis of cyclic carbonates reaction but very few is dedicated to explaining the limitations of molar masses of PHUs. This article aims at demonstrating that the low molar masses can be explained by the existence of side reactions and the uncomplete conversion of monomers during the polymerization. These conclusions were obtained after complete DSC and NMR studies that evidence that the incomplete conversion of monomers and therefore the low molar masses are caused mainly by hydrogen bonding and partly by the formation of urea.



II. Introduction

Polyurethanes (PUs) are the 6th most widely used polymers [1]. Yet, isocyanate monomers used for their synthesis are toxic. Therefore, the syntheses of PUs raise increasing health and environmental concerns and become a societal issue [2, 3]. For example, methylene diphenyl-4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), two of the most widely used isocyanates in PU industry, have been classified as CMR (Carcinogenic, Mutagenic and Reprotoxic)[4]. For this reason, the development of isocyanate-free alternatives to PUs is currently intensely investigated both in academia and in the industrial community [5-8]. The aminolysis of cyclic carbonates is one of the most promising alternatives for the synthesis of isocyanate-free PUs, which leads to Polyhydroxyurethanes (PHUs). Endo *et al.* [9-13], Figosky *et al.* [14-16] and some of us [17-24] have greatly contributed to the PHUs chemistry. In the literature five-membered (C5), six-membered (C6) [9, 25, 26], seven-membered (C7) [27] and eight-membered (C8) [28] cyclic carbonates were investigated. C5 cyclic carbonates are the most widely used compared to C6, C7 and C8 because they can be easily synthesized from the corresponding epoxide function using a simple carbonation reaction [10, 29]. On the other hand, C6 and C7 cyclic carbonates require several synthetic steps synthesis that could also involve toxic reactants. Despite their promises, PHUs suffer from some limitations. Indeed, even if the use of catalysts allowed reaching quite a high reactivity during the aminolysis of C5-cyclic carbonate, this reaction faces conversion limitations that prevent the access to high molar mass PHUs [27, 29-31].

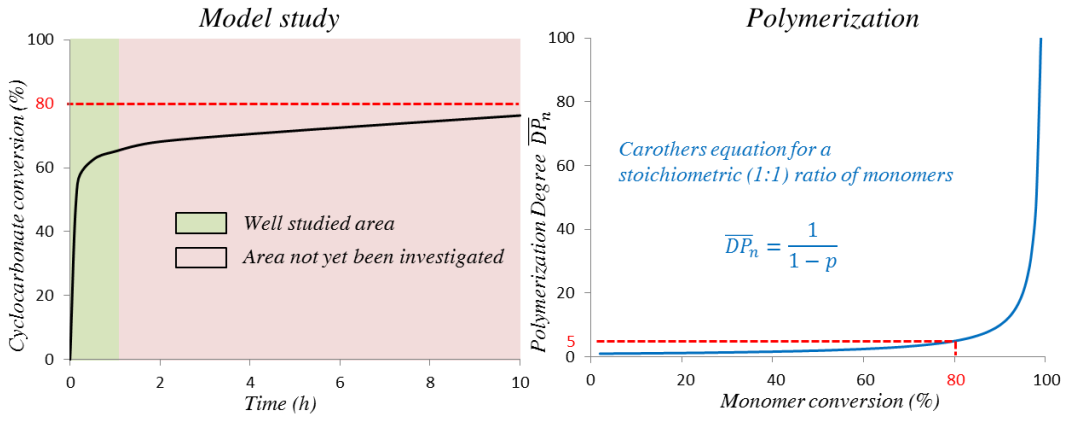


Figure II-37 On the left, cyclic carbonate conversion on a model study corresponding to the reaction of propylene carbonate with cyclohexylamine catalyzed with TBD.[18] On the right, evaluation of the degree of polymerization from Carothers' equation.

Several teams have mainly focused their work on the reactivity of the reaction corresponding to the green area Figure II-37. Numerous amines and cyclic carbonates have been proposed in

order to improve the reactivity of cyclic carbonate aminolysis [9, 27, 32, 33]. Moreover, catalytic studies have been conducted to improve the reactivity as well [18, 24, 34, 35]. Interesting results were observed at the beginning of the reaction but the final conversions generally remain close to 80%. This conversion corresponds to a degree of polymerization of only 5, based on Carothers' equation.

Therefore, only PHU polymers with low molar mass are synthesized. The question that needs to be addressed concerns the red area Figure II-37: what prevents monomers from getting high conversions? Some of us have already tried to explain the low molar masses obtained on linear PHUs [36] with glycerol carbonate in a model study. The presence of a free hydroxyl function in this monomer makes it less stable than etherified or esterified analogues. Therefore, glycerol carbonate is sensitive to degradations or side reactions. Herein, we proposed an in-depth study of the possible phenomena that may explain the limitation of conversion of cyclic carbonates and the low molar masses observed for PHUs. The carbonation of the amine [37-39] and secondary reactions such as the formation of urea [18, 33, 36, 40, 41], the formation of CO_2 *in-situ* [42] and the formation of oxazolidinone [36, 43] account for the modification of the stoichiometric (1:1) ratio of the monomers and prevent from getting PHUs of high molar masses. Another phenomena, namely the presence of strong hydrogen bonds might explain the low molar masses observed. To the best of our knowledge, this hypothesis has not been studied, yet. Here-after, we present a complete new DSC study of the reaction of polycyclic carbonates with polyamines that reveals the presence of two enthalpies of reaction. Thanks to the results obtained by DSC and a complete NMR study, we propose that the second enthalpy of reaction is caused mainly by hydrogen bonding and partly by the formation of urea. This unprecedented result explains the low conversions obtained for PHUs.

III. Experimental section

Materials

IPDI and the mixtures of triols ($1000<\bar{M}n<5000$ g.mol^{-1}) were kindly provided by JUXTA. 2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) noted JEFFAMINE® EDR-148 was obtained from Hunstman. Trimethylolpropane triglycidyl ether (TMPTGE), Poly(propylene oxide) diglycidyl ether $\bar{M}n \approx 380$ g.mol^{-1} (PPODGE380), Poly(propylene oxide) diglycidyl ether $\bar{M}n \approx 640$ g.mol^{-1} (PPODGE640), 1,4-butanediol diglycidylether and 1,3-cyclohexanebis(methylamine) (CBMA) were purchased from Sigma Aldrich. Deuterated

solvents ($CDCl_3$, DMSO-d_6, DMF-d_7, Methanol-d_4, THF-d_8) were purchased from Euriso-top (Saint-Aubin, France).

^{1}H and ^{13}C NMR spectra

The chemical structures of the molecules were determined using ^{1}H, ^{13}C, COSY, HSQC and HMBC NMR-spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Chemical shifts were given in ppm.

IR spectroscopy

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectrometer (FTIR). The characteristic IR vibrations mentioned in the text are reported in cm^{-1} and correspond to the most intense bands.

DSC analyses

The thermal properties of each polymer prepared were investigated by Differential Scanning Calorimetry (DSC). All analyses were carried out on a Netzsch DSC200 calorimeter. Cell constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the inert gas. Samples were placed in pierced aluminum pans and the thermal properties were recorded at 10 °C.min^{-1} for the enthalpy of reaction study.

TGA analysis

ThermoGravimetric Analyses (TGA) were performed on a Q50 from TA Instrument. The samples were heated in an alumina crucible from room temperature to 650 °C under a nitrogen flow (60 mL.min^{-1}). The experiments were carried out with a heating rate of 10 °C.min^{-1}.

General procedure for the cyclic carbonate synthesis

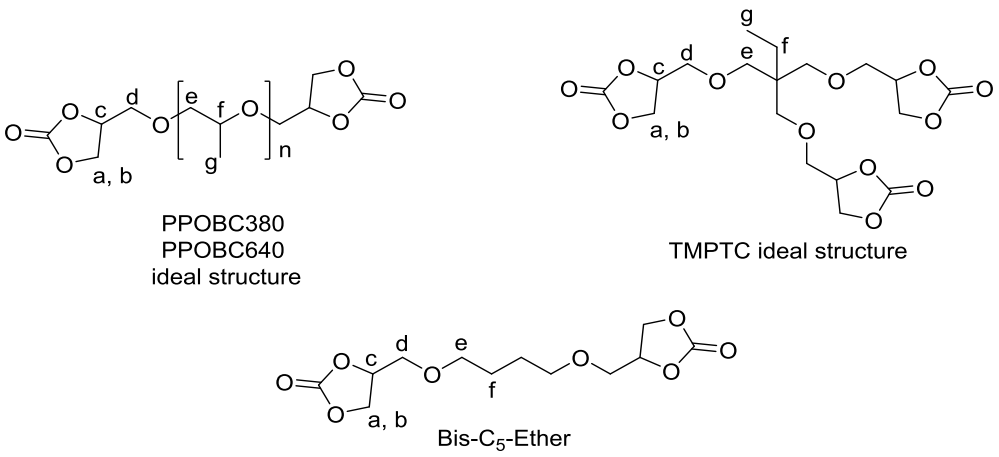


Figure II-38 Monomers synthesized for the study by epoxy carbonation

In a round-bottom flask (500 mL), poly(propylene oxyde) diglycidyl ether (PPODGE380 or PPODGE640 or 1,4-butanediol diglycidylether) or trimethylolpropane triglycidyl ether (1 eq, 100 g) and LiBr (5 mol%) were dissolved in DMF (150 mL). The solution was introduced into a reactor and the atmosphere was replaced with CO_2 (P= 15 bar). The solution was then allowed to stand at 80 °C with continuous stirring for 36 h. DMF was removed under vacuo (70 °C, P= 10 mbar). Then, the crude mixture was washed several times with water and brine to remove LiBr salt. The pure product TMPTC was obtained as brown oil in 76% yield. PPOBC380 was obtained as brown oil in 82% yield. PPOBC640 was obtained as brown oil in 87% yield. Bis-C5-Ether was obtained as a white solid in 96% yield.

^{1}H NMR PPOBC380(400 MHz, $CDCl_3$): δ: 1.06 (m, 7H, H_g); 3.24-3.90 (m, 18H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

^{1}H NMR PPOBC640. (400 MHz, $CDCl_3$): δ: 1.06 (m, 23H, H_g); 3.24-3.90 (m, 32H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

^{1}H NMR TMPTC(400 MHz, $CDCl_3$): δ: 0.81 (t, 3H, H_g); 1.34 (m, 2H, H_f); 3.20-4.00 (m, 12H, H_d, H_e); 4.25-4.60 (m, 6H, H_a, H_b); 4.82 (m, 3H, H_c).

^{1}H NMR Bis-C_5-Ether (DMSO-d_6, 400 MHz) δ (ppm) = 4.91 (m, 2H, H_a), 4.52(t, 2H, J=8.4 Hz, H_b), 4.25 (dd, 2H, J=8.3 Hz, J=5.9 Hz, H_c), 3.59 (m, 4H, H_d), 3.46 (m, 4H, H_e), 1.54 (m, 4H, H_f)

^{13}C NMR Bis-C_5-Ether (DMSO-d_6, 400 MHz): δ (ppm) = 155.0, 75.5, 70.5, 69.5, 66.11, 25.6.

Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl acetate: C_5-Acetate

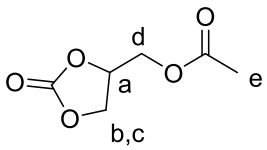
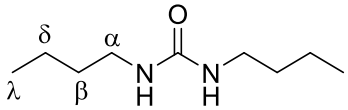


Figure II-39: Structure of C_5-Acetate

In a two-neck-round bottom-flask (50 mL), 4-(hydroxymethyl)-1,3-dioxolan-2-one (3 g, 25.40 mmol) and pyridine (2.21 g, 27.94 mmol) were dissolved in dry dichloromethane (15 mL). Acetic anhydride (2.85 g, 27.94 mmol) dissolved in dichloromethane (15 mL) was added dropwise to the mixture. The reaction was then allowed to stand at room temperature under continuous stirring for 12h. The crude mixture was washed twice with brine, dried over anhydrous magnesium sulfate and concentrated under vacuum. The pure product (2-oxo-1,3-dioxolan-4-yl)methyl acetate was obtained quantitatively as a transparent liquid in 93% yield.

Synthesis of dibutylurea



In a round bottom flask are introduced the butylamine, the propylene carbonate and TBD and heated at 120 °C. After 24 hours the urea is precipated in iced water. After several washing of the precipitate with water the urea is obtained with 100% yield.

^{1}H NMR dibutylurea (400 MHz, DMSO-d_6) δ 5.71 (t, 2H, J = 5.5 Hz, H_α), 2.95 (m, 4H, H_β), 1.37-1.19 (m, 8H,H_δ), 0.86 (t, 6H J = 7.2 Hz, H_γ).

^{13}C NMR dibutylurea (400 MHz, DMSO-d_6) δ 158.1, 38.9, 32.2, 19.5, 13.7.

Titration of the epoxy equivalent weight titration by ^{1}H NMR

The epoxide equivalent weight (EEW) is the amount of resin (in grams) containing one gram-equivalent of epoxy functions. It was determined by ^{1}H NMR spectroscopy. First, a solution of DMSO-d_6 containing toluene as an internal standard was prepared (c = 52.9 mmol.L^{-1}). Then a known amount of TMPTGE (about 90 mg) and the toluene containing DMSO-deuterated solution (around 800 mg) were weighed and transferred into a NMR tube. Two characteristic epoxy signals at 3.07 ppm and 2.71 ppm were chosen. The EEW is calculated

with Equation II-7 by comparing the integral ($\int H_{toluene}$) corresponding to the CH_3 protons of toluene with the integral ($\int H_{epoxy}$) of the two methylene protons of the epoxy.

Equation II-7
$$EEW = \left(\frac{\int H_{toluene}}{\int H_{epoxy}} \times \frac{2}{3}\right)\left(\frac{m_{epoxy}}{m_{toluene}}\right)(M_{toluene})$$

The titration was replicated four times and revealed an EEW of 137 ± 1 $g.eq^{-1}$ which corresponds to a 2.3 epoxy functions per molecule [44].

Titration of the carbonate equivalent weight titration by ^1H NMR

The carbonate equivalent weight (CEW) is the amount of resin (in grams) containing one gram-equivalent of carbonate functions. It was determined using the procedure used for the determination of the EEW. Three characteristic cyclic carbonate signals at 4.94 ppm, 4.53 ppm and 4.26 ppm were chosen. The CEW is calculated using Equation II-8 by comparing the integral ($\int H_{toluene}$) with the integral ($\int H_{cyclic\ carbonate}$) of the three cyclic carbonate protons.

Equation II-8
$$CEW = \left(\frac{\int H_{toluene}}{\int H_{cyclocarbonate}}\right)\left(\frac{m_{cyclocarbonate}}{m_{toluene}}\right)(M_{toluene})$$

The titration was replicated four times and revealed a CEW of 178 ± 1 $g.eq^{-1}$ for TMPTC, 236 ± 1 $g.eq^{-1}$ for PPOBC380, and 344 ± 6 $g.eq^{-1}$ for PPOBC640.

IV. Result and discussion

To the best of our knowledge the cyclic carbonate / amine system reactivity measured by DSC has not yet been compared to the isocyanate/alcohol system or the epoxy/amine system commonly used for room temperature reactions. The cyclocarbonate/amine system is among the best alternative to remove isocyanates in PUs. Therefore, it seemed important to us to compare both reactivities. The epoxy/amine system was also investigated because it is a highly used room temperature system and it also corresponds to the aminolysis of an heterocycle. The different systems were analyzed as follow: the two reactive monomers were mixed together at 0 °C, in a (1/1) ratio. Hence, 1/1 epoxy-/NH-functions, OH-/NCO-functions and, cyclic carbonate-/NH_2-functions were considered. Next, the monomer mixtures were introduced in DSC pans and analyzed. The samples were analyzed from -100 °C to 250 °C with a 10 $°C.min^{-1}$ rate. The results of the first DSC heating ramp are presented Figure II-40.

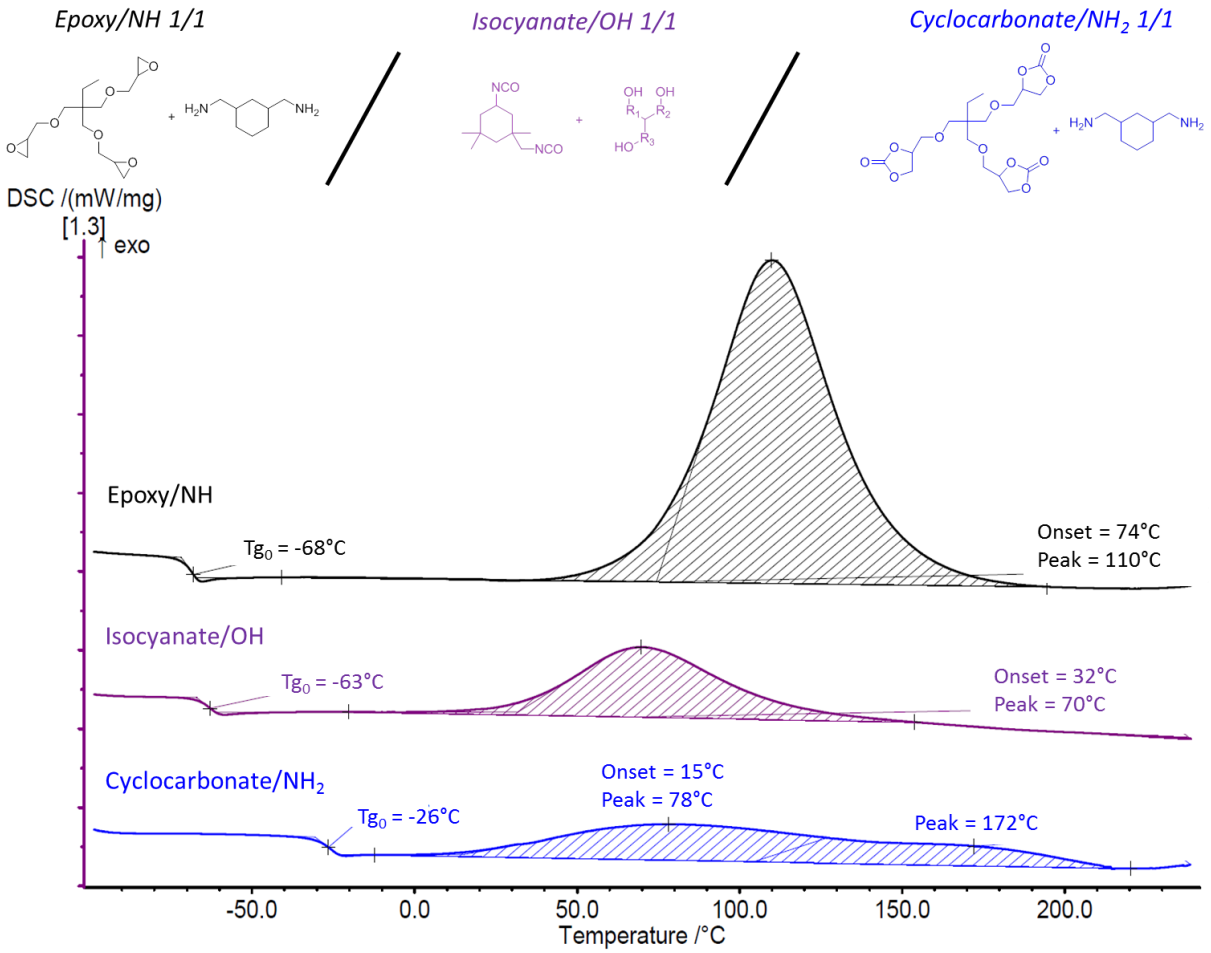


Figure II-40 Enthalpy of reaction study of several reactive systems monitored by DSC: epoxy/amine, isocyanate/alcohol, cyclic carbonate / amine.

Equation II-9

$$\frac{1}{Tg_0} = \frac{w_1}{Tg_1} + \frac{w_2}{Tg_2}$$

To study a reaction from the enthalpies of reaction it is necessary to control that the reaction did not start at the beginning of the heating ramp, after the mixing at 0 °C. Therefore, the Flory equation (Equation II-9) is used to control the degree of advancement of the reaction at the beginning of the first heating ramp. When $Tg_{0theoretic}$ = $Tg_{0experimental}$ the degree of advancement of the reaction is considered equal to zero. The $Tg_{0theoretic}$ calculated with the equation was compared to the $Tg_{0experimental}$ of the mixture of the two monomers. As presented in

Table II-3 except for the carbonate/amine system where the $Tg_{0theoretic}$ > $Tg_{0experimental}$, the two other systems display $Tg_{0theoretic}$ and $Tg_{0experimental}$ values close to each other of. In the case of the carbonate/amine system the difference observed between the two values might result from the heterogeneity of the mixture. Indeed, the TMPTC is highly viscous. Therefore, the mixing of the two monomers at 0 °C is difficult. Nevertheless, for less viscous systems such as PPO-

dicyclic carbonates, $Tg_{0theoretic}$ and $Tg_{0experimental}$ were close (SI - Figure II-47). To conclude, all the systems, present a degree of advancement nil at the beginning of the DSC analysis meaning that the enthalpies of reaction presented Figure II-40 totally describe the full reaction.

Table II-3 $Tg_{0theoretic}$ calculation of the three systems and comparison to the $Tg_{0experimental}$

System	w (%)	Tg (°C)	$Tg_{0theoretic}$ (°C)	$Tg_{0experimental}$ (°C)
Epoxy	82	-62	-66	-68
Amine	18	-93		
Isocyanate	50	-59	-63	-63
Alcohol	50	-68		
Carbonate	72	-12	-16	-26
Amine	28	-94		

As expected, the epoxy/amine reaction starts at a much higher temperature than the isocyanate/alcohol reaction, with a peak temperature of 110 °C and 70 °C, respectively. Nevertheless, the enthalpy of reaction of epoxy/amine is larger than the one of the isocyanate+alcohol reaction. The cyclic carbonate / amine system displays a broader ethalpy peak with two enthalpies of reaction. Interestingly, the first peak of enthalpy of reaction appears at a temperature of 78 °C comparable to the enthalpy of reaction of the isocanate/alcohol system. This result proves that the cyclic carbonate / amine and the isocyanate/alcohol reaction both start at the same temperature. Therefore, once the cyclcic carbonate / amine reaction is catalayzed with the apropriate catalyst similar reactivities should be observed with classical room temperature polyurethane systems. The latter, are also catalyzed to avoid secondary reactions of isocyanates with water or to simply speed up the reaction. The presence of the second enthalpy of reaction correspond to another reaction that is needed to reach full conversion of monomers. This second enthalpy of reaction may explain the low conversions observed for the PHUs. In the following study, we focused on this second enthalpy of reaction observed at 172 °C for the cyclic carbonate / amine system.

The evolution of enthalpies for the cyclic carbonate / amine and the epoxy/amine systems were also monitored by DSC over time at 25 °C. In another system, PPODGE380 and PPOBC380 were reacted with 1,3-cyclohexanebis(methylamine) (CBMA). Several DSC pans were prepared with the two couples of monomers. Then, they were analyzed at different time using the procedure previously described. TMPTC was replaced by PPOBC380, which is less viscous to get more homogeneous preparations. SI - Figure II-48 shows clearly the progressive disappearance of the first cyclic carbonate / amine enthalpy to reveal only the

second one. The evolution of the % enthalpy area over time is presented in Figure II-41. The % enthalpy area of the cyclic carbonate / amine system decreases rapidly compared to the epoxy/amine system, reaching 50% within two hours. Nevertheless, the % enthalpy area reaches a plateau at 50 %, whereas the % enthalpy of the epoxy/amine system keeps decreasing over time (SI - Figure II-49). A parallel can be drawn with the limitation of the enthalpy area and the low conversions generally observed for cyclic carbonate / amine systems.

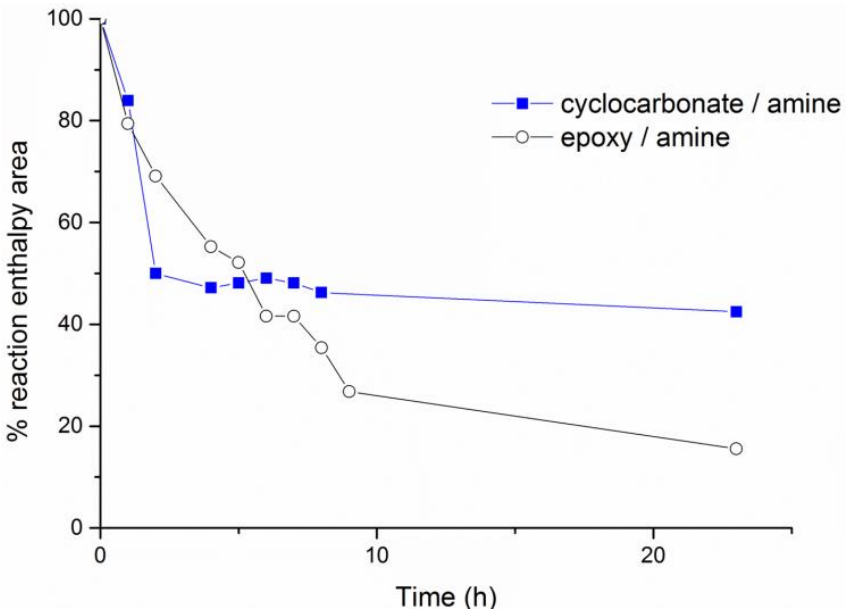


Figure II-41 PPODGE380/CBMA and PPOBC380/CBMA evolution of enthalpy over time at room temperature

Several phenomena can be responsible for the second enthalpy of reaction. It is not a degradation process, since the TGA of the cyclic carbonate / amine material displays only a 5% degradation at 250 °C. In the following, all these possibilities various secondary reactions or hydrogen bonding will be considered.

The degree of advancement of the solvent free PPOBC640 stoichiometric (1:1) reaction with CBMA at room temperature was calculated using ^{1}H NMR spectroscopy (Figure II-42). The integrations of the peaks $\int H_z$ and $\int H_a$, corresponding respectively to the CH_2 in α position of the amine of the CBMA as well as to the CH_2 in α position of the amine at the chain end of the PHU were compared with the integration $\int H_a$ corresponding to the CH_2 proton integral at α position to the carbamate function (Figure 5). The degree of advancement is calculated using (Equation II-10). For this system, after 24h of reaction at room temperature, p = 0.66. Then, with Carothers' equation, the degree of polymerization of the reaction $\overline{DP_n}$ was calculated (Equation II-11). r corresponds to the stoichiometric ratios of monomers; the ratio

is 1 when both monomers are introduced with a stoichiometric composition 1:1. The $\overline{DP_n}$ calculated from Equation II-12 is 3, corresponding to $\overline{M}n$ = 2,600 g.mol^{-1} calculated by ^{1}H NMR. Therefore, at the end of the first enthalpy of reaction the degree of advancement of the reaction is low, and only short PHU chains are obtained.

Equation II-10 $$p = \frac{\int H_a}{\int H_a + \int H_{a'} + \int H_z} = 0.66$$

Equation II-11 $$\overline{DP_n} = \frac{1+r}{1+r-2rp}$$

Equation II-12 $$\overline{DP_n} = \frac{1}{1-p}$$

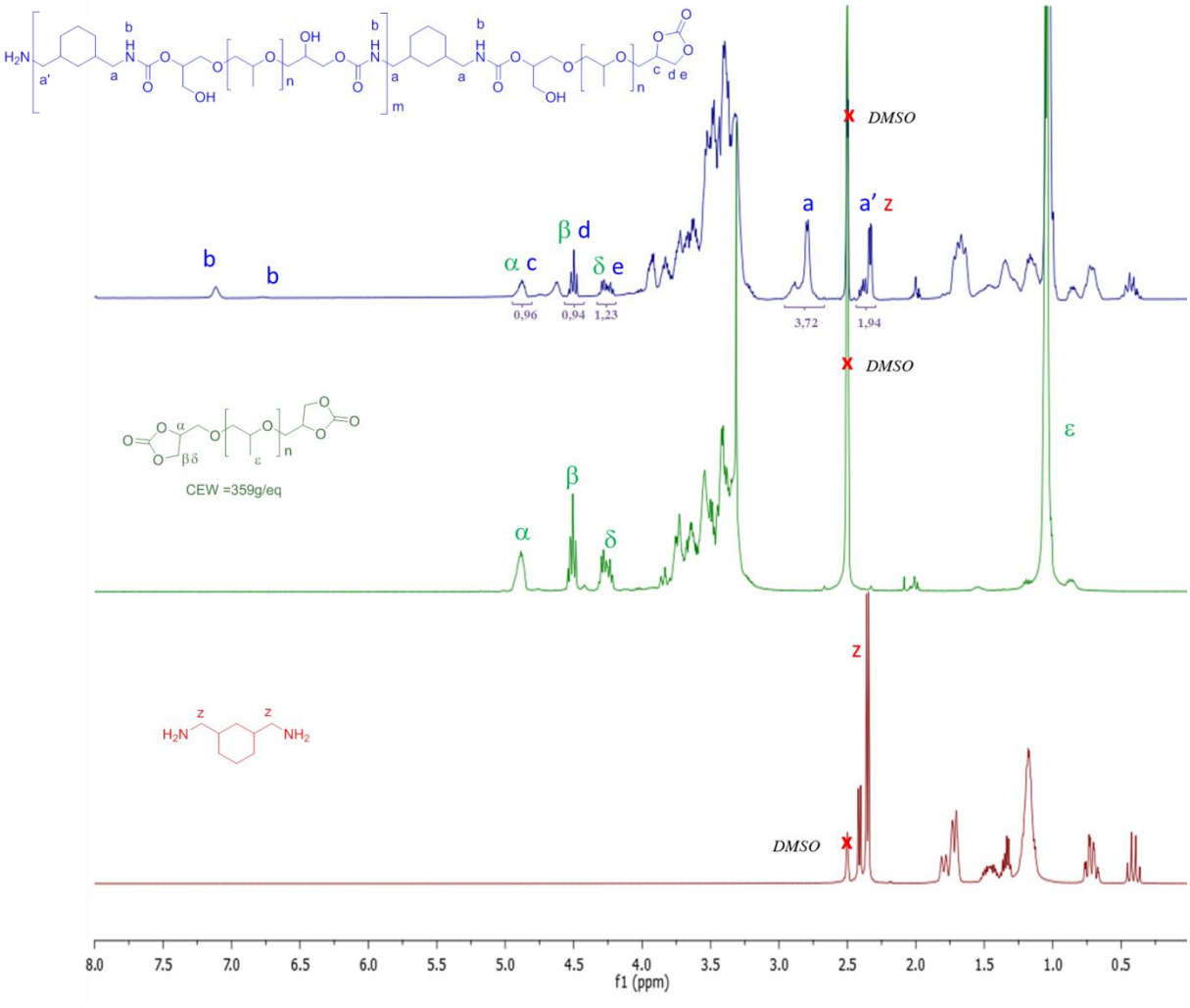


Figure II-42 ^{1}H NMR spectra in DMSO-d6, of CBMA (bottom), PPOBC640 (middle), and the corresponding PHU obtained at room temperature after 24h without solvent (top)

Both IR and ^{1}H NMR studies were carried out on PHU material at several temperatures in order to explain the second enthalpy of reaction. The PHU obtained from PPOBC640 with

CBMA at room temperature was placed 1h at 80 °C, then 1h at 120 °C and 1h at 150 °C. The obtained materials were analyzed by ^{1}H NMR spectroscopy (Figure II-43, Figure II-44). Figure II-43 reveals the conversion of amine functions into carbamates over temperature. Figure II-44 discloses the formation of the secondary compounds over temperature. Unfortunately, the IR spectra were identical (SI - Figure II-50) and did not bring any insight for the reaction.

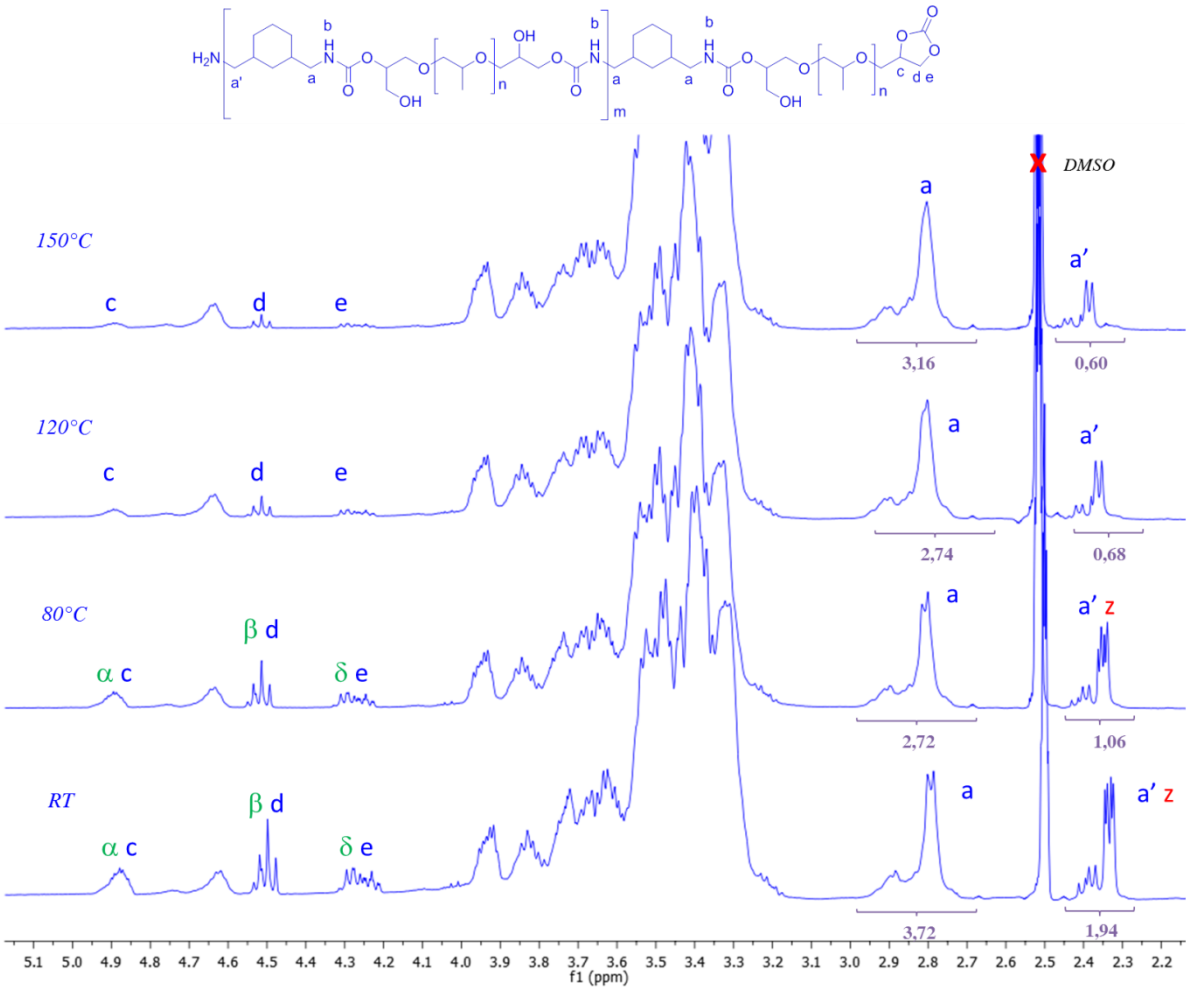


Figure II-43 ^{1}H NMR spectra in DMSO from 2 to 5 ppm of PHUs obtained from PPOBC640 with CBMA at different temperatures

Figure II-43 clearly evidences the increase of the degree of advancement with temperature. Using the protons area ($\int H_z$) of the CBMA and the integrations ($\int H_a$, $\int H_{a'}$) of the PHU protons, the degree of advancement was calculated: it increases from 65% at room temperature to 72% at 80 °C, 80% at 120 °C and 84% at 150 °C. Thus, a maximum degree of polymerization $\overline{DP}_n$= 6 and a molar mass of $\overline{M}n$ = 5,200 g.mol^{-1} were calculated by ^{1}H NMR. Nevertheless, the temperature increase entails the formation of a secondary product. Figure II-44 illustrates the intensity increase for the signal at 5.76 ppm from 120 °C. The area of the

integration measured for the peak was too low to be relevant. Accordingly, the identification of the secondary compound required additional investigations.

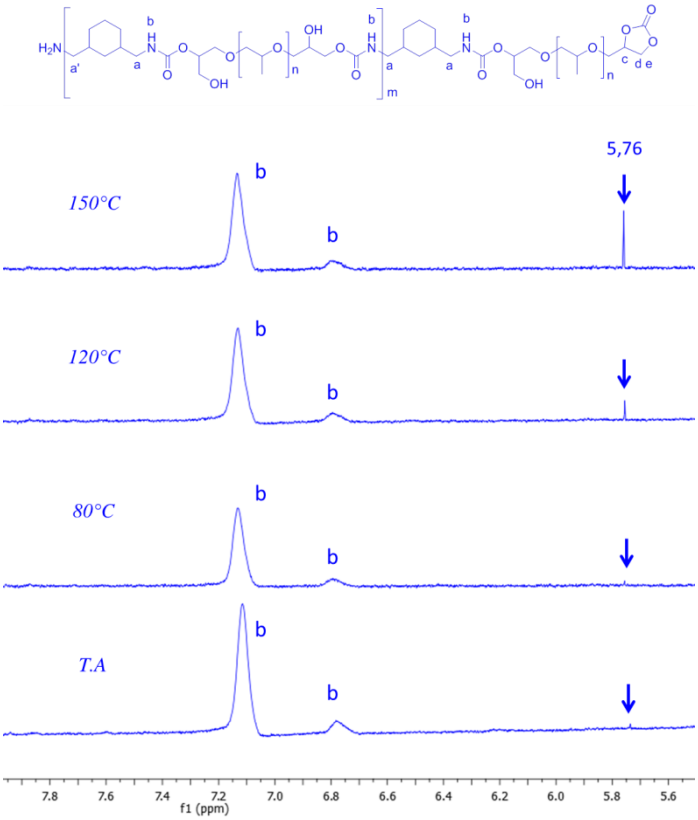


Figure II-44 ^{1}H NMR spectra in DMSO from 5.5 ppm to 7.9 ppm of a PHU obtained from PPOBC640 with CBMA at different temperatures

IV.1 Carbonation of the amine

Carbonation of the amine can be responsible for the partial cyclic carbonate aminolysis. In fact, an amine can react with the CO_2 present in the air. This reaction leads to the formation of an unreactive salt formed between a carbamate anion and an ammonium cation Scheme II-4[37-39]. This carbonation reaction consumes amines and leads to a stoichiometry gap which prevent reaching high molar mass according to Carothers' equation.

$$CO_2 + 2\ RNH_2 \longrightarrow RNHCOO^- + RNH_3^+$$

Scheme II-4: Reaction between CO_2 and amine

The carbonation of the amine is also a well-known process in epoxy coatings. In a recent study performed by our team [45], the carbonation of common aliphatic amines was studied. This study describes the carbonation of the CBMA within 30 minutes in the presence of air. Moreover, this reaction was shown reversible at 90 °C. Therefore, this process might explain

the second enthalpy of reaction. In fact, during the mixing process the amine may carbonate. Then during the heating step the amine salt decarbonates and produces the reactive primary amine that gives a second enthalpy of reaction by reacting with the remaining cyclic carbonates. Nevertheless, this hypothesis does not stands for several reasons. First, the infrared analysis of the PHU obtained at room temperature (SI - Figure II-50) does not show any characteristic bands of carbonated amine such as strong bands between 1600 and 1300 cm^{-1} and a band near 2500 cm^{-1} [46-48]. Secondly, the decarbonation process causes CO_2 release, and the formation of bubbles after annealing at 120 °C and 150 °C is not visible. Finally, for epoxy/amine systems, the carbonation of the amine is a well-known process. Therefore, the second enthalpy of reaction visible for the carbonate/amine system would also be visible on the DSC of the epoxy/amine system (Figure II-40). Hence, the carbonation of the amine is not responsible for the second enthalpy of reaction.

IV.2 Secondary reactions

Side reactions can also explain the presence of the second enthalpy of reaction. In the literature, several side reactions for the cyclic carbonate / amine reaction have been described, such as the transcarbonation, the formation of urea, the formation of oxazolidinone and the formation of CO_2 *in-situ*. To confirm or infirm the presence of side products, ^1H NMR (Figure II-44) as well as an IR analyses (SI - Figure II-50), were recorded on the polyhydroxyurethanes at several temperatures.

IV.2.1 Transcarbonation reaction

With sufficient energy, primary alcohols could undergo trans-urethanation to yield secondary alcohols of lower energy as described by Steblyanko *et al.* [11] (Figure II-45). This side reaction would lead to the modification of the ratio of primary and secondary alcohols. In our case, the heating step does not change the ratio between primary and secondary alcohols. Therefore, the trans-urethanation reaction is not responsible for the second enthalpy of reaction.

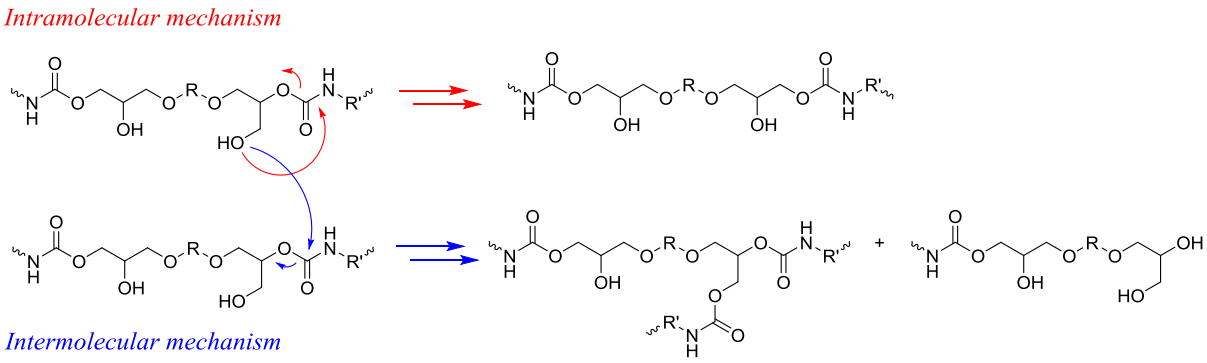


Figure II-45 Mechanism of trans-urethanation

IV.2.2 Formation of CO_2 *in-situ*

In a Huntsman report [42], the formation of CO_2 *in-situ* is described. Instead of reacting with the carbonate function, the amine can directly attack the carbon at α position to the carbonate (Figure II-46). The CO_2 formed *in-situ* can then carbonate the amine as discussed previously.

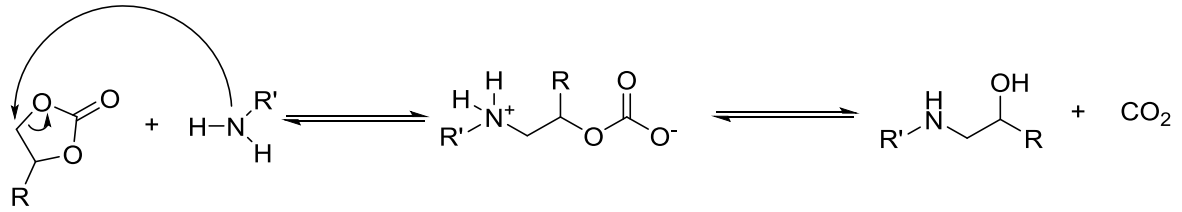


Figure II-46 formation of CO2 in-situ mechanism

MOPAC calculations were carried out on the cyclic carbonate to evaluate the partial charges on the carbonyl as well as the carbon in α position of the carbonate (Figure II-47). As expected, the carbon of the carbonyl bears a positive charge. The carbon at α position of the carbonate bears a negative charge. Therefore, the amine attack on the carbonyl remains much more favorable. This observation is also verified by the HSAB theory. Indeed, the primary amine and the carbonyl are both considered as hard acid/base. Therefore, they will react preferentially with each other. Moreover, in the case of the formation of CO_2 *in-situ*, CO_2 is released, therefore, the formation of bubbles would be visible at room temperature or after the heating stage, such a phenomenon was not observed. In conclusion, the second enthalpy of reaction is not caused by the formation of CO_2 *in-situ*.

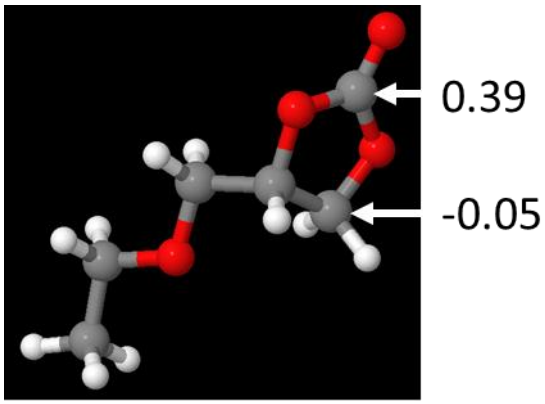


Figure II-47 MOPAC calculation of the partial charges

IV.2.3 Formation of oxazolidinone

The formation of oxazolidinone has been described by Clements *et al.*[43] and Besse *et al.* [36] The reaction pathway is presented in Figure II-48. This side reaction generally occurs at 80 °C under catalyst free conditions.

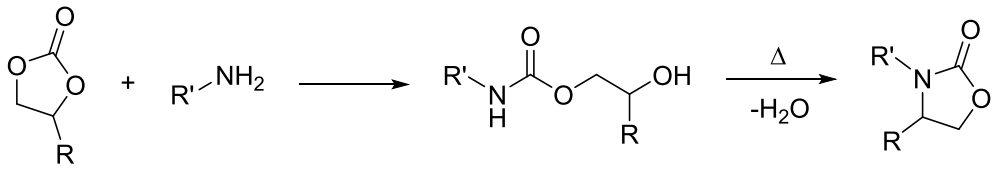


Figure II-48 Formation of oxazolidinone

The presence of oxazolidinone Figure II-49 would lead to the formation of new signals close to the chemical shift of the cyclic carbonate protons [49] around 4 ppm. Nevertheless, the presence of new signals corresponding to the formation of an oxazolidinone were not visible on the ^{1}H NMR spectra Figure II-43.

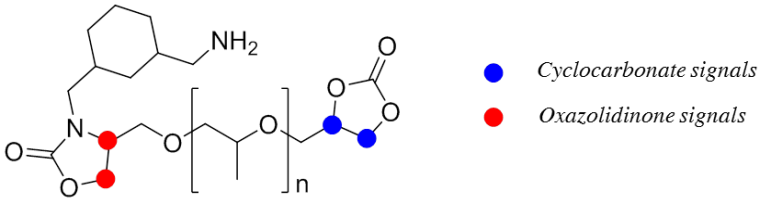


Figure II-49 Example of oxazolidinone obtained from PPOBC and CBMA

IV.2.4 Formation of urea

Trans-urethane reactions have been reported in numerous publications [18, 26, 33, 36, 40, 41]. It corresponds to the nucleophile attack of the amine on the formed urethane function to yield an urea (Figure II-50). This reaction is generally observed for temperatures higher than 100 °C.

The formation of an unreactive urea and a terminal alcohol leads to PHUs of low molar masses.

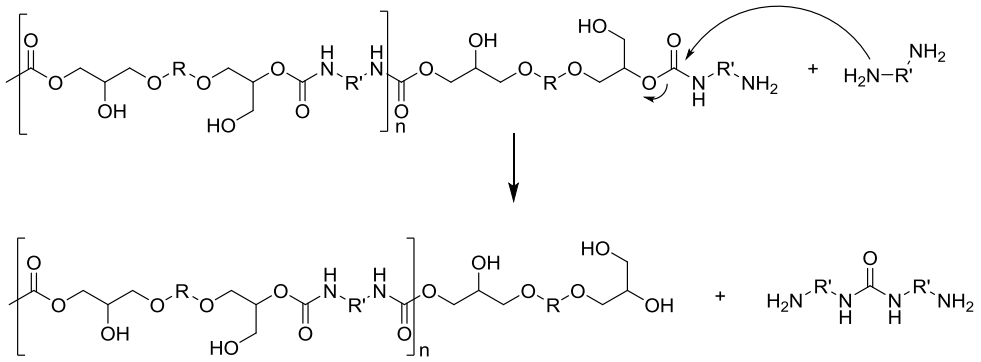


Figure II-50 Mechanism of formation of urea

To confirm the presence of urea signals in the ^{1}H NMR spectra (Figure II-44), a model urea, namely the dibutylurea, was synthesized. The ^{1}H and ^{13}C NMR spectra of the dibutylurea are reported in the SI - Figure II-52 and SI - Figure II-53. The urea NH chemical shift appears at 5.71 ppm. This chemical shift is almost identical as the signal assigned to the side product observed (Figure II-44) at 5.76 ppm. Therefore, at temperatures higher than 80 °C, the formation of urea is clearly observed. Nevertheless, even if ureas are formed, their quantity in the PHU is really low. In fact, the ^{1}H NMR signal is weak (Figure II-44), and no significant changes in the IR spectra are visible.

To confirm the formation of urea, two prepolymers were synthesized and analyzed by DSC. For the first one, an excess of CBMA was reacted with PPOBC640 to yield an amino-telechelic oligomer. This oligomer contains a major amount of unreacted primary amines that can further react to yield ureas. For the second one, an excess of PPOBC640 was reacted with CBMA to yield a cyclocarbonato-telechelic oligomer. The latter reaction was used as a reference for the study. The two ^{1}H NMR spectra (SI - Figure II-54 and SI - Figure II-55) confirm the absence of carbonates in the amino-telechelic oligomer and the absence of amine in the cyclocarbonato-telechelic oligomer. The oligomers, as well as the materials obtained from the reaction of PPOBC640 with CBMA at room temperature were analyzed by DSC from -100 °C to 250 °C with a 10 °C.min^{-1} rate (Figure II-51).

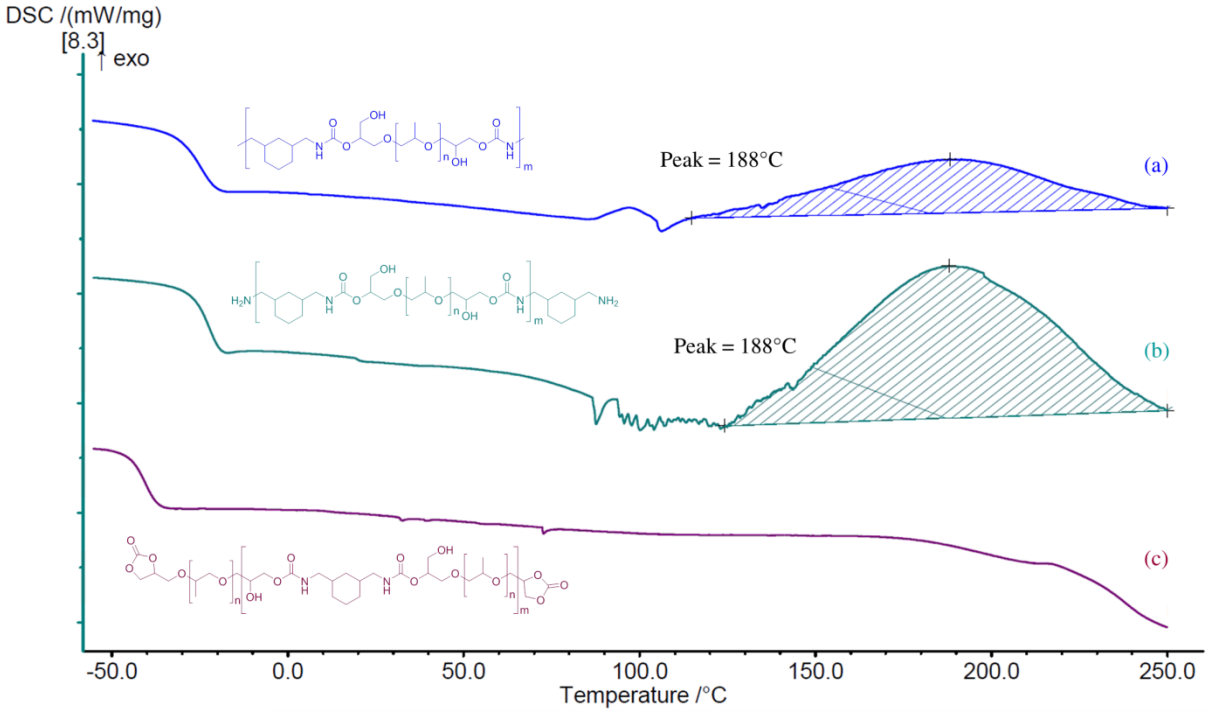


Figure II-51 DSC analyses of a stoichiometric room temperature synthesized PHU (top), an amino-telechelic PHU (middle), a cyclocarbonato-telechelic PHU (bottom)

As previously noticed, the second enthalpy of reaction is still visible on the PHU obtained after 24h at room temperature (Figure II-51a). As expected, cyclocarbonato-telechelic oligomer doesn't show any enthalpy of reaction (Figure II-51c). Nevertheless, the amino-telechelic oligomer shows an enthalpy of reaction at 188 °C, the same temperature as the stoichiometric (1:1) PHU material (Figure II-51b). In this case, the enthalpy of reaction can only be caused by the reaction of terminal amines with the carbamate functions to yield the corresponding ureas. The small bumps in the DSC curve of the amino-telechelic prepolymer (Figure II-51b) between 90 °C and 110 °C correspond to the amine decarbonation. In fact, the prepolymer contains a large quantity of unreacted primary amines and it was not stored under nitrogen, leaving the possibility to the amine to carbonate with the CO_2 present in the air. As already reported by Blain *et al.* [45], the amine decarbonation is visible around 90 °C. The amino-telechelic oligomer obtained after heating at 200 °C was also analyzed by ^{1}H NMR. The analysis confirms the formation of urea with a NH signal at 5.85 ppm (SI - Figure II-56). The IR spectrum (SI - Figure II-51) confirms the presence of urea. Actually, two carbonyl bands are visible on the spectra: the one at 1699 cm^{-1} corresponds to the band of the $\nu_{C=O}$ urethane and the one at 1645 cm^{-1} corresponds to the band of the $\nu_{C=O}$ urea as described by Cannon [50]. To conclude, these analyses confirm the formation of urea at temperatures higher than 80 °C. When an excess of amine is used the enthalpy of reaction of the formation of urea

correlates with second reaction of enthalpy observed for the synthesis of PHU. Nevertheless, for the stoichiometric (1:1) PHU material only traces of urea are visible on the ^{1}H NMR spectra (Figure II-44). Moreover, the urea amount is so low that it does not induce any changes on the IR spectra (SI - Figure II-51). Therefore, the second enthalpy of reaction is only partly due to the formation of urea and might be caused by another parameter such as hydrogen bonding.

IV.3 Hydrogen bonding

The formation of hydrogen bonds is the last considered alternative phenomenon that could explain the second enthalpy of reaction. In fact, PHUs contain many more hydrogen bonds than regular PUs, due to the presence of hydroxyl functions hanging off the polymer chain. The ^{1}H NMR study (Figure II-43) demonstrates that the progress of the reaction can be improved by heating the material. Therefore, the second enthalpy of reaction could correspond to a system gelation caused by hydrogen bonds that limits the degree of advancement. Then, when a sufficient quantity of energy is brought to the system, the polymer chains get mobility and the reaction goes on. To validate this assumption 25% weight of diglycerol and triglycerol were added to a mixture of PPOBC380/CBMA in order to limit the chain interactions. The mixtures were analyzed by DSC from -100 °C to 250 °C at 10 °C.min^{-1} (Figure II-52).

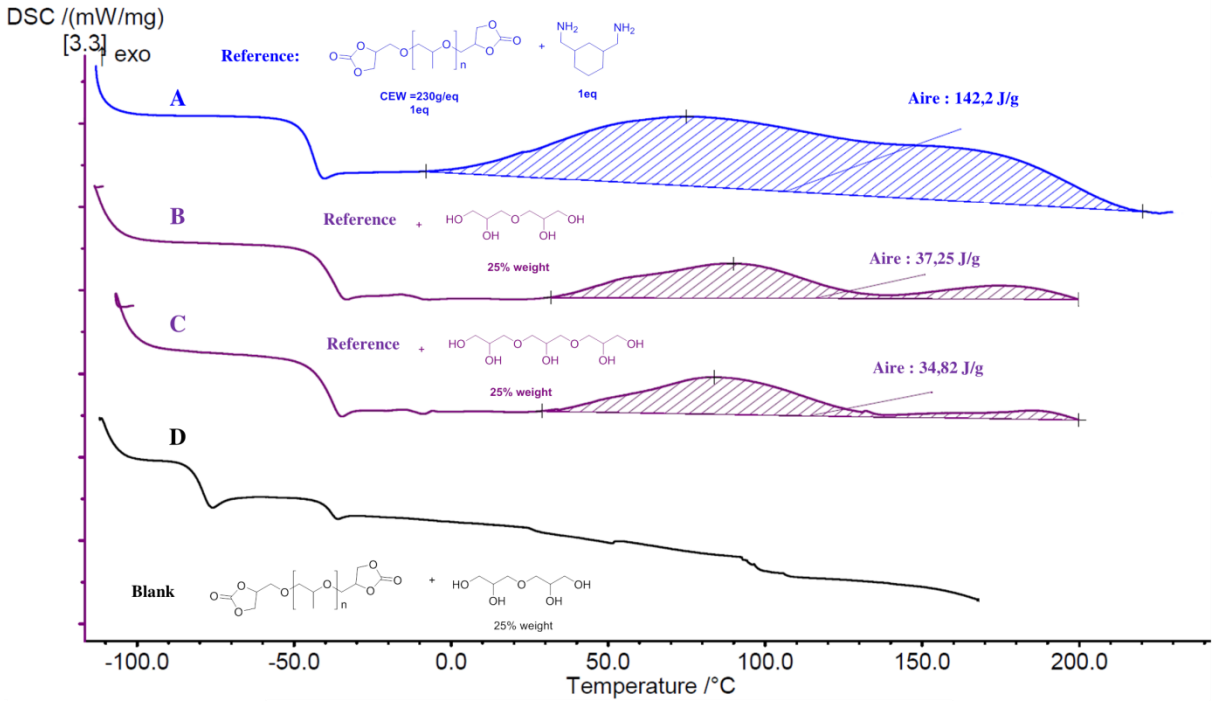


Figure II-52 Diglycerol (B) and triglycerol (C) effect over the enthalpy of reaction of PPOBC380 with CBMA (A)

Diglycerol and triglycerol were chosen as plasticizers for their high boiling point and degradation temperature to avoid any perturbation of the DSC analyses. These plasticizers create hydrogen bonding with the polyhydroxyurethane and inherently reduce the hydrogen bonding inter- and intra-molecular between PHU chains, giving back mobility to the system (Figure II-53). PPOBC380 was also mixed with diglycerol and heated up to 170 °C to ensure that there are no secondary reactions between the cyclic carbonate and the hydroxyl groups of the diglycerol. The absence of enthalpy of reaction between cyclic carbonates and diglycerol (Figure II-52D) validates the previous statement.

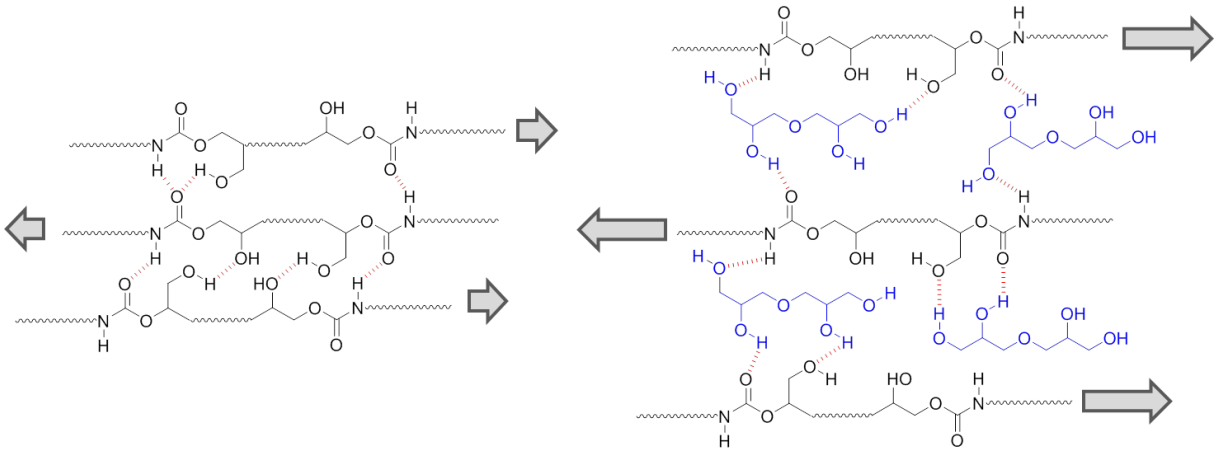


Figure II-53 Diglycerol effect on the PHU chains mobility

Figure II-52 clearly evidences the effect of diglycerol and triglycerol on the cyclic carbonate / amine reaction. In fact, the second enthalpy of reaction has nearly disappeared. Moreover, areas of the enthalpies of reaction (curve B, C Figure II-52) are much lower than the reference (Figure II-52A). Two reasons may explain this result. Firstly, by adding 25% weight of glycerol, the system is more diluted. Secondly, the formation of hydrogen bonds between the cyclic carbonate and the protic additives increase the positive charge on the carbonyl and favor the aminolysis of the cyclic carbonate as mentioned by Garipov *et al.* [51].

To conclude, protic additives present two advantages. The first one, improves the aminolysis of the cyclic carbonate and consequently the reactivity of the system as described by Garipov *et al.* [51]. Secondly, protic additives compete with intra- and inter- chains hydrogen bonds leading to the loss of the second enthalpy of reaction. The PHU recovers chain mobility and can continue to react leading to higher degree of advancement of polymerization. A temperature increase induces the same effect as demonstrated earlier (Figure II-43). Therefore, the formation of a hydrogen bond network is mainly responsible for the second enthalpy of reaction whereas the formation of ureas plays a little role for the second enthalpy of reaction in the PHU.

To confirm these previous results, a study on model compounds was carried out in deuterated NMR solvents. The (2-oxo-1,3-dioxolan-4-yl)methyl acetate was mixed with 2,2'-(ethane-1,2-diylbis(oxy))bis(ethan-1-amine) noted JEFFAMINE® EDR-148 at room temperature in several NMR solvent (Figure II-54). The cyclic carbonate conversion was monitored by ^{1}H NMR using the cyclic carbonate characteristic protons area at 5.08 ppm, 4.67 ppm and 4.49 ppm.

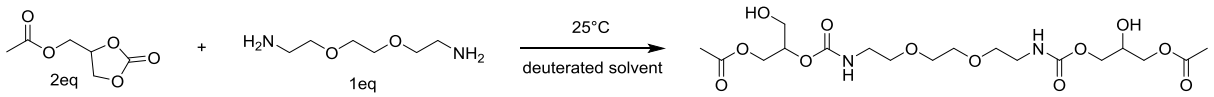


Figure II-54 Reaction conditions to study the solvent effect over the cyclic carbonate conversion

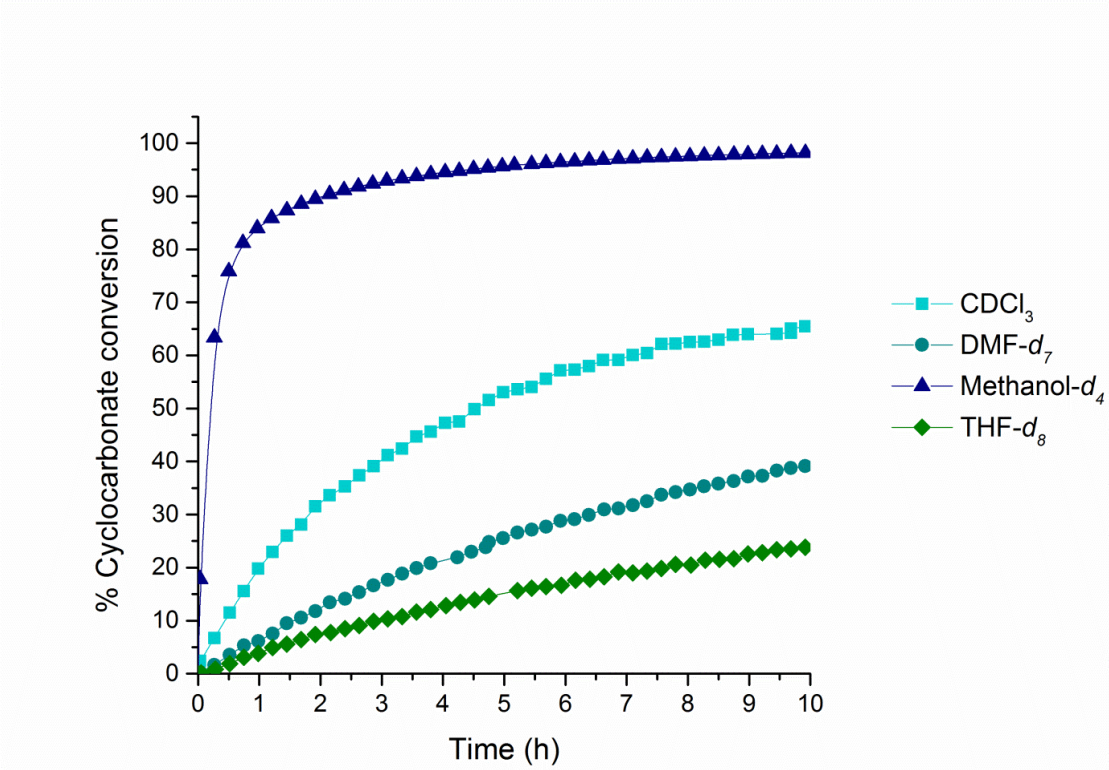


Figure II-55 Cyclic carbonate conversion monitored by ^{1}H NMR in several deuterated solvents, reaction of (2-oxo-1,3-dioxolan-4-yl)methyl acetate with Jeffamine EDR148.

Figure II-55 reveals that methanol-d_4 is the best solvent compared to the three other solvents, namely DMF-d_7, $CDCl_3$ and THF-d_8. The use of methanol allows a 95% cyclic carbonate conversion within 4 hours and 99% conversion after 10h. On the other hand, in the three other solvents, the conversions do not exceed 60% conversion. Hence, the model study confirms the previous results obtained by DSC with oligoglycerol. In fact, in a first part the activation of the cyclic carbonate by the protic solvent allows a conversion of 84% within 1h versus less than 20% for the other solvents. Then, in a second part, the limited self-association leads to 99% conversion.

Owing to the performance of methanol in the model study, protic solvents were also tested on the PHU synthesis by reaction between CBMA and Bis-C5-Ether. Di-functionality was confirmed by ^{1}H NMR (Figure II-56) for both monomers that were mixed in stoichiometric proportions (1:1). The solvent used for the reaction was EtOH in order to heat the reaction up to 80 °C. After 24h at 80 °C, the polymer was precipitated in ethyl acetate and dried at 70 °C

in an oven under vacuum. The amount of residues present in the filtrate were insignificant. The PHU ^{1}H NMR is presented Figure II-56. Traces of solvent (EtOAc, EtOH) are still visible on the spectra. To remove the remaining traces of solvent, the polymer was cryogrinded and dried in an oven under vacuum. The PHU spectra obtained after this procedure is presented on theSI - Figure II-57. Except the proton signals $\int H_e$, $\int H_g$, $\int H_h$ and $\int H_j$ that might contain water traces, the other integrations correspond to their assigned protons. Signals were assigned by 2D COSY (SI - Figure II-58), HMBC (SI - Figure II-59) and HSQC (SI - Figure II-60) NMR. The signal a is composed of two signals corresponding to the CBMA isomers. The two signals a corelate with two different carbone atoms distant 44.5 and 46.8 ppm as displayed in HSQC NMR (SI - Figure II-60) suggesting that the two signals do not belong to different isomers. Nevertheless the CBMA 2D HSQC NMR (SI - Figure II-61) displays the same patterns for the signal z. This observation confirms that the signal a corresponds to two isomers. Signals d and m were assigned using HMBC spectroscopy (SI - Figure II-59). They correlate with the carbonyl group. It is possible to differenciate the signals m and d, because the two peaks m correlate with the same carbon in HSQC (SI - Figure II-60). Using the COSY correlation, k correlates with m. Signals l and f do not correlate with any proton or carbon, therefore they are hydroxyl protons. The main product is always the secondary alcohol, therefore the peak with the highest integration at 4.90 ppm corresponds to the peak l.

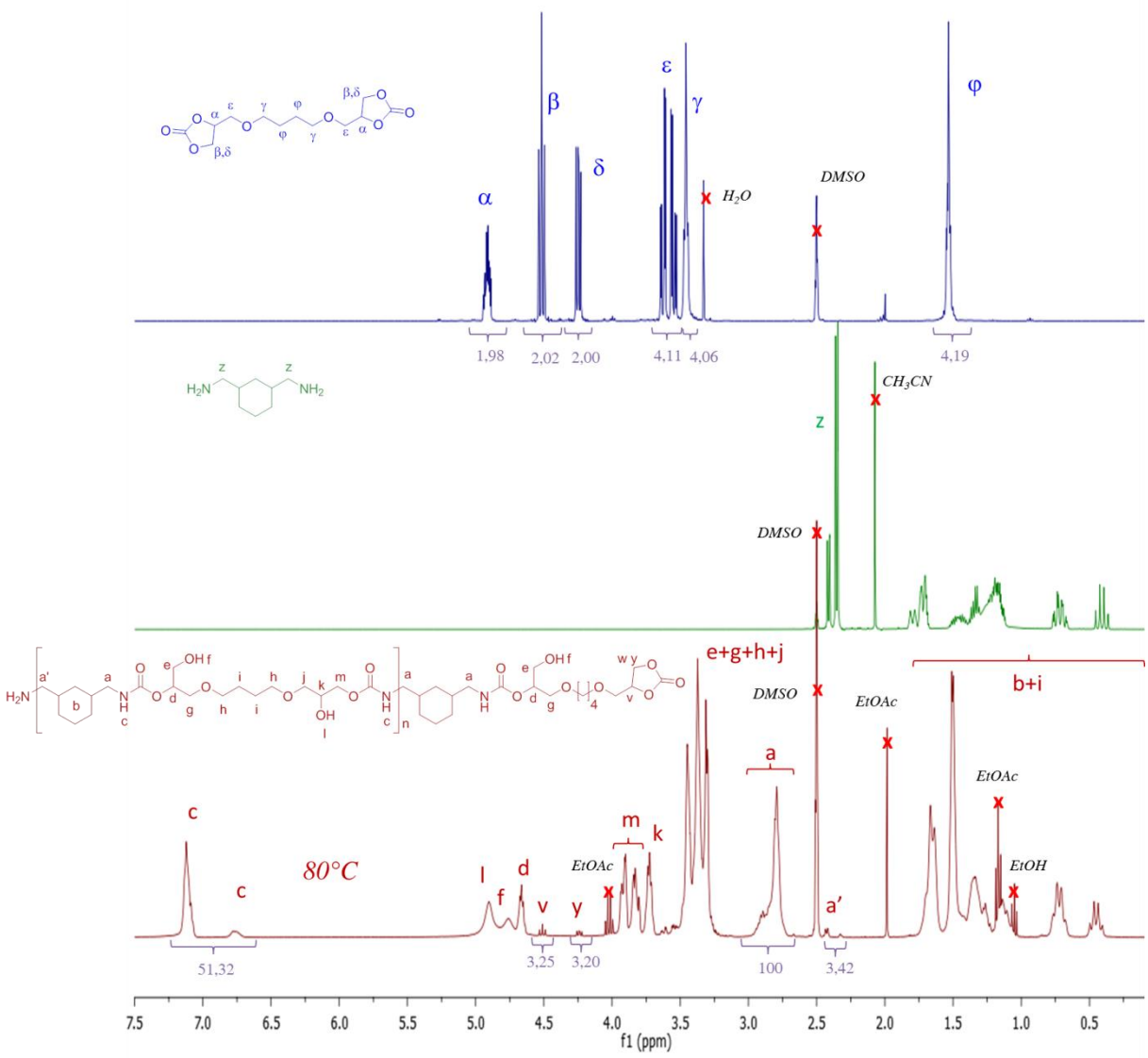


Figure II-56 PHU ^{1}H NMR obtained from a short bis-cyclic carbonate and CBMA at 80 °C in DMSO-d_6

The monomer conversion, p, is calculated from $\int H_a$ corresponding to the CH_2 at α position to the amine at the chain end of the PHU and $\int H_{a'}$ corresponding to the CH_2 at α position to the carbamate, p = 0.97. Thus, $\overline{DP_n}$ = 33 and the molar mass calculated by ^{1}H NMR is $\overline{M_n}$ = 14,300 g.mol^{-1}. From this result we can assess that protic solvents (MeOH/EtOH) have a positive influence on the cyclic carbonate conversion.

V. Conclusion

This study reveals two enthalpies of reaction in DSC during the first heating ramp when 1,3-cyclohexanebis(methylamine) is reacted with polycyclic carbonates. Moreover, a second analysis clearly shows that the first enthalpy rapidly disappears whereas the second enthalpy remains over time. We have considered several hypotheses in order to explain this second

enthalpy which is linked to the partial conversion generally observed in model studies of aminolysis of cyclic carbonate as well as the low molar masses obtained for PHU. Among these hypotheses we have considered the carbonation of the amine, side reactions and hydrogen bonding to explain the two enthalpies of reaction. To sum up, the first enthalpy corresponds to the reaction of cyclic carbonates with amines as described in the literature. The second one corresponds partly from the formation of urea and mainly from the reaction of cyclic carbonates with amine but only when sufficient energy is brought to the system to compete with the inter-chains hydrogen bonding. Therefore, the temperature rise allows to reach higher molar mass PHUs but it must remain below 100 °C in order to avoid the formation of ureas. Moreover the use of protic solvent such as methanol or ethanol allows to reach 99% conversion on model study with a monomer conversion up to p = 0.97 for PHU at 80 °C. The use of plasticizers such as diglycerol or triglycerol can be considered for the synthesis of PHU in mass. These two molecules will limit intra- and inter- chains hydrogen bonding and improve the monomer conversion to achieve a high degree of polymerization.

VI. Acknowledgements

The Association Nationale de la Recherche et de la Technologie (ANRT), the Agence Nationale de la Recherche (ANR) and Juxta are deeply acknowledged for their financial support. The authors thank Mr. Cyril Bourgogne for his contribution with MOPAC calculations. The authors wish to thank Huntsman for supplying EDR-148.

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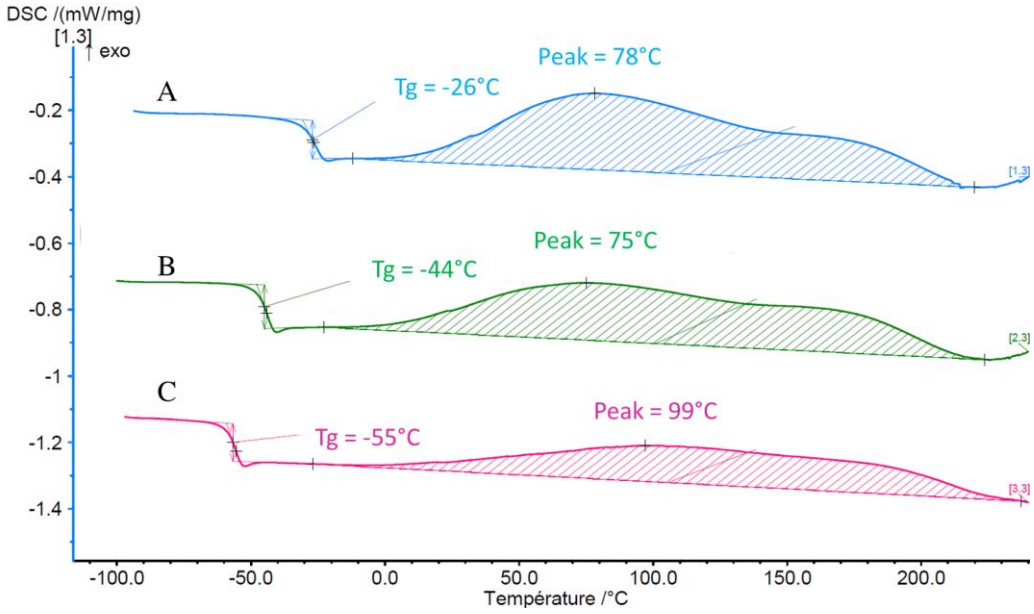
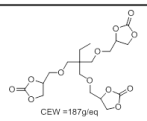
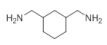
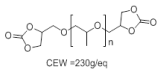
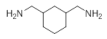
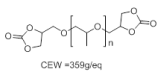
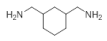
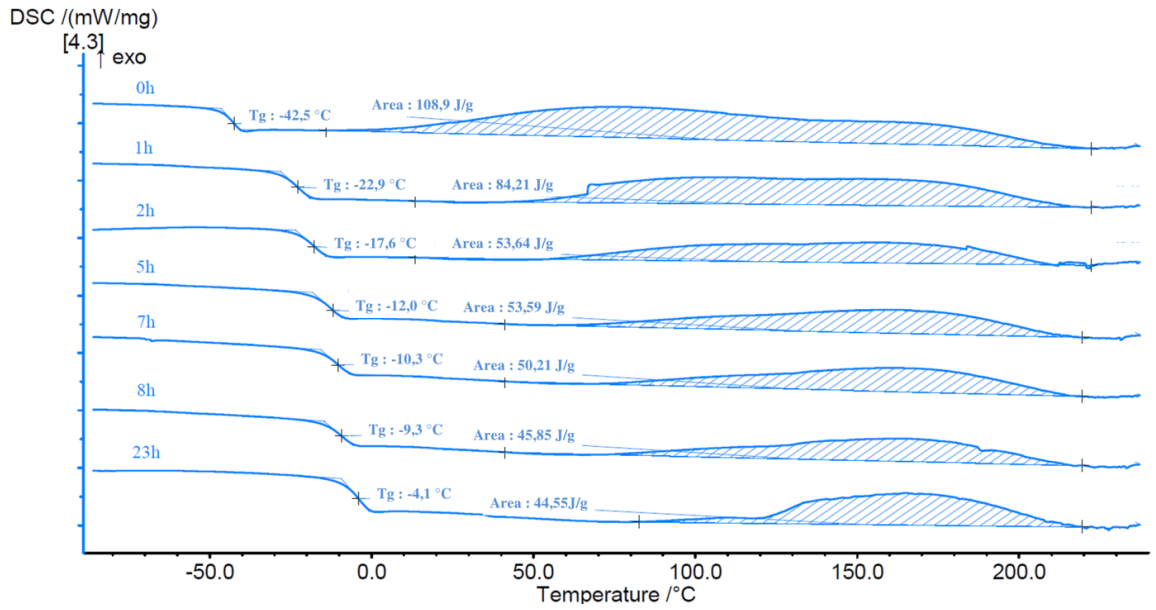
VIII. Supporting Informations

VIII.1 Enthalpy of reaction measured by DSC on the first heating

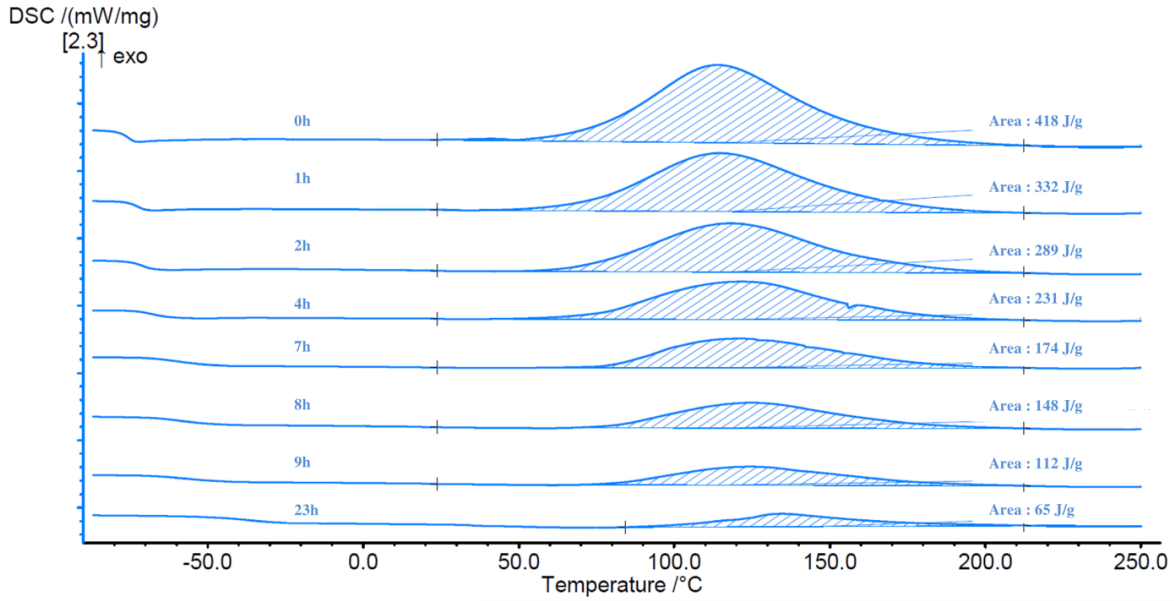


	System	w (%)	Tg (°C)	$Tg_{0theoric}$ (°C)	$Tg_{0experimental}$ (°C)
A	 CEW =187g/eq	0.72	-12	-16	-26
		0.28	-93		
B	 CEW =230g/eq	0.76	-39	-45	-44
		0.24	-93		
C	 CEW =359g/eq	0.83	-46	-50	-55
		0.17	-93		

SI - Figure II-47: Enthalpies of reaction and $Tg_{0theoric}$ calculated by DSC

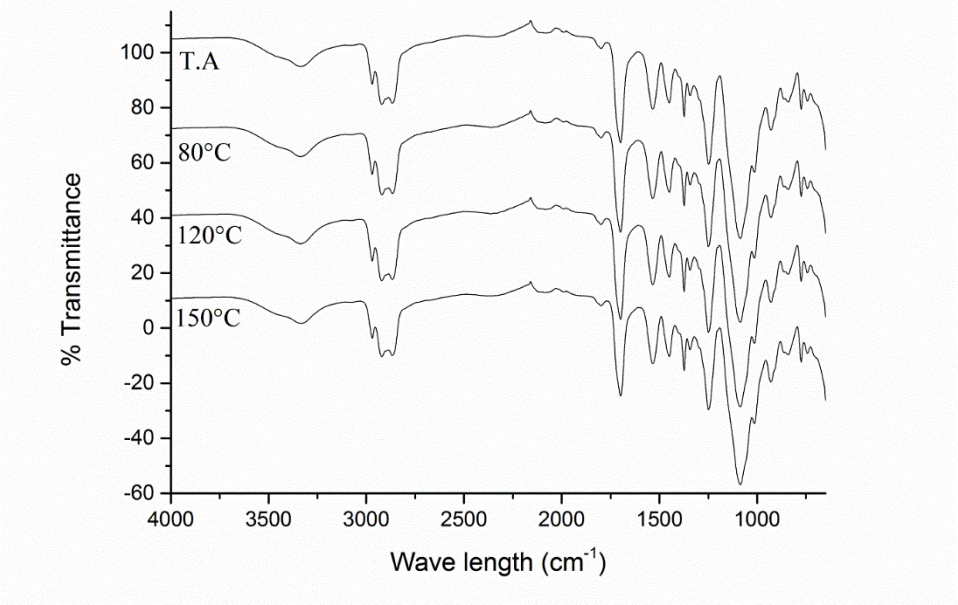


SI - Figure II-48: PPOBC380 aminolysis cinetic reaction with CBMA at 25 °C enthalpy of reaction evaluation with DSC

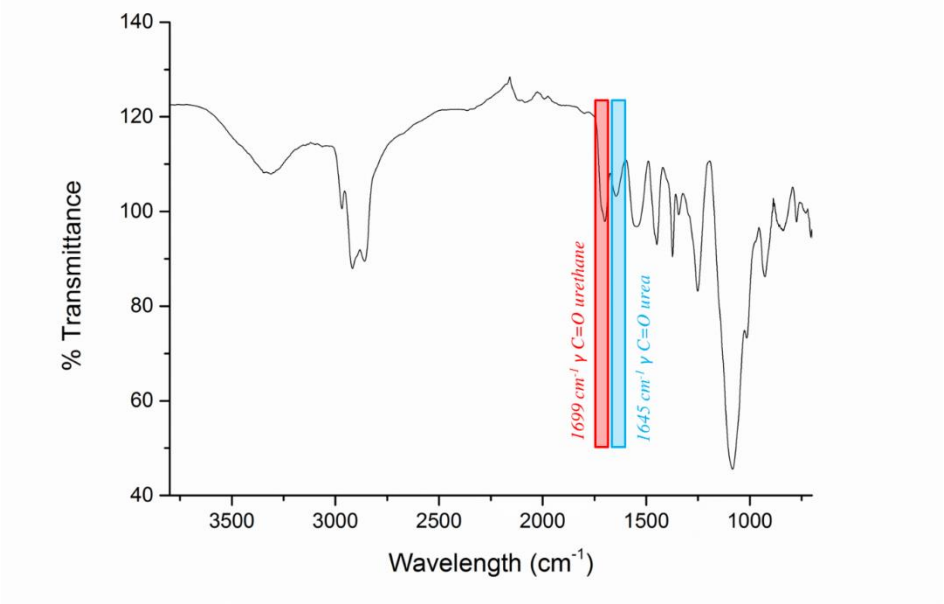


SI - Figure II-49: PPO380-diglycidylether reaction with CBMA at 25 °C enthalpy of reaction evaluation with DSC

VIII.2 Infrared spectra

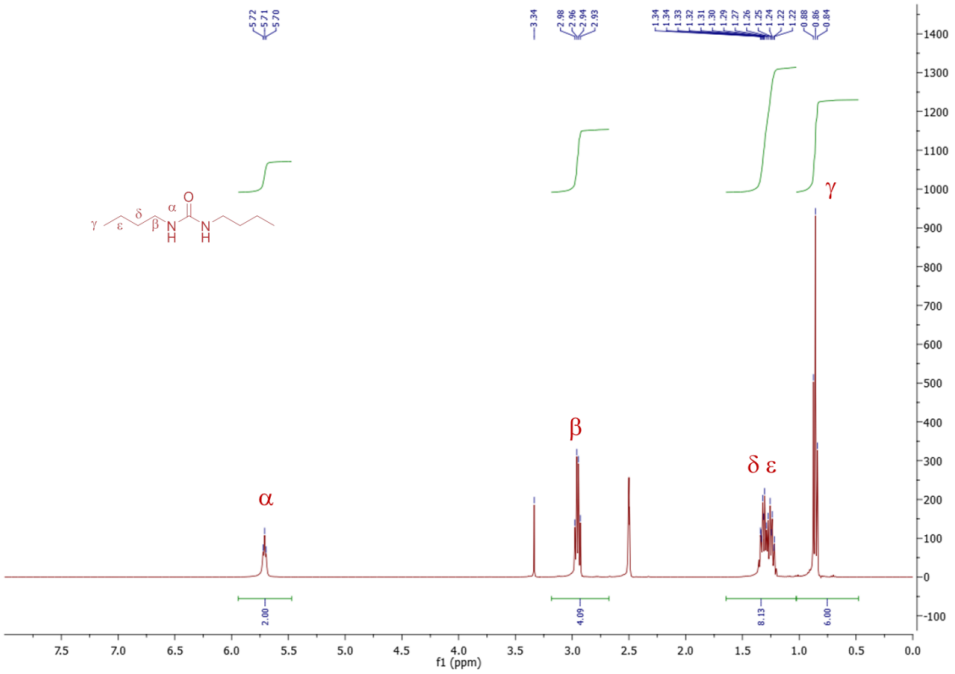


SI - Figure II-50: IR spectra obtained from PPOBC640 with CBMA at different temperatures

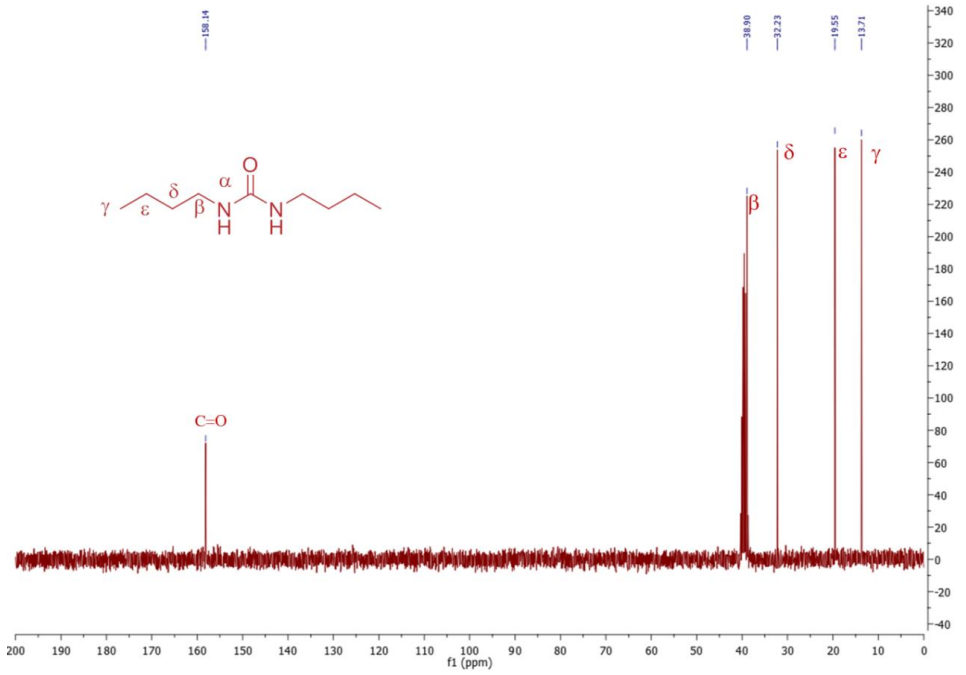


SI - Figure II-51: IR spectra of aminotelechelic prepolymer after heating at 200 °C

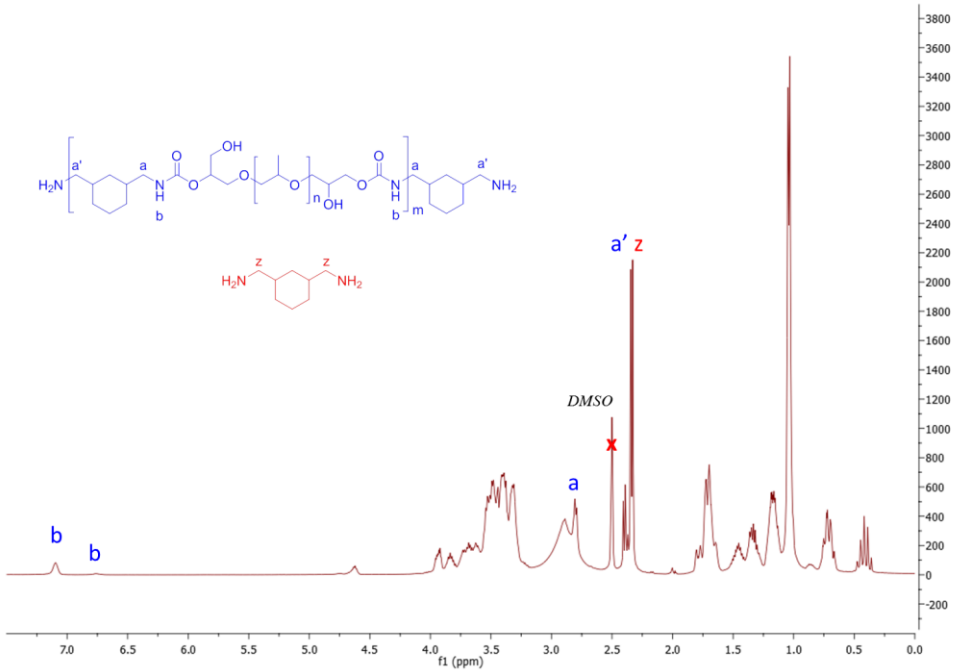
VIII.3 NMR spectra



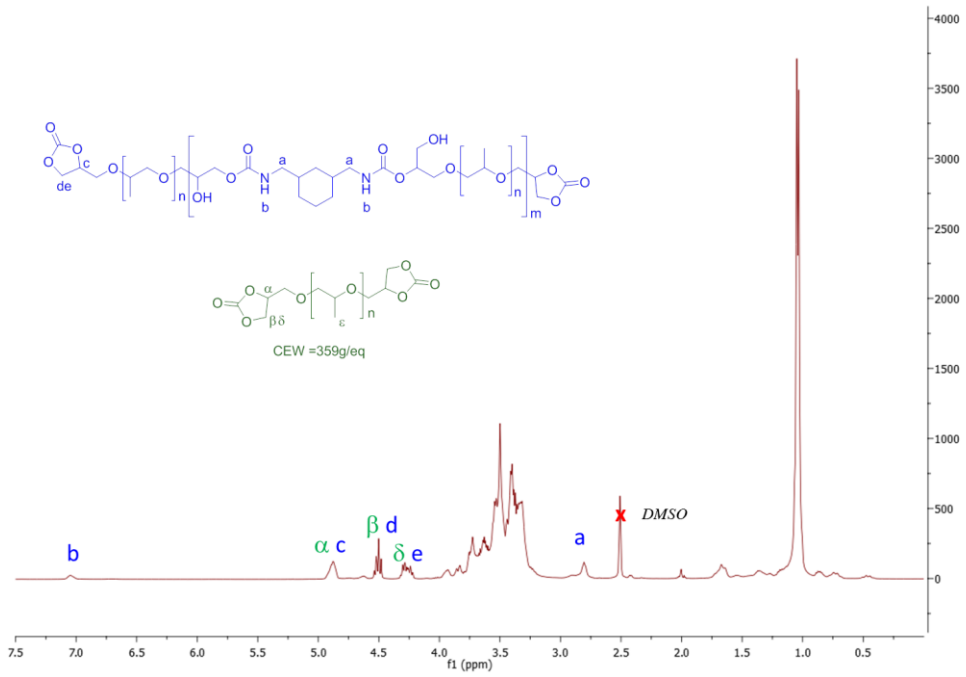
SI - Figure II-52: Dibutyl urea ^{1}H NMR in DMSO-d_6



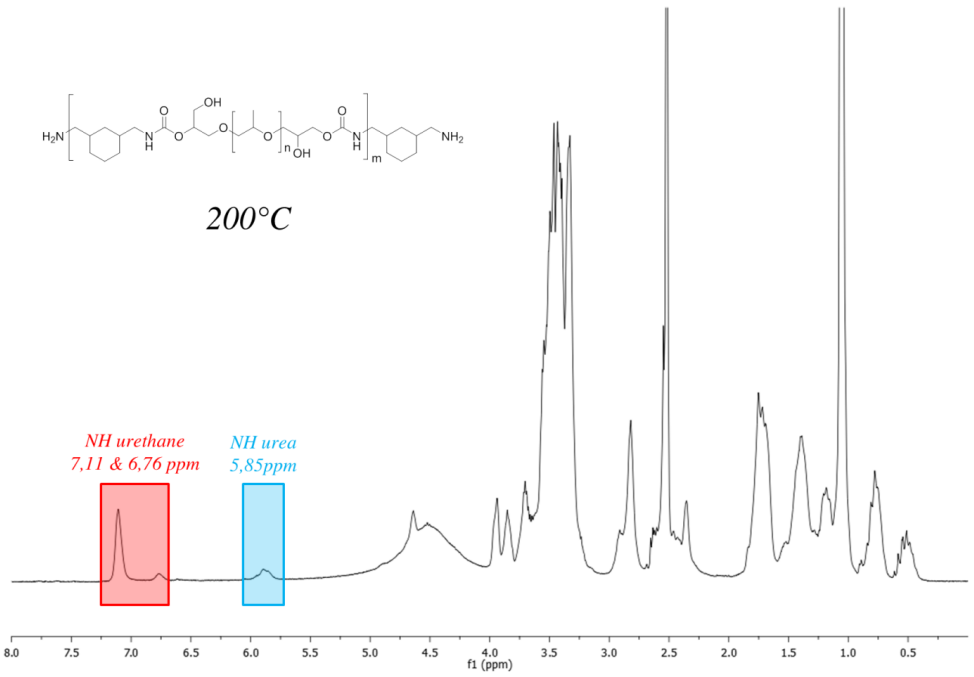
SI - Figure II-53: Dibutylurea ^{13}C NMR in DMSO-d_6



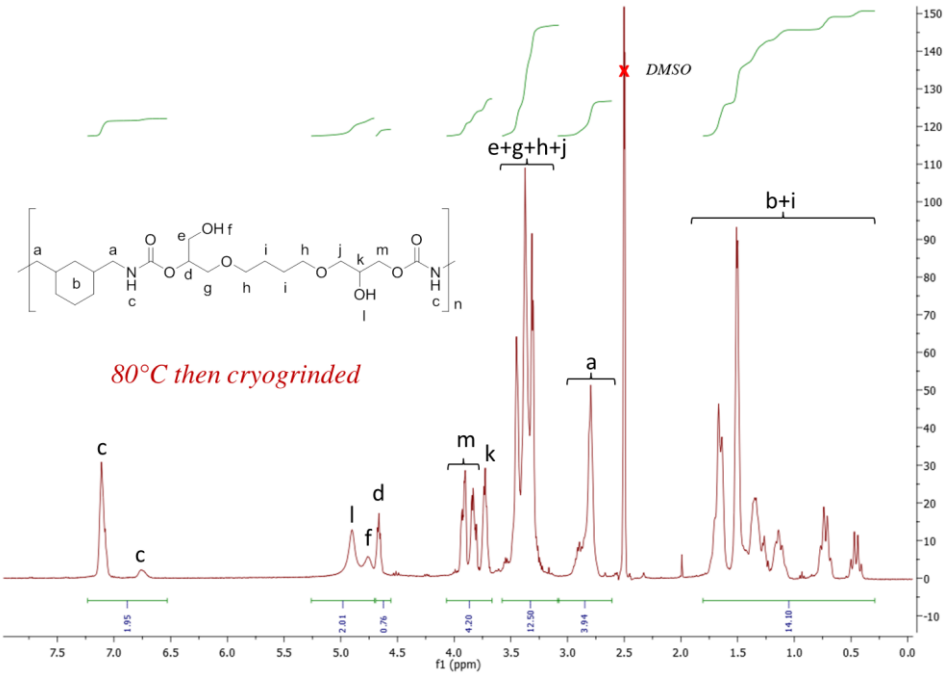
SI - Figure II-54: Room temperature aminotelechelic prepolymer ^{1}H NMR spectra in DMSO-d_6



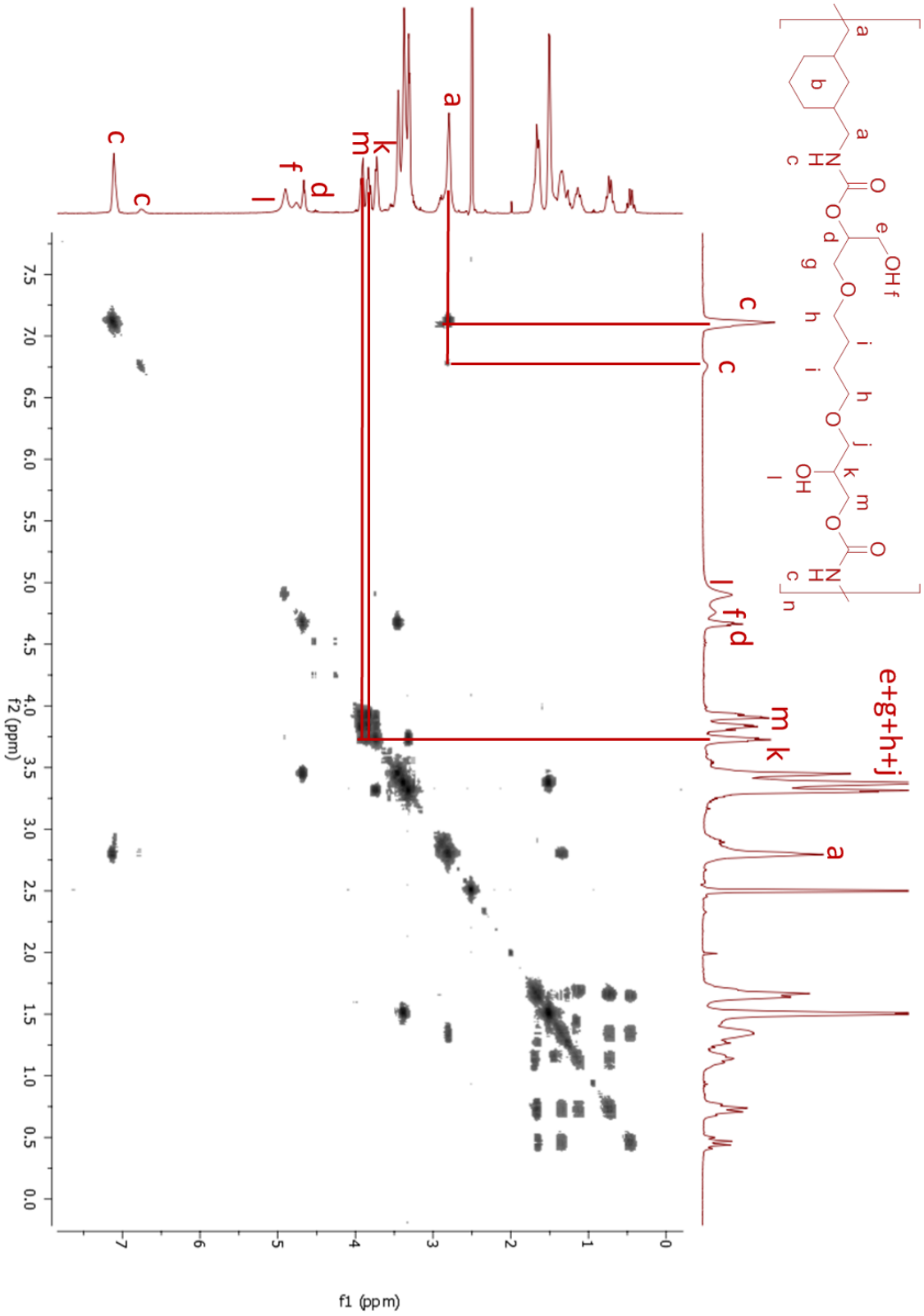
SI - Figure II-55: Room temperature cyclic carbonatetelechelic prepolymer ^{1}H NMR spectra in DMSO-d_6



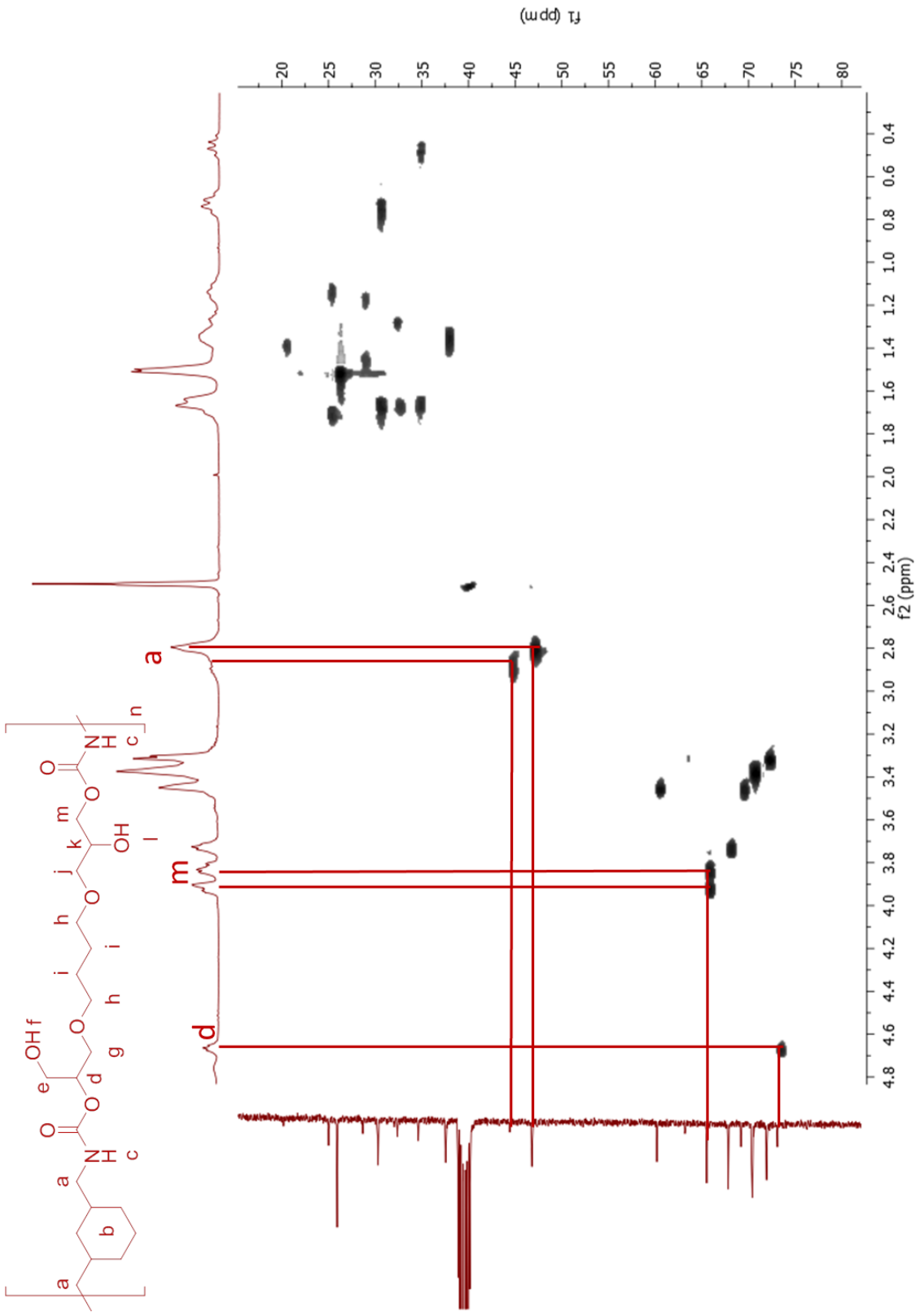
SI - Figure II-56: Aminotelechelic prepolymer after heating at 200 °C ^{1}H NMR spectra in DMSO-d_6



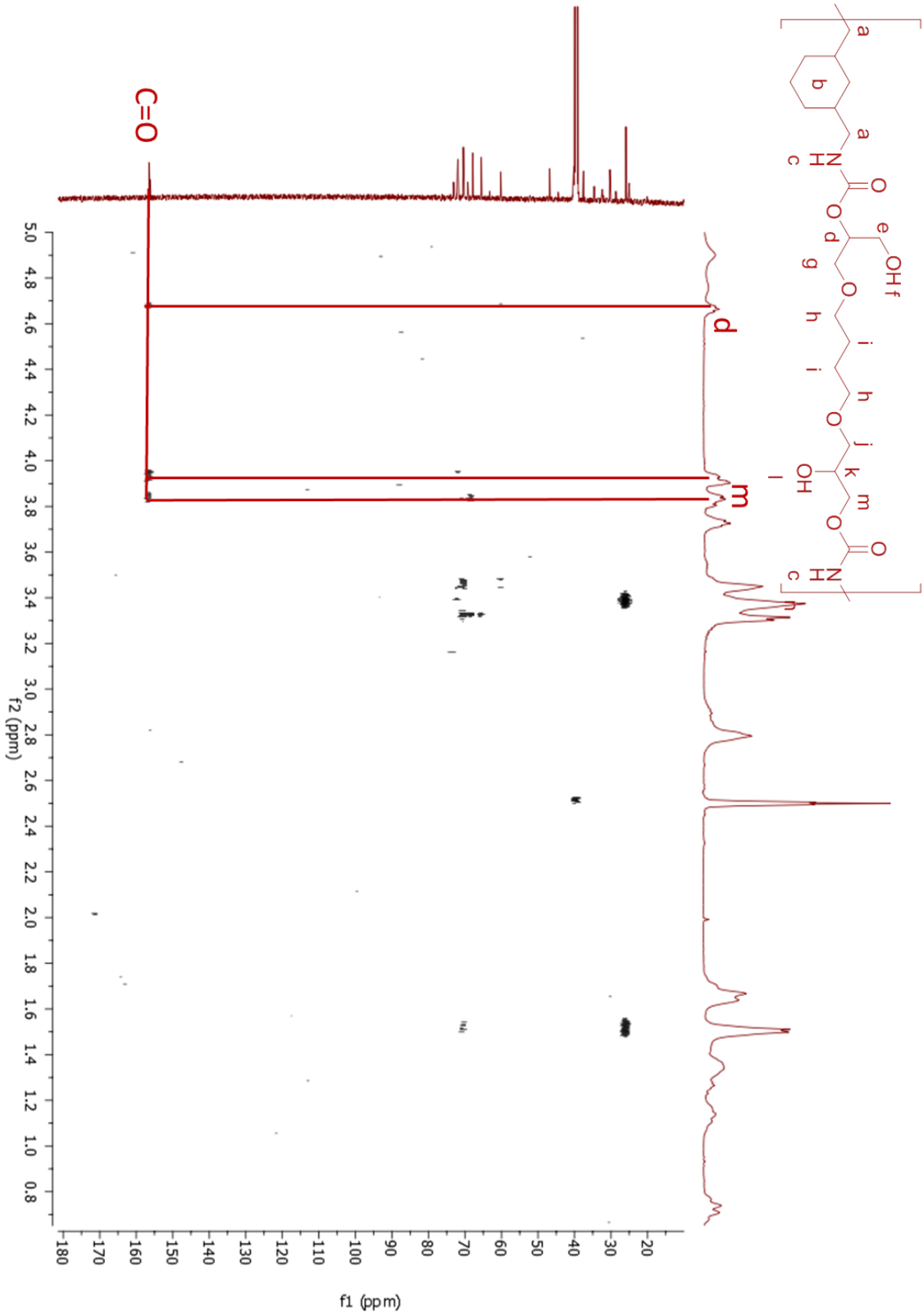
SI - Figure II-57: PHU obtained from the reaction of Bis-C5-Ether with CBMA at 80 °C in a mixture of MeOH/EtOH (1/9) after several cryogrinded and drying ^{1}H NMR in DMSO-d_6



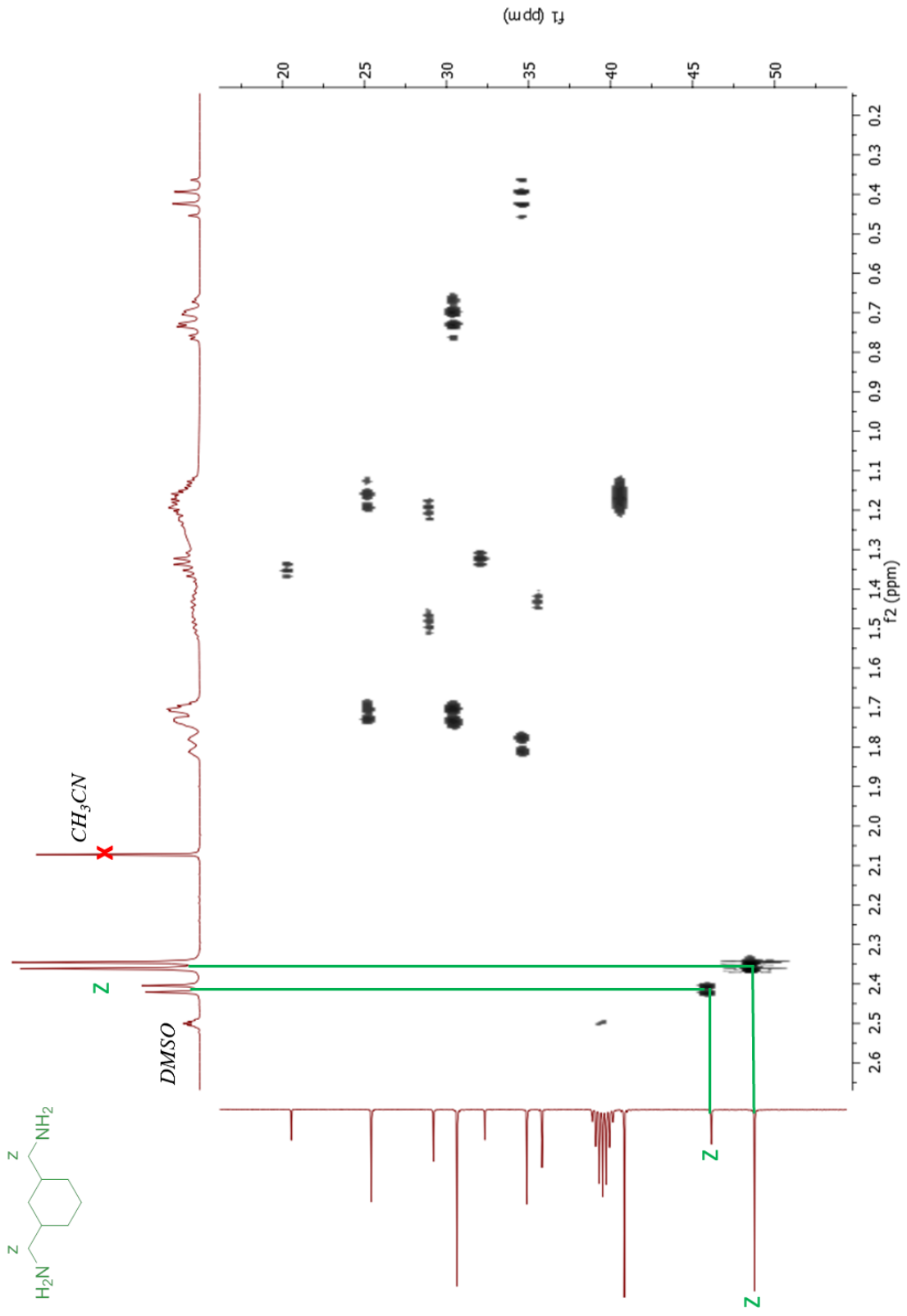
SI - Figure II-58: PHU obtained from the reaction of Bis-C5-Ether with CBMA after several cryogrinded and drying 2D COSY NMR in DMSO-d_6



SI - Figure II-59: PHU obtained from the reaction of Bis-C5-Ether with CBMA after several cryogrinded and drying 2D HSQC NMR in DMSO-d_6



SI - Figure II-60: PHU obtained from the reaction of Bis-C5-Ether with CBMA after several cryogrinded and drying 2D HMBC NMR in DMSO-d_6



SI - Figure II-61: CBMA HSQC NMR in DMSO-d_6

Conclusion Partie 2

Cette seconde partie a permis de mettre en évidence que la polymérisation en masse de carbonates cycliques par des amines à température ambiante conduit à des polymères PHUs de faibles masses molaires. Cela est principalement dû au faible degré d'avancement de la réaction.

Afin d'expliquer ce faible degré d'avancement, de nombreuses hypothèses ont été envisagées telles que la carbonatation de l'amine, les réactions secondaires ou les liaisons hydrogène. Ces dernières semblent être à l'origine de ce faible avancement de réaction et confirme les résultats obtenus dans la première partie. Ces interactions inter- et intra-chaînes limitent la diffusion des espèces lors de leur polymérisation.

Conclusion Chapitre II

Dans ce second chapitre, la synthèse, la caractérisation et les limites des polyhydroxyuréthanes ont été étudiées. Ces travaux ont montrés que le choix du précurseur carbonate cyclique ainsi que le choix du solvant sont des paramètres importants dans la vitesse de réaction et son avancement.

En effet, la réactivité des carbonates cycliques en combinaison avec une amine est influencée par leur structure et la nature de leurs substituants. Les composés di-thio-carbonates cycliques (CCs) et les carbonates cycliques à 6 membres (CC6) sont plus réactifs que leur analogue à 5 membres (CC5). Néanmoins, leur synthèse nécessite l'utilisation de composés dangereux et nocifs pour l'utilisateur. Par conséquent, les CC5 restent plus prometteurs. L'activation de ces derniers peut en effet être réalisée en jouant sur la nature de leur substituant. Les études ont montré que les groupements esters activent de manière conséquente ces précurseurs mais conduisent à des réactions secondaires. Par conséquent, les CC5 activés par des groupements éthers sont privilégiés pour la formation de PHUs à température ambiante.

La synthèse des carbonates cycliques est réalisée par carbonatation de précurseurs époxydés selon un procédé économiquement viable. Ces composés époxydés sont d'ailleurs disponibles commercialement sous une grande variété de structures chimiques permettant de moduler les propriétés des matériaux PHUs.

Néanmoins, les deux études menées et présentées dans ce chapitre ont mis en évidence la difficulté de synthétiser des PHUs en masse à température ambiante en raison du faible degré d'avancement de la réaction. Ce faible degré d'avancement est principalement lié à la création d'interactions hydrogène inter- et intra-chaînes limitant la diffusion des espèces au cours de la polymérisation.

Afin de redonner de la mobilité aux chaines lors de la polymérisation, quatre possibilités sont envisageables :

- Effectuer la réaction à chaud. L'apport d'énergie augmente l'agitation des molécules lors de la polymérisation et casse les liaisons hydrogène. Néanmoins, il est important de rester à des températures inférieures à 100°C pour éviter la formation de produits secondaires tels que les urées;

- Effectuer la réaction dans un solvant protique afin de limiter l'effet des liaisons hydrogène inter- et intra-chaînes ;
- Ajouter des composés hydroxylés tels que du di- ou tri-glycérol en tant que plastifiant qui auront les mêmes effets qu'un solvant protique ;
- Ajouter à la formulation un agent permettant une homogénéisation du système au cours de la polymérisation et inhibant l'effet des liaisons hydrogène.

Ces différentes voies impliquent des choix de procédés par les industriels et limitent les applications de ces polymères. Afin de contourner cette problématique, une nouvelle approche de synthèse de matériaux contenant des motifs hydroxyuréthane peut être envisagée. Cette nouvelle chimie sera développée dans le chapitre IV de ce manuscrit.

Mais avant cela, la formulation de matériaux PHUs pour des applications adhésifs et mousses ainsi que leurs propriétés thermiques, mécaniques et d'adhésion sont présentées dans le chapitre suivant.

Chapitre III. Formulations de Matériaux PHUs pour des Applications Adhésifs et Mousses

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Introduction Chapitre III

Dans le chapitre précédent, il a été démontré que la synthèse de PHUs de hautes masses molaires est principalement limitée par la diffusion des espèces lors de leur polymérisation. Afin de contourner ces inconvénients, deux procédés de formulation sont envisageables : formuler les polymères à température élevée ou utiliser un additif limitant les effets des liaisons hydrogène lors de la polymérisation. De plus, des précurseurs polyfonctionnels peuvent être utilisés afin d'obtenir des matériaux PHUs réticulés et ainsi augmenter leurs masses molaires de manière infinie.

Ce chapitre décrit, par l'intermédiaire de trois publications acceptées dans *European Polymer Journal*, la formulation de matériaux PHUs réticulés à partir de composés polyfonctionnels pour différentes applications. Pour une raison de procédé de synthèse, de réactivité et de limitation de réactions secondaires, les composés carbonates cycliques utilisés dans ces études sont des composés porteurs de fragments éthers de fonctionnalités et de longueurs de chaînes différentes, issus de la carbonatation de leurs analogues époxydés.

Dans une première partie, ce chapitre décrit la formulation et la caractérisation thermique et mécanique de matériaux PHUs. Les propriétés d'adhésion de ces matériaux sont ensuite évaluées sur différents supports.

Dans une seconde partie, la formulation de mousses PHUs et leurs propriétés mécaniques et thermiques sont étudiées.

Les propriétés des matériaux PHUs ainsi formulés sont comparées à des matériaux PUs de référence ayant des structures comparables.

Partie 1 - Formulations et caractérisations de matériaux PHUs pour des applications adhésifs

L'entreprise Bostik est un des leaders mondiaux dans la synthèse d'adhésifs polyuréthanes. Dans une optique de développement durable et de protection de ses employés et des consommateurs, l'entreprise souhaite substituer tout ou partie des isocyanates dans ses formulations d'adhésifs polyuréthanes.

Par conséquent, un travail de formulation de matériaux PHUs a été développé à partir des résultats obtenus dans les chapitres précédents de ce manuscrit. Ces matériaux ont été caractérisés structurellement, thermiquement, mécaniquement et thermo-mécaniquement. Enfin, la capacité d'adhésion de ces PHUs a été étudiée sur différents supports et comparée à des polyuréthanes de référence possédant des structures chimiques similaires. Toutes ces caractéristiques sont développées dans la suite de ce manuscrit. Ce travail a fait l'objet d'une publication scientifique acceptée dans *European Polymer Journal*.

Promising mechanical and adhesive properties of isocyanate-free poly(hydroxyurethane)

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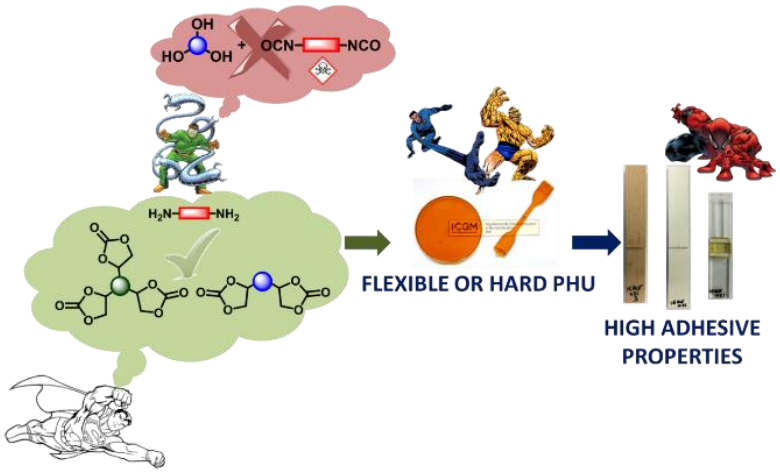
I. Abstract

A series of poly(hydroxyurethane) (PHU) materials were synthesized by step growth polymerization of cyclic carbonates and diamines. Trimethylolpropane tris-carbonate and various poly(propylene oxide) bis-carbonates were copolymerized with EDR-148 or 1,3-cyclohexanebis(methylamine) (CBMA). Thermal, mechanical and thermo-mechanical properties of PHU materials were characterized by DSC, TGA, durometer, dynamometer and DMA. Moreover, for the first time, we report adhesive properties of PHU synthesized without isocyanate on wood, aluminum and glass supports. All these properties were compared to reference polyurethane materials, synthesized from poly(propylene oxide) triol polymerized with hexamethylenediisocyante (HDI) or 1,3-bis(isocyanatomethyl)cyclohexane (CBMI), in order to compare the materials properties of similar chemical structure. PHUs exhibit outstanding adhesion properties due to the presence of hydroxyl groups hanging off the main polycarbonate chain.



II. Introduction

Since the discovery of the synthesis reaction of Polyurethanes in 1947 by Otto Bayer and coworkers [1], between diisocyanates and polyols, the polyurethane (PU) production have not stopped to increase to reach a global production of 18 million tons in 2016 [2]. PU ranks 6th among all polymers based on annual worldwide production. Owing to the facile variation of structure of polyols and diisocyanates, PU were readily tailored for diversified applications ranging from flexible and rigid foams, elastomers, thermoplastics, thermosets, adhesives, coatings, sealants, fibers… [3-5].

Despite this undeniable success, increasing concerns related to the use of (poly)isocyanate monomers as key reagents for the synthesis of PU have stimulated the search for alternative synthetic strategies that could afford macromolecules with similar properties without requiring the use of toxic isocyanate building blocks. In fact, the European regulation REACH is very vigilant on the harmfulness of PU synthesis [6]. Actually, the two most widely used isocyanates in PU industry, methylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as CMR (Carcinogen, Mutagen and Reprotoxic) [7].

Therefore, this context has led to the development of non-isocyanate polyurethane (NIPU). Thus, one first routes relies on the ring opening polymerization of aziridines with carbon dioxide. This route is the less dependent on isocyanates, but its main problem concerns the high toxicity of aziridines [8]. Another way to produce NIPU consists in the rearrangement of acyl azide followed by polycondensation with alcohol functions. However, during the polymerization, isocyanates are formed in situ [9, 10] which cannot fully prevent any toxicity. Other ways emerged, especially the polycondensation by transurethanization between diols and bicyclic carbonates, which still leads to the release of by-products during polymerization [11-15]. Hence, the reaction between a bicyclic carbonate and a diamine represents one of the most promising alternatives to the conventional synthesis of PUs [12, 15-37]. The resulting materials are called polyhydroxyurethanes (PHUs). Indeed, the macromolecular chain contains one hydroxyl group hanging off the chain for each generated urethane group.

The main problem concerning the synthesis of PHU relies on the low reactivity of carbonate/amine reaction and low molar masses of synthesized thermoplastic PHUs. Many studies reported in the literature have been conducted to enhance the reactivity of cyclic-carbonates with electro-withdrawing substituents [26, 34, 36, 38-44] or by using six-, seven-, eight-membered or thio-cyclic carbonates. But the synthesis of these compounds requires the use of

harmful and toxic products such as phosgene or its derivatives for six-, seven- or eight-membered cyclic carbonates or carbon disulfide for thio-cylic carbonate. Hence, in order to increase the kinetic reactions, Blain *et al.* [45] and Lambeth *et al.* [46] describes, in their works, the synthesis of PHU from 5-membered cyclic carbonate in presence of catalysts such as thiourea and 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD). However, despite numerous studies dedicated to enhance the reactivity of carbonate/amine reaction, actually, the preparation of the PHU materials with total conversion of carbonate at room temperature has been reported only for the synthesis of PHU foams [47]. Indeed, during the formation of PHU, hydrogen bonds are created between hydroxyl groups and carbamate groups, fixing the reaction mixtures. The use of blowing agent allows homogenizing the reaction and reaching total conversion of cyclic-carbonates. However, this is only valid for the foams and not for the other types of PHU materials.

Since the PHU thermoplastics do not exhibit high molar masses from five member carbonates and amines, cross-linking of PHU by polyfunctional carbonate cross-linker with di- or poly-amines can be envisaged to afford PHU thermoset rubbers [48, 49]. So far, PHU materials were reported for various applications such as coatings and the barrier properties [50], thermosets or thermoplastics [48, 49], rigid [51] and flexible [47, 52] foams. The only study in literature which reports adhesive properties is based on hybrid PHU-PU materials with TDI [53]. Moreover, only a handful of studies report mechanical characterizations of PHU materials [48, 49, 54, 55]. To the best our knowledge, the preparation and the characterization of PHU adhesives without isocyanate was never reported in literature. Therefore, we aspired to synthesize and characterize the first PHU adhesives. This pioneered work is very interesting since it is important to study for the first time the influence of hydroxyl groups of PHUs on adhesion properties and compare to PUs in order to assess potential interest for adhesive applications.

To synthesize a series of various PHUs, we chose five-membered cyclic carbonates since their synthesis does not require any phosgene derivative, in combination with diamines. We selected three commercially available five-membered cyclic carbonates: trimethylolpropane tris-carbonate (TMPTC) used as cross-linking agent, and two polypropylene oxide bis-carbonate of different molar masses (PPOBC380 and -640). PHUs were obtained by step growth polymerization of this three five-membered cyclic carbonates, in combination with aliphatic (EDR-148) or cycloaliphatic (CBMA) diamines. We characterized the thermal and mechanical properties of synthesized PHUs prior the characterization of the adhesive

properties on wood, aluminum and glass substrates. All these properties were compared to structural analogous PU reference synthesized from polyols and diisocyanate.

III. Experimental Section

Materials

Poly(propylene oxide) diglycidyl ether ($\overline{M}n$=380 g.mol^{-1} PPODGE-380 and $\overline{M}n$=640 g.mol^{-1} PPODGE-640), trimethylolpropane triglycidyl ether (TMPTGE), lithium bromide (LiBr), dimethylformamide (DMF), 1,3-cyclohexanebis(methylamine) (CBMA), dibutyltin dilaurate (DBTDL), hexamethylediisocyanate (HDI), 1,3-bis(isocyanatomethyl)cyclohexane (CBMI), ethyl acetate, tetrahydrofuran (THF) and toluene were purchased from Sigma Aldrich. 2,2'-(ethylenedioxy)diethylamine (EDR-148) was obtained from Huntsman. Poly(propylene oxide) triol (Triol 420) was obtained from Dow Chemical. Deuterated solvents ($CDCl_3$ and DMSO-d_6) were purchased from Eurisotop (Saint-Aubin, France).

Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: around 10 mg of product for ^{1}H, ^{13}C and ^{19}F experiment in around 0.5 mL of $CDCl_3$ or DMSO-d_6.

Fourier Transform Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectroscopy (FTIR) spectrometer. The characteristic IR absorptions mentioned in the text were strong bands are reported in cm^{-1}.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating of 10 °C.min^{-1}. Approximately 10 mg of samples was placed in an aluminum pan and heated from room temperature to 580 °C under a nitrogen or air flow (60 mL.min^{-1}).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. 10-15 mg samples were sealed in

aluminum pans. The thermal properties were analyzed at 20 °C.min^{-1} in the range between -100 and 150 °C to observe the glass transition temperature at the second ramp. All the reported temperatures are onset values.

Dynamic Mechanical Analyses

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Uniaxial stretching of samples (3 x 5 x 12 mm^3) was performed while heating at a rate of 3 °C.min^{-1} from -80 °C to 200 °C, keeping frequency at 1 Hz.

Crosslinking density (ν) was calculated on the basis of the relation between average molecular weight of effective networks chains (Mc) and density of the polymer (ρ) (Equation III-1).

Equation III-1 $$\nu = \frac{\rho}{M_c}$$

From rubber elasticity theory [56, 57], the uniaxial stretching were studied on the rubbery plateau at T_α+50, and at very small deformations. Under these hypotheses, the crosslinking density ($\nu_{E'}$), can be obtained from Equation III-2 and Equation III-3, where E' is the storage modulus, R is gas constant and T_α is the temperature, in K, of transition from vitreous to elastic domain of material determined at the maximum of the tan δ curve [58].

Equation III-2 $$E' = \frac{3\rho RT}{M_c}$$

Equation III-3 $$\nu'_e = \frac{E'_{at\ T\alpha+50}}{3RT_{\alpha+50}}$$

Hardness

Shore A or D hardness were measured on respectively a Shore durometer HDA 100-1 and HDD 100-1 from Sauter. Samples with dimensions 1 cm thickness were prepared for the measurement. An average of five measurements was performed.

Tensile test

Mechanical tensile tests performed on a Zwick/Roell Zwicky line testing machine with a 2.5 kN loading cell in order to determine mechanical properties of materials. A laser Xtens extensometer was used for monitoring the strains and to obtain the Young's modulus. Traction speed was performed at 1 mm.min^{-1} until 3% at strain length for Young's modulus and 100 mm.min^{-1} until materials rupture. Tests need plane dog bone specimens, of a 75 mm length, 25.0 length of narrow portion, 12.5 mm width of ends, 4.0 width of narrow portion and a thickness of around 2 mm according to standard ISO37. Thickness is measured at three points

on each sample and the lowest value is uploaded in the measurement software. After the test, this value is corrected owing to the rupture zone on the sample. Results are an average of measurements performed on three samples.

General procedure for syntheses of cyclic-carbonates: PPOBC380, PPOBC640 and TMPTC

The cyclic carbonate were syntheses with the same method that reported in our previous study [47]. In a round-bottom flask (500 mL), poly(propylene oxide) diglycidyl ether (PPODGE-380 or -640) or trimethylolpropane diglycidyl ether (TMPTGE) (1 eq, 100 g) and LiBr (5 mol%) were dissolved in DMF (150 mL). The solution was introduced onto a reactor and the atmosphere was replaced with CO_2 (P=15 bar). The solution was then allowed to stand at 80 °C with continuous stirring for 36 h. DMF was removed by distillation under vacuum (70 °C, P= 10 mbar). The pure product (PPOBC380 and PPOBC640) was obtained quantitatively as brown oil with a 76% yield.

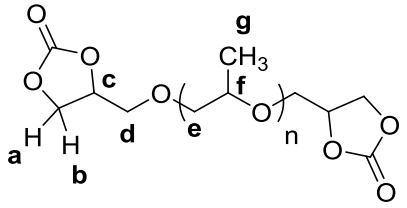


Figure III-1: PPOBC380 and -640 idealized structure

^{1}H NMR PPOBC380 (400 MHz, $CDCl_3$, ppm): δ: 1.06 (m, 7H, H_g); 3.24-3.90 (m, 18H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

^{1}H NMR PPOBC640 (400 MHz, $CDCl_3$, ppm): δ: 1.06 (m, 23H, H_g); 3.24-3.90 (m, 32H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

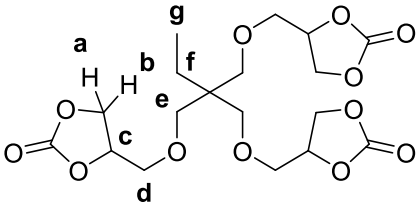


Figure III-2: TMPTC idealized structure

^{1}H NMR TMPTC (400 MHz, $CDCl_3$, ppm): δ: 0.81 (t, 3H, H_g); 1.34 (m, 2H, H_f); 3.20-4.00 (m, 12H, H_d, H_e); 4.25-4.60 (m, 6H, H_a, H_b); 4.82 (m, 3H, H_c).

Titration of the cyclic carbonate by ^{1}H NMR

A specified amount of cyclic carbonate (TMPTC, PPOBC380 or -640) (around 50 mg) and a standard solution of DMSO with toluene (around 60 mg of toluene dissolved in 10 mL of DMSO-d_6) were weighed into an NMR tube. Once the ^{1}H NMR acquisition was completed, characteristic peaks of carbonate a, b and c (4.51, 4.29 and 4.92 ppm respectively) and CH_3 (2.32 ppm) of toluene were integrated. The integration of CH_3 of toluene was fixed to 300. Carbonate equivalent weight (CEW) of TMPTC, PPOBC380 and -640 were calculated according to Equation III-4, where m_{C5} – mass of cyclic carbonate introduced into the NMR tube, $n_{function\ of\ carbonate}$ – molar amount of function carbonate in cyclic carbonate, I_a, I_b, I_c – integrations of characteristics peaks a, b and c of carbonate, $n_{toluene}$ – molar amount of toluene introduced in standard solution, I_{CH3} – integration of peak CH_3 of toluene. The CEW values for each cyclic carbonate were obtained in triplicate determinations.

Equation III-4
$$CEW = \frac{m_{C5}}{n_{function\ of\ carbonate}} = \frac{m_{C5} \times I_{CH3}}{(I_a + I_b + I_c) \times n_{toluene}}$$

Titration of the isocyanate by ^{1}H NMR

The procedure to titrate isocyanate function of HDI and CBMI is the same that described for cyclic carbonate. Indeed, characteristic peaks observed are the CH_2 in α of NCO situated at 3.30 ppm for HDI and 3.35 ppm for CBMI. Isocyanate equivalent weight (IEW) was calculated according to Equation III-5 where $m_{isocyanate}$ – mass of isocyanate introduced into the NMR tube $n_{function\ of\ isocyanate}$ – molar amount of function isocyanate in HDI or CBMI, I_{CH3} – integration of peak CH_3 of toluene, I_{CH2} – integrations of characteristic peaks CH_2 in α of NCO, $n_{toluene}$ – molar amount of toluene introduced in standard solution. The IEW values for each isocyanate were obtained in triplicate determinations.

Equation III-5
$$IEW = \frac{m_{isocyanate}}{n_{function\ of\ isocyanate}} = \frac{2}{3}\frac{m_{isocyanate} \times I_{CH3}}{I_{CH2} \times n_{toluene}}$$

Synthesis of PHU materials and adhesives

First, the cyclic carbonate compounds (TMPTC and PPOBC380 and -640) were stirred mechanically under vacuum for 2 min at 2,000 rpm with a Speed Mixer in a plastic pot. Once the homogeneous mixture was obtained, di-amine (EDR-148 or CBMA) was added and the mixture was stirred for 1 min at 2,000 rpm under vacuum, then the mixture was poured into a silicone mold for TGA, DSC, DMA, hardness, Swelling Index and Gel Content characterization or PTFE mold in order to obtain plane bone-dog specimens for tensile test. For the adhesive properties, the reaction mixture cyclic carbonate / amine was applied onto

wood, aluminum covered of epoxy paint or glass. The PHU materials and adhesives were crosslinked at 80 °C during 12 hours then 150 °C during 30 minutes.

Synthesis of PU materials and adhesives

The Triol 420 and DBTDL catalyst were mixed together in a plastic cup and stirred at during 2 min at 2,000 rpm under vacuum with mechanical stirrer at room temperature. The stirring was stopped for the addition of isocyanate adducts (HDI or CBMI) before continuing at the same speed for 1 min under vacuum. The reaction mixture was poured into a silicone mold for TGA, DSC, DMA, hardness, Swelling Index and Gel Content characterization or PTFE mold in order to obtain plane bone-dog specimens for tensile test. For the adhesive properties, the reaction mixture was applied onto wood and aluminum covered of epoxy paint surface.

Swelling Index and Gel Content

Swelling Index: three samples (30mg each) were separately put into 30 ml THF for 24 h. The swelling index, SI, is given by Equation III-6, where m_0 is initial mass of tab and m_1 is mass of tab after swelling in solvent.

Equation III-6 $$SI=\frac{m_1-m_0}{m_0}\times 100$$

Gel content: After SI measurement, the three tabs are dried in a ventilated oven at 50 °C during 24 h. The gel content GC is given by following Equation III-7, where m_0 is initial mass of tab and m_2 is mass of tab after drying.

Equation III-7 $$GC=\frac{m_2}{m_0}\times 100$$

Wood, aluminum and glass bonding and lap shear strength testing

The adhesive was applied onto the surfaces of wood, aluminum or glass specimens with a bonding area of 12.5 x 25 mm. The two coated pieces of wood, aluminum or glass surfaces were stacked together for the adhesives to be cured at 80 °C/12h and 150 °C/30min for PHU and at room temperature during 24h for PU adhesives (Figure III-3). Specimens were conditioned at 23 °C with relative humidity of 50% for one day. The lap shear strength tests were carried out on the Zwick/Roell Zwicky Machine. The specimens were gripped by two screw-type flat-plate grips and pulled at a shear rate of 100 $mm.min^{-1}$. Specimens were prepared in triplicate and the average lap shear strength was reported.

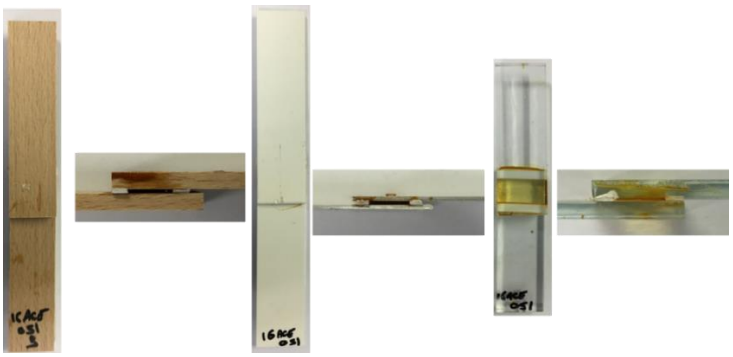


Figure III-3: Wood, aluminum and glass bonding specimens

IV. Results and Discussion

IV.1 Synthesis and characterization of raw materials

IV.1.1 Cyclic carbonate

The three cyclic carbonates were synthesized from commercial epoxy compounds, poly(propylene oxide) diglycidyl ether (PPODGE380 and PPODGE640) and trimethylolpropane triglycidyl ether (TMPTGE) by carbonation process in presence of lithium bromide and dimethylformamide (DMF) (Figure III-4). The syntheses and the complete characterizations of these products were described in our previous paper [47]. TMPTGE is an interesting compound because it comes from a biobased triol, trimethylolpropane. Indeed, the trimethylolpropane can be obtained by biotechnical and chemical processes based on raw materials like sugars [59, 60]. The three five-membered cyclic carbonates were noted respectively poly(propylene oxide) biscarbonate (PPOBC380 and PPOBC640) and trimethylolpropane triscarbonate (TMPTC). These cyclic carbonate are currently commercially available at Specific Polymers Company.

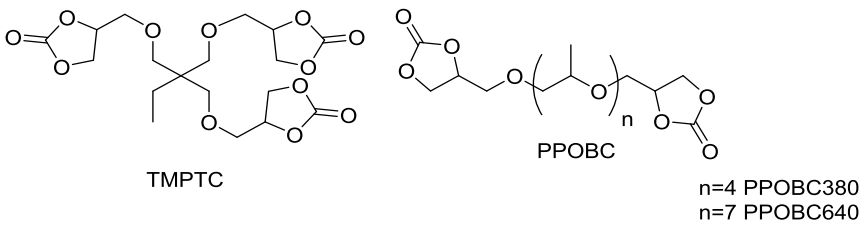


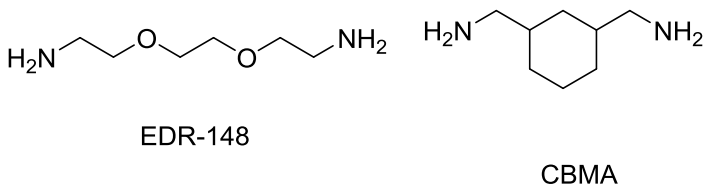
Figure III-4: Cyclic carbonate structures

In order to determine precisely the carbonate functionality (CEW: Carbonate Equivalent Weight) of each carbonated monomer, ^{1}H NMR titration with standard solution (DMSO-d_6

with few milligram of toluene) was achieved. CEW, degree of polymerization, functionalities and molar masses of cyclic carbonates were summarized in Table III-1.

IV.1.2 Amine

In order to synthesize polyhydroxyurethane materials, two reactive commercial amines were used: EDR-148, a primary aliphatic diamine commercialized by Hunstman Company and CBMA, a primary cycloaliphatic diamine purchased from Sigma Aldrich (Figure III-5). Webster *et al.* [61] and Diakoumakos *et al.* [62] showed that primary aliphatic amines are the most reactive amines for reaction with cyclic carbonate. However, the carbonation phenomenon of amines with CO_2 of air is well known [63], therefore, these diamines have been previously distilled under vacuum at 120 °C and stored under argon. ^{1}H NMR analyses of EDR-148 (ESI 4) and CBMA (ESI 5) confirm the purity and the di-functionality of these diamines. In order to formulate isocyanate-free polyurethane materials, the Amine Hydrogen Equivalent Weight (AHEW) of diamines was calculated from Equation III-8 where M is the molar mass of diamine and nb active H is the number of active hydrogen of the amine (1 by NH_2 function in the case of cyclic carbonate / amine reaction).



EDR-148 CBMA

Figure III-5: Amines structures

Equation III-8 $$AHEW = \frac{M}{nb\ active\ H}$$

IV.1.3 Polyol

To compare the properties of PHU materials, two classical polyurethane materials were synthesized from polyol and isocyanate. The polyol used is a poly(propylene oxide) noted Triol 420 whose structure is given in Figure III-6 and ^{1}H NMR in SI - Figure III-6. The hydroxyl content used for polyurethane formulation was given by supplier and is reported in Table III-1. However, to formulate polyurethanes, the hydroxyl equivalent weight (OHEW) was calculated from Equation III-9 with M_{KOH} - molar mass of KOH and IOH - hydroxyl content of Triol 420. The value of OHEW is also reported in Table III-1.

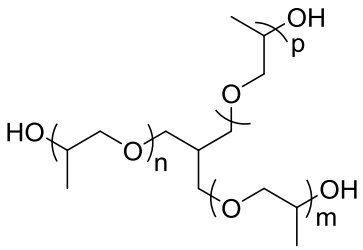


Figure III-6: Structure of Triol 420

Equation III-9 $$OHEW = \frac{M_{KOH}}{IOH.10^{-3}}$$

IV.1.4 Isocyanate

To synthesize PU material references with an analogous structure compared to PHU materials, two diisocyanates with similar structures than EDR-148 and CBMA amines were used: hexamethylene diisocyanate (HDI) and 1,3-bis(isocyanatomethyl) cyclohexane (CBMI) (Figure III-7). The ^{1}H NMR analyses of HDI (SI - Figure III-7) and CBMI (SI - Figure III-8) confirm the purity and difunctionality of these compounds. As for cyclic carbonates, the isocyanate functionality (IEW: Carbonate Equivalent Weight) of each diisocyanate monomers was determined by ^{1}H NMR titration with standard solution (DMSO-d_6 with few milligram of toluene). IEW, functionalities and molar masses of diisocyanates were summarized in Table III-1.

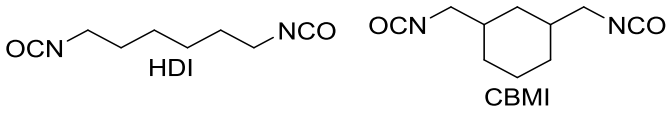


Figure III-7: Diisocyanate structures

Table III-1: Characteristics of raw materials

Reactants	IOH (mgKOH.g-1)	CEW/OHEW (g.eq-1)	AHEW/NCOEW (g.eq-1)	Carbonate or amine functions	M (g.mol-1)
Triol 420	3831	146	-	≈3	4201
PPOBC380	-	235	-	≈2	3522
PPOBC640	-	350	-	≈2	6612
TMPTC	-	183	-	2.6	4763
HDI	-	-	77	2	1683
CBMI	-	-	84	2	1943
EDR-148	-	-	74	2	1481
CBMA	-	-	71	2	1421

[1]: Dow chemical, Huntsman or Sigma Aldrich data; [2]: Molar mass calculated by ^{1}H NMR; [3]: Molar mass calculated from M=CEW x Carbonate function

IV.2 Synthesis and characterization of PHU materials

IV.2.1 Synthesis of PHU materials

In this study, several formulations of PHU materials were achieved from the five reactants without any solvent or catalyst. These formulations depend on the amine structure (aliphatic: EDR-148 or cycloaliphatic: CBMA) and the cyclic carbonate ratios (TMPTC and PPOBC380 or -640) incorporated in the material. Reactions were conducted at 80 °C during twelve hours and 150 °C during 30 min. PHUs materials are noted M-1 to M-10.

The presence of crosslinking carbonate (TMPTC) was crucial to obtain solid materials. In fact, the PHU materials obtained with only di-functional cyclic carbonates and di-amines present lower molar masses [24, 36, 40, 44, 64, 65]. Moreover, the long aliphatic carbon backbone of PPOBC380 and -640 confers flexibility to materials. Therefore, PPOBC640 brings more flexibility to the materials that PPOBC380. These PHU materials were prepared by using formulations based on molar equivalents of reactants (Table III-2). PHU materials were firstly structurally characterized by infrared spectroscopy, then, the degree of cross-linking of each formulation was estimated by measurement of swelling index (SI) and gel content (GC) of each polymer. Thermal and thermo-mechanical properties of materials were determined by thermogravimetric (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). PHU polymers were also characterized by tensile test with dynamometers for their mechanically properties and with durometer for their hardness. Finally, the adhesive properties of these materials were compared on three substrates: wood, aluminum and glass. All characteristics were compared to two PU material references synthesized from poly(propylene oxide) triol (Triol420) and hexamethylene diisocyanate (HDI), PU_{HDI}, or 1,3-bis(isocyanatomethyl)cyclohexane (CBMI), PU_{CBMI}, with DBTDL as catalyst at room temperature during 24 hours. These precursors were chosen to obtain polyurethanes with structures analogous to PHUs, thus allowing for meaningful comparison of their properties.

Table III-2: PHU materials formulation in molar equivalent

Reactants	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	M-9	M-10
TMPTC	1	0.75	0.50	0.75	0.50	1	0.75	0.50	0.75	0.50
PPOBC380	-	0.25	0.50	-	-	-	0.25	0.50	-	-
PPOBC640	-	-	-	0.25	0.50	-	-	-	0.25	0.50
EDR-148	1	1	1	1	1	-	-	-	-	-
CBMA	-	-	-	-	-	1	1	1	1	1

IV.2.2 Structural characterization of PHU materials

The PHU material pictures in Figure III-8 showed that all the PHU materials are visually homogeneous.

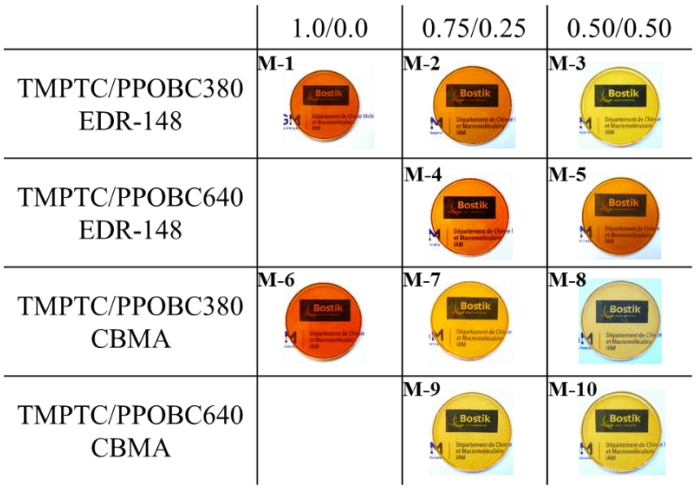


Figure III-8: PHU materials samples

In order to check the advancement of reaction between cyclic carbonate and amine, infrared spectroscopy analysis of PHU materials was performed after curing. Figure III-9 and Figure III-10 present respectively the overlaying infrared spectra of cyclic carbonate, amine and PHU materials for EDR-148 and CBMA. The spectra of all PHU materials are similar. On the PHU material spectra, we observe the total disappearance of band at 1612 and 1617 cm^{-1} corresponding to NH_2 of EDR-148 and CBMA respectively. Moreover, we observe the decreasing of band at 1791 cm^{-1} corresponding to elongation of carbonate group C=O bond stretching of TMPTC, PPOBC380 and -640. These residual band could correspond to cyclic carbonate end-groups on polymers. These bands could also correspond to residual non-reacted free cyclic carbonate monomers.

In order to demonstrate full conversion of reaction and absence of residual monomers, we performed swelling index (SI) and gel content (GC) measurements on PHU materials (Table III-3). The results gave information on crosslinking degree of materials. Indeed, lowest SI and highest GC correspond to the maximum crosslinking of polymer. The variation of swelling index of PHU materials depends on two parameters: the TMPTC/PPOBC ratio and the length of PPOBC used to formulate PHU materials. Indeed, TMPTC, with a functionality higher than 2, increases crosslinking degree of polymers. Hence, the distance between crosslinking nodes is reduced and the solvent penetrates less easily in materials, which leads to lower SI. Similarly, the length of PPOBC influences the distance between the nodes of crosslinking and

the crosslinking density. Moreover, the structure of diamine influences the SI of material. The cycloaliphatic structure of CBMA (or CBMI) increases the size between crosslinking nodes of PHU and PU materials, which increases the SI, compared to materials formulated with EDR-148 (or HDI).

Concerning gel contents, all PU and PHU materials exhibit high gel contents (91-99%), which indicates a high crosslinking of networks, without free monomers and a quantitative conversion of polymerization. Therefore, bands of C=0 carbonate in synthesized PHU materials correspond to carbonate groups at the end of macromolecular chains of PHU materials.

The total disappearance of NCO band of HDI or CBMI at 2243 cm^{-1} on the overlaying spectra of PU material references (SI - Figure III-9), and their high GC values indicate also a quantitative conversion of reaction between alcohol and isocyanate and that the materials were synthesized at maximum of crosslinking.

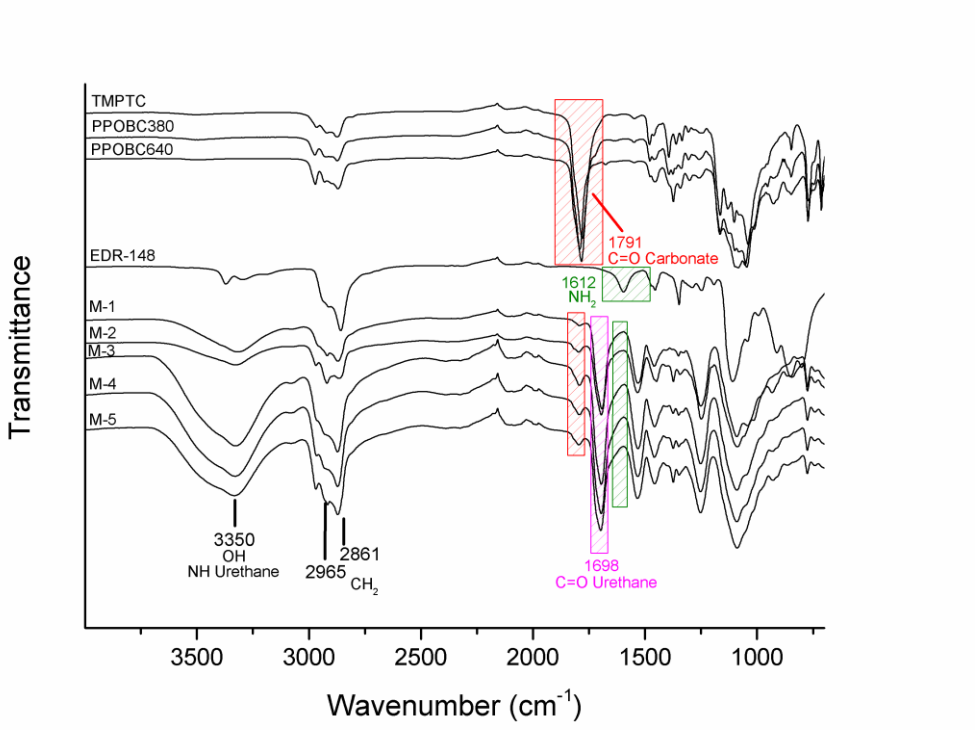


Figure III-9: Overlay of infrared spectra of raw materials and PHU materials synthesized with EDR-148

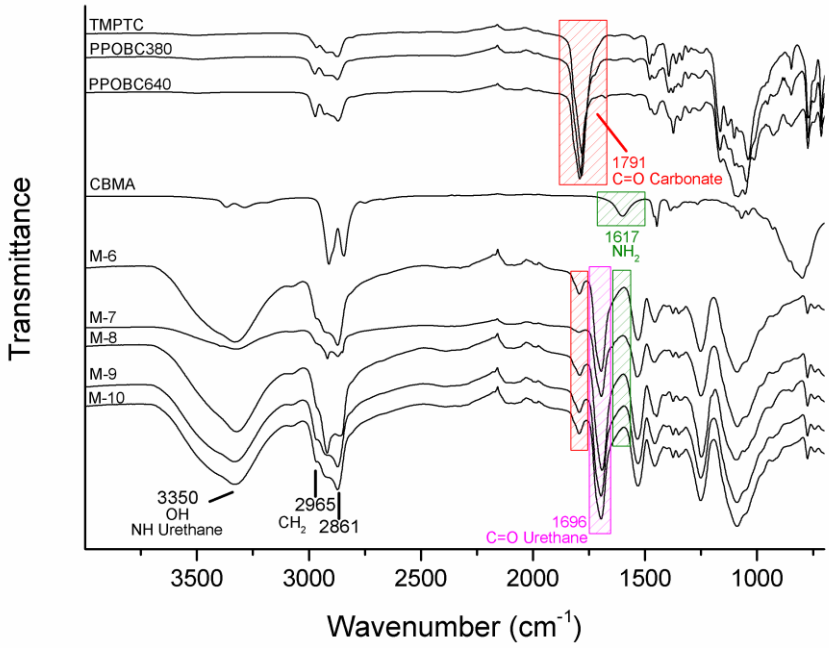


Figure III-10: Overlay of infrared spectra of raw materials and PHU materials synthesized with CBMA

Table III-3: Main characteristic values of PU and PHU materials synthesized from cyclic carbonate, EDR-148 and CBMA

Materials	*Composition*	*SI*[1] *%*	*GC*[2] *%*	*Tg (°C)*	*Tα (°C)*	*E'*[3] *(10^5 Pa)*	*$\nu_{E'}$*[4] *(mol.m^{-3})*
PU_{HDI}	Triol 420/HDI	189	97	10	17	56.4	626
M-1	TMPTC/EDR-148	64	96	34	43	53.6	665
M-2	0.75TMPTC/0.25PPOBC380/EDR-148	89	97	26	30	24.3	301
M-3	0.50TMPTC/0.50PPOBC380/EDR-148	138	91	18	29	11.6	144
M-4	0.75TMPTC/0.25PPOBC640/EDR-148	131	93	16	27	10.2	127
M-5	0.50TMPTC/0.50PPOBC640/EDR-148	301	91	-4	7	10.2	127
PU_{CBMI}	Triol 420/CBMI	218	96	32	35	64.4	785
M-6	TMPTC/CBMA	78	97	76	99	34.2	424
M-7	0.75TMPTC/0.25PPOBC380/CBMA	230	99	63	70	31.5	256
M-8	0.50TMPTC/0.50PPOBC380/CBMA	315	92	50	55	10.9	91
M-9	0.75TMPTC/0.25PPOBC640/CBMA	199	92	51	69	22.4	278
M-10	0.50TMPTC/0.50PPOBC640/CBMA	313	93	21	43	14.3	177

[1]: Swelling Index; [2]: Gel Content; [3]: E' at Tα+50 °C; [4]: Crosslink density

IV.2.3 Thermal characterization of PHU materials

First of all, PU and PHU materials were characterized by DSC in order to determine their glass transition temperature (Tg) (Table III-3, SI - Figure III-10 - SI - Figure III-13). Hence, materials were submitted at two temperature ramps between -100 and 150 °C. During the first

dynamic ramp temperature, from -100 to 150 °C, no residual exothermic reaction was observed for all PHU materials, which proves, in addition to IR analysis and GC values, that the materials are nearly totally crosslinked. After a cooling back to -100 °C, Tg were measured during the second dynamic ramp temperature to 150 °C. PHUs exhibited various Tg values, owing to the different monomers and their various ratios, ranging from hard and brittle materials, characterized with high Tg, to flexible and elastic ones, with lower Tg. These differences can be explained by three parameters. Firstly, the amine structure: PU or PHU materials formulated with CBMI and CBMA have a Tg of 32 and 76 °C respectively, whereas those formulated with HDI or EDR-148 have a lower Tg (10 and 34 °C respectively). Indeed, the cycloaliphatic structure of CBMI or CBMA reduces polymer chains mobility and confers rigidity to the materials, whereas HDI or EDR-148 brings flexibility. The second parameter is the chain length of PPOBC. The longer is the aliphatic chain of PPO, and the more it brings flexibility to materials which lowers its Tg. Finally, the third parameters that influences the Tg is the crosslinking agent (TMPTC) amount in the materials. Increasing ratios of TMPTC lead to more crossinked materials with higher Tg.

Thermal stability of PHU materials was also characterized by TGA on the temperature range between 23 °C (room temperature) and 580 °C, under inert (N_2) and oxidative (Air) atmosphere. The results are summarized in Figure III-11 and the curves are shown inSI - Figure III-15. The thermal stability of these PHU materials is similar to other PHU materials reported in literature [24, 66]. Moreover, the oxidative atmosphere has no influence on the thermal stability of these materials. However, PU materials exhibit a slightly higher thermal stability than PHU materials. It may be explained, in the case of PHU materials, by the weakening of bond between carbonyl carbon and oxygen in urethane group due to the influence of OH-groups [67]. We demonstrated in a previous work, than thermal decomposition of PHU and PU polymers is similar [47].

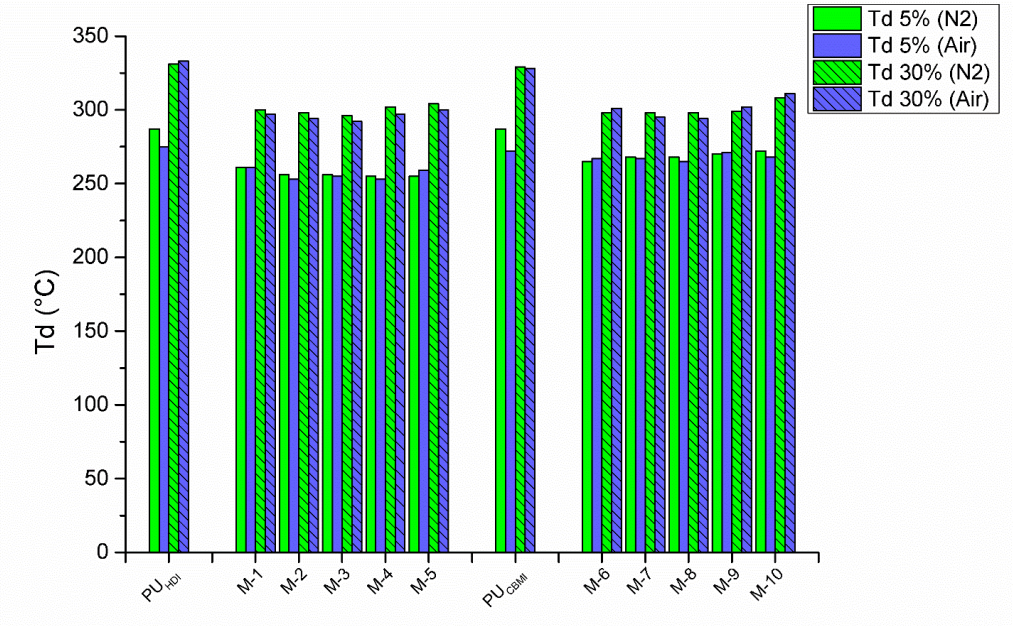


Figure III-11: Main degradation temperatures of PU and PHU materials

IV.2.4 Thermo-mechanical characterization of PHU materials

The thermo-mechanical properties of the materials were investigated using DMA. Figure III-12 shows storage modulus E' and loss factor tan δ as a function of temperature for PU and PHU materials. From these curves, E' in vitreous and elastic domain are similar for all PHU materials. The transition from vitreous to elastic domain corresponds to the α transition relaxation, associated to the glass transition temperature, when the chains in the amorphous region begin to coordinate large scale motions. Temperature Tα of the α transition is determined at the maximum of the tan δ curves (Table III-3). Tα values follow the same trend than Tg values determined by DSC and hardness in function of TMPTC amounts and amine structures. The tan δ peak form reflects homogeneity of material: a symmetrical and narrow tan δ reveals a homogeneous material [68]. Consequently, tan δ reveals that the PU and PHU materials are homogeneous. Usually, the crosslinking density ($\nu_{E'}$ determined from Equation III-3) of carbonate networks increases with the cross-linker content (TMPTC) for PHU materials. Hence, crosslinking density of PHU materials formulated with 100% TMPTC and CBMA are respectively 2.8 and 4.4 times higher than crosslinking densities of PHU materials formulated with 25% and 50% of PPOBC640. Indeed, the structure of TMPTC presents a cyclic carbonate functionality of 2.6, which decreases the distance between urethane groups in the materials, and increases the crosslinking density. The crosslinking density varies also with the structure of amine. Indeed, the PHU material formulated with 100% TMPTC and EDR-148 presents a crosslinking density 1.6 times higher than PHU material formulated with

CBMA and the same amount of TMPTC. These crosslinking density values follow the same trend than SI values.

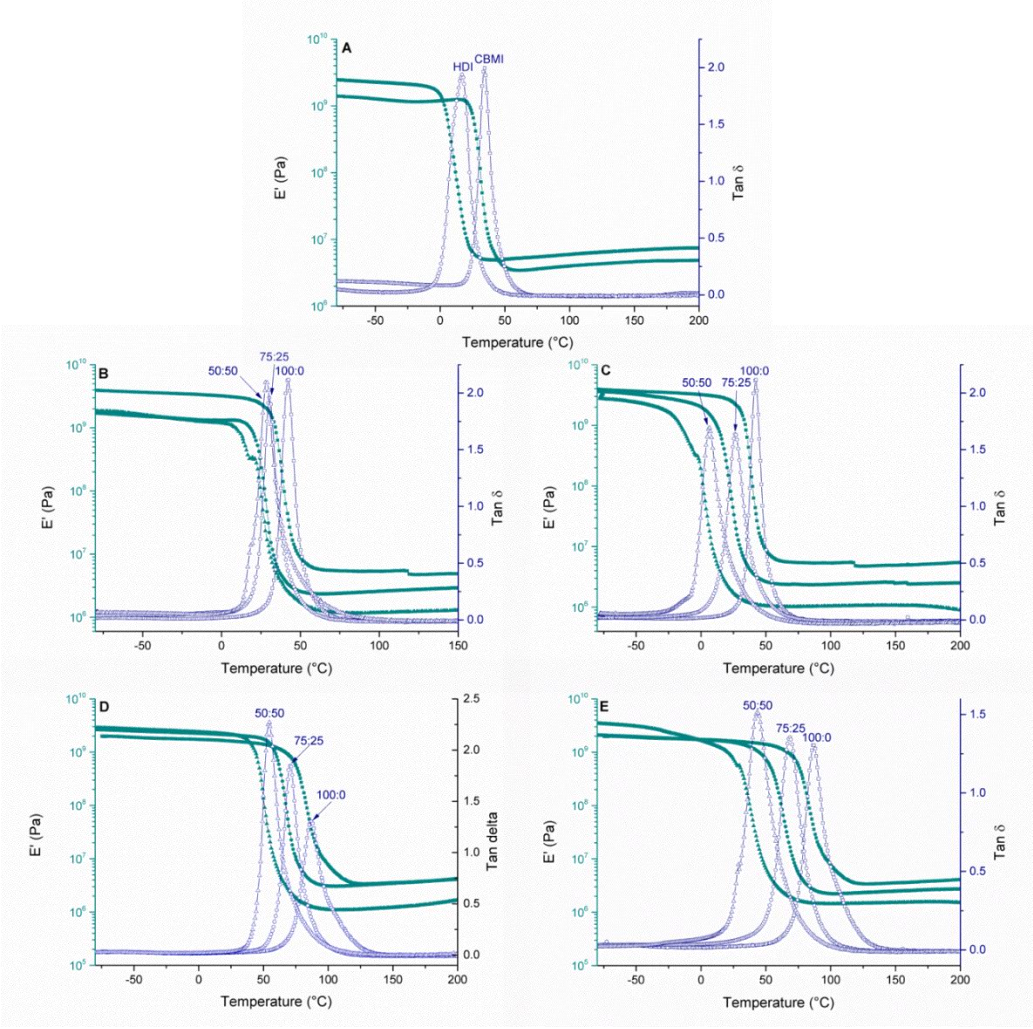


Figure III-12: DMA of PU (A) and PHU materials synthesized with TMPTC, PPOBC380 (B) or PPOBC640 (C) and EDR-148 and TMPTC, PPOBC380 (D) or PPOBC640 (E) and CBMA

IV.2.5 Mechanical properties of PHU materials

Synthesized PU and PHU materials were characterized to determine Shore A and D hardness and their strain at break, tensile strength and Young's modulus with dynamometer for tensile test.

Shore A and D values are given in Table III-4. The hardness values of materials follow the same tendency than glass transition temperatures. This range of hardness is explained by the same parameters: amine structure, chain length of PPO in PPOB380 and -640 and crosslinker amount (TMPTC). Thus, the higher is the Tg and the higher are both the rigidity and the hardness.

The mechanical properties of PU and PHU materials were then characterized by tensile test. Figure III-13 shows the tensile test curves obtained throughout the traction of materials. The strain at break, tensile strength and Young's modulus results are summarized in Table III-4. From these results, these materials present different mechanical behaviors. The M-6, M-7, M-8 and M-9 materials are brittle materials [69]. These PHU were formulated with CBMA which confers rigidity to materials. Moreover, these materials were analyzed below their glass transition temperature. Therefore, these materials are hard and brittle leading to an inelastic fracture (high modulus, low deformation). However the M-10 material formulated also with CBMA presents a different behavior which could be due to a formulation with 50% of PPOBC640. Indeed, the long aliphatic chain of PPOBC640 confers flexibility to material and decrease the Tg. This material was analyzed above its Tg. Therefore, the Young's modulus is lower than for M-6, M-7, M-8 and M-9 and the strain at break is higher. This leads to a ductile break: beyond of proportional limit of stress-strain curves, flowing chain; the sample deforms irreversibly and undergoes a striction phenomenon [69]. The section materials decreases under effect of the jaws of the tensile testing machine holding the sample, causing stress concentration. It results in flowing chains and an intern friction leading to a temperature increase. This behavior is also observed for the PHU materials formulated with EDR-148 (M-1, M-2, M-3, M-4 and M-5). However, the M-1 material presents a surprising behavior. Beyond the plasticity plateau, we observe a striction propagation intervening at inferior stress. At the end of tensile test, we observe an increase of stress reflecting the behavior of crosslinking node.

Concerning the behavior of PU materials, PU_{HDI} has a lower strain at break (28%) than PU_{CBMI}. This is due to the use of HDI which does not bring enough structure and rigidity to the materials compared to aliphatic ring of CBMI in PU_{CBMI} (140%). PU_{HDI} is a soft and brittle polymer while PU_{CBMI} is a soft and resistant polymer. Of course, these typical behaviors are also conditioned by the deformation speed and temperature. A same material can be ductile at low deformation speed and high temperature and presents a fragile break at low temperature and high deformation speed.

To conclude on this part, a range of isocyanate-free polyurethane with different hardness values and mechanical behaviors was formulated. The mechanical property results in terms of tensile test of PHU polymers are very interesting compared to classical PU materials. Although the low molar mass often reported in the literatures for PHUs, their mechanical properties of these materials are similar to their analogous PU probably owing to the

hydrogen bonding interactions created between hydroxyl and urethane groups generated by ring opening of cyclic carbonate.

Table III-4: Main mechanical properties of PU and PHU materials synthesized with cyclic carbonates, EDR-148 and CBMA

Material	*Formulation*	*Hd[1] (Sh A)*	*Hd[1] (Sh D)*	*Str. at Br.[2] (%)*	*Ten. Stre.[3] (MPa)*	*Young's Mod.[4] (MPa)*
PU_{HDI}	Triol 420/HDI	69 ± 3	23 ± 4	28*	1.56*	6.47*
M-1	TMPTC/EDR-148	94 ± 1	55 ± 1	130 ± 10	10.5 ± 1.4	14.4 ± 3.4
M-2	0.75TMPTC/0.25PPOBC380/EDR-148	87 ± 5	33 ± 3	150 ± 5	4.24 ± 0.21	3.4 ± 0.1
M-3	0.50TMPTC/0.50PPOBC380/EDR-148	44 ± 6	-	170 ± 13	1.32 ± 0.07	1.06 ± 0.11
M-4	0.75TMPTC/0.25PPOBC640/EDR-148	54 ± 2	-	99 ± 3	1.54 ± 0.02	2.3 ± 0.1
M-5	0.50TMPTC/0.50PPOBC640/EDR-148	25 ± 3	-	140 ± 3	0.62 ± 0.02	0.74 ± 0.11
PU_{CBMI}	Triol 420/CBMI	88 ± 4	58 ± 2	140 ± 8	7.87 ± 1.90	5.5 ± 0.8
M-6	TMPTC/CBMA	99 ± 3	100 ± 1	3 ± 1	75.1 ± 13.1	2370***
M-7	0.75TMPTC/0.25PPOBC380/CBMA	99 ± 2	100 ± 2	3 ± 1	77.1 ± 12.5	2310 ± 90
M-8	0.50TMPTC/0.50PPOBC380/CBMA	95 ± 5	92 ± 4	2**	46.4 ± 4.5	-****
M-9	0.75TMPTC/0.25PPOBC640/CBMA	97 ± 3	85 ± 5	5**	54.7±4.6	845±53
M-10	0.50TMPTC/0.50PPOBC640/CBMA	87 ± 4	22 ± 2	280 ± 7	6.3 ± 0.6	1.04 ± 0.45

[1]: Hardness; [2]: Strain at Break; [3]: Tensile Strength; [4]: Young's Modulus; Tensile tests were performed with 5 samples for each formulation *: not errors because just one samples were tested, the jaws of machine tensile machine cutting samples; **: errors were between 0 and 1 and, therefore, incompatible with significant digits of values***: not errors because only one samples has a strain at break superior at 3%; ****: not sample has a strain at break superior at 3%

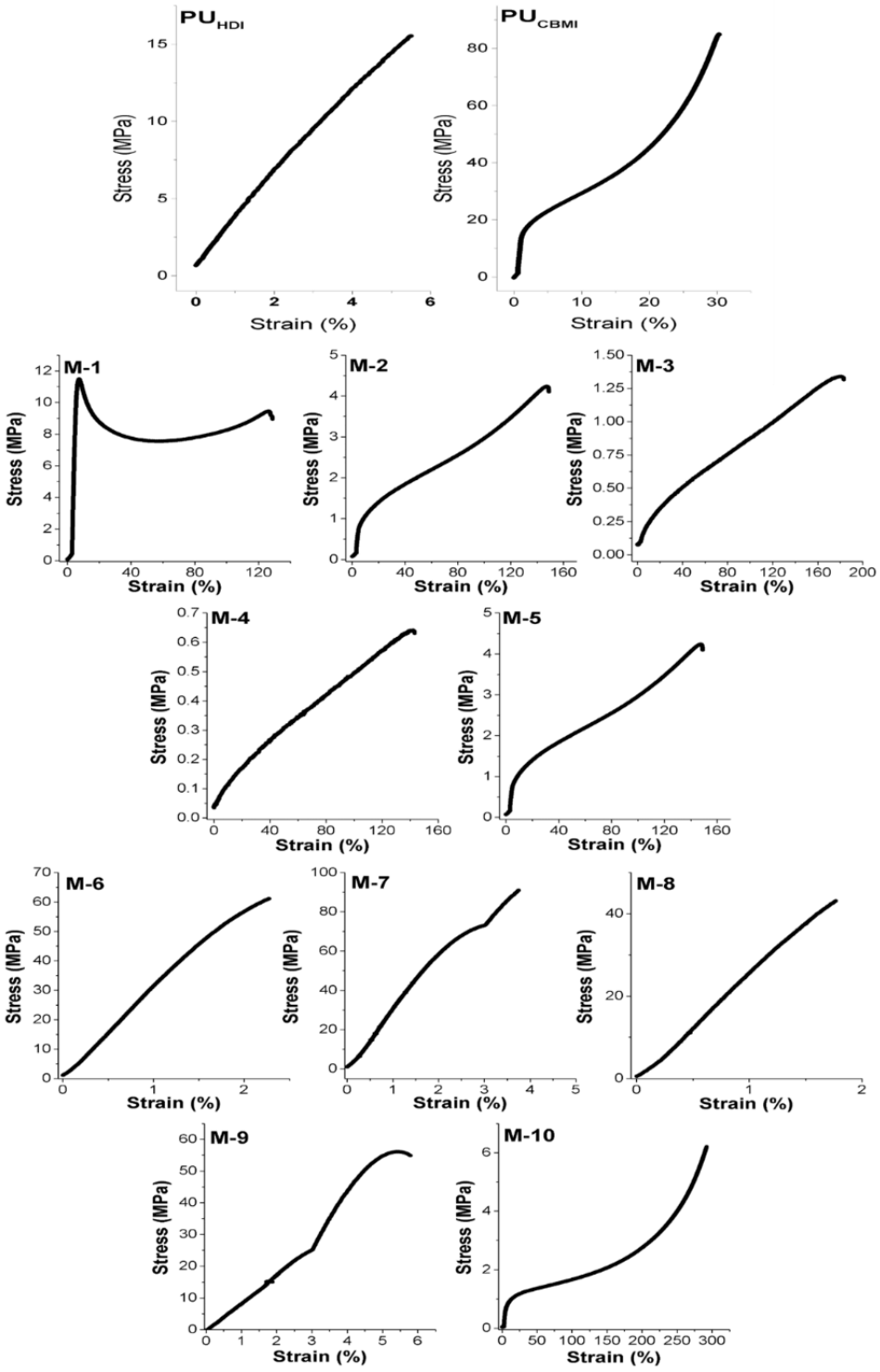


Figure III-13: Tensile test curves of PU and PHU materials

IV.2.6 Adhesive properties characterization of PHU materials

To the best our knowledge, the adhesion properties of PHUs were never reported in literature.

Even if, recently, Leitsch *et al.* [53] report the good adhesive properties of PU/PHU hybrid polymers, these materials contain isocyanate and thus are not really isocyanate-free PUs. Hence, adhesive properties of our PHU materials synthesized without isocyanate were studied on different supports (glass, wood and aluminum covered of epoxy paint) and compared with PU references. Figure III-14 and Figure III-15 give the adhesive shear forces obtained on wood and aluminum for PHU and PU references materials.

The results for the glass support are not given because the glass doesn't resist to traction and no failure is observed for the adhesive. In other terms, the shear force needed to break the PHU adhesives is higher than the shear force required to break the glass support. In addition of Van der Waals bonds which are created between polymers and support, these excellent adhesive properties of PHU materials can be explained by the creation of hydrogen bonds between Si-O groups at the surface of glass and hydroxyl groups of PHU created by ring opening of cyclic carbonate by amine. Therefore, these PHU materials could be used as glazing gaskets in building or automobile industry for example.

Concerning the wood (beech wood) support, we also obtained excellent adhesive properties of PHU materials. In fact, Figure III-14 compares the shear force of PHU synthesized with both EDR-148 and CBMA with respective analogous PU_{HDI} and PU_{CBMI}. Firstly, concerning PHU synthesized with EDR-148 (M-1 to M-5), the shear force of M-1 is higher than the PU_{HDI} and other PHU materials. This M-1 material is synthesized with 100% of TMPTC and corresponds to the most crosslinked material, which thus contains the highest content of urethane and hydroxyl groups. As in the case of glass, on the wood surface, hydrogen bonds created with hydroxyl groups of PHU and the wood could explain the higher adhesive properties of this material compared to PU_{HDI}. The others PHU materials were synthesized with different contents of PPOBC380 or -640 and present peel force values lower that M-1. The peel force decreases when the flexible chain amount from PPO of PPOBC380 or -640 in the materials increases. In this case, the higher is the cross-linking density and the higher are the adhesive properties. The long, non-functional aliphatic chains of PPOBC380 or -640 allows the flexibility of materials and the decrease of the adhesive properties. Concerning the materials synthesized with CBMI (PU_{CBMI}) and CBMA (M-6 to M-10), we notice that the shear force to peel bonding is higher than PU with HDI or PHUs with EDR-148 for PHU. These materials

exhibit higher Tg and hardness and increased adhesive properties. Only M-10 PHU with low content of TMPTC and PPOBC640 present a lower shear forces to break bonding. Moreover, the shear force for bonding break of M-8, M-9 are those of wood break. In fact, during traction of these materials, the wood breaks before the bonding. The difference of adhesive between different support is explained by the interaction (Van der Waals bonds, hydrogen bonds …) created between the polymer and the support. In the case of glass or wood, hydrogen bonds were created between glass and wood. Moreover, wood, with a porous surface allows a better mechanical anchoring of the adhesive and an increasing of contact surface between support and polymers. Therefore, the adhesive properties on wood are better than on glass.

The third support tested is aluminum covered of epoxy paint (Figure III-15). Hence, the less hydrogen bonds could be created at the interface between the polymer and the support. Therefore, the bonding is less resistant with aluminum support than glass or wood. However, the adhesive properties of PU_{HDI} and PHU_{CBMI} are similar, considering the relative errors. As for the wood, the adhesive properties of PHU on aluminum decrease when the content in flexible chains increases.

In addition to the difference in terms of shear force in the bonding support, we also observed differences in the failure mechanism of adhesive in function of the support. In the case of wood, PU_{HDI} and PU_{CBMI} materials undergo an adhesive failure whereas all PHU polymers undergo a cohesive failure, which is very promising. Indeed, the best adhesives require a cohesive failure [70-72]. Hence cohesive failure occurs within the adhesive materials and material remains bonded to both sides of the substrates used in the test. Adhesive failure occurs when the adhesive shears completely away form the substrate. This mechanism takes place for shear of PU and PHU polymers bonding on painted aluminum.

To conclude on this part, the isocyanate-free PHU materials investigated in this study exhibited highly tunable adhesive properties, with a substantial fraction yielding excellent adhesion on wood, glass and painted aluminum supports.

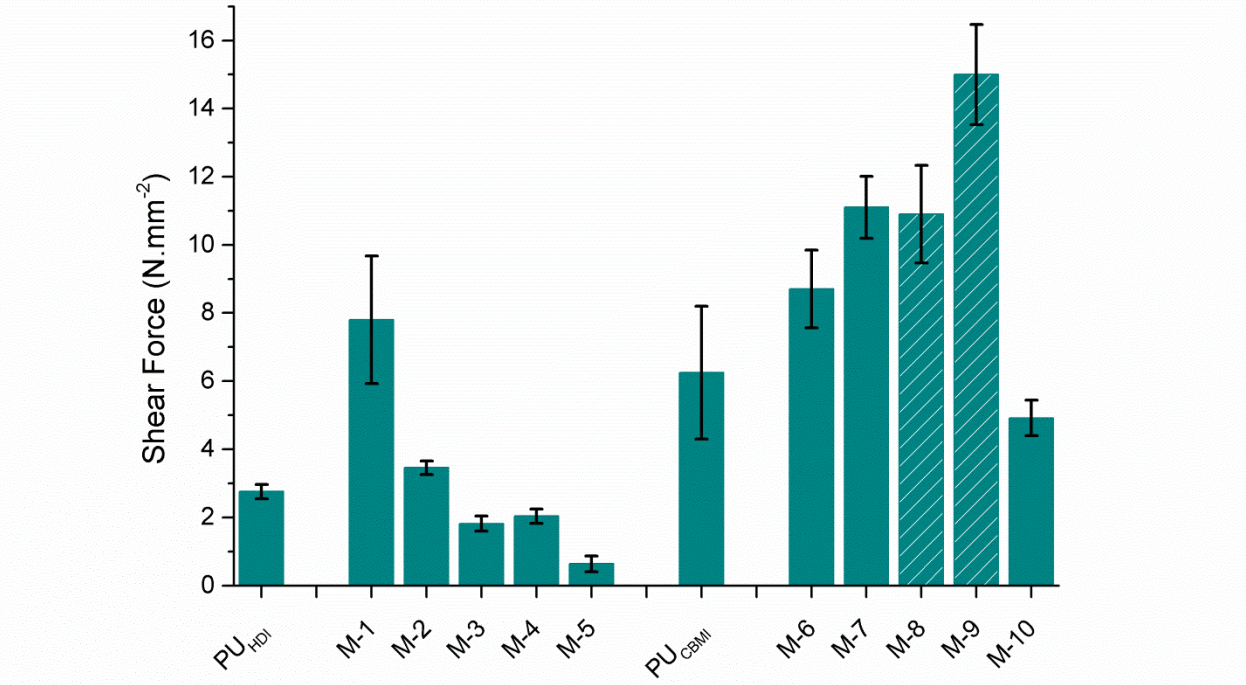


Figure III-14: Adhesive properties of PU and PHU materials on wood. Error bars are the representative standard deviation of each sample set considering 3-5 samples. Shaded bars correspond to failure of support

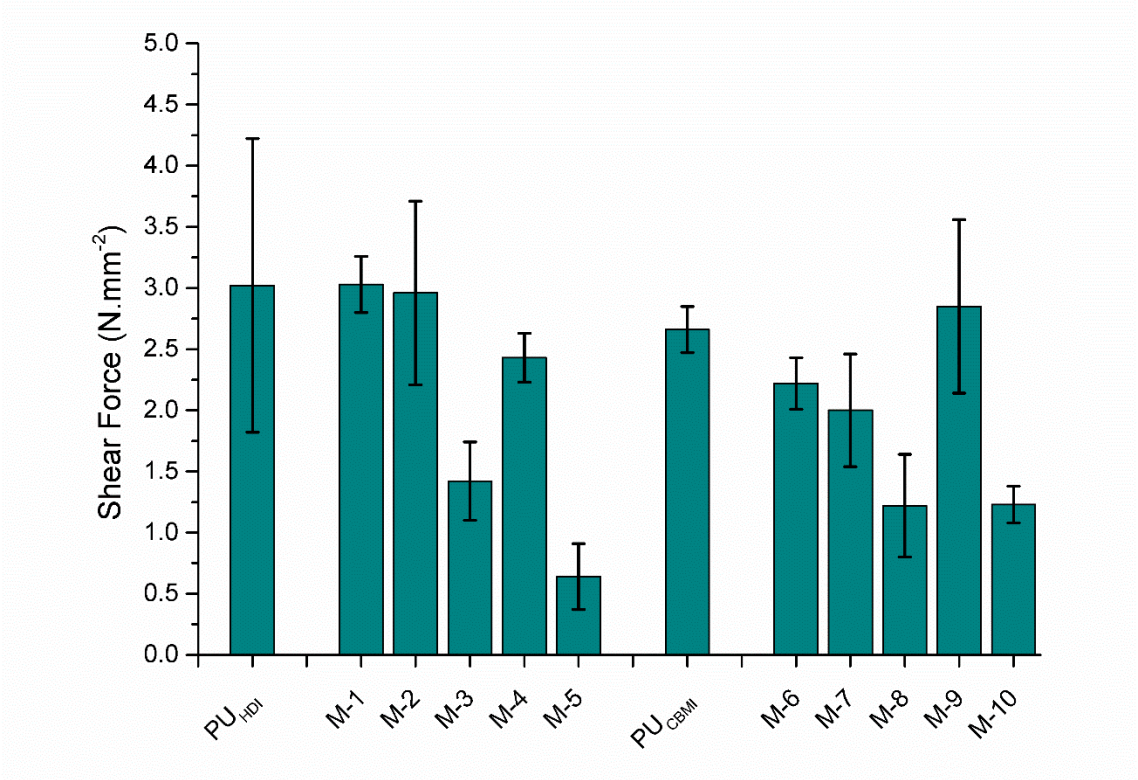


Figure III-15: Adhesive properties of PU and PHU materials on aluminum covered of epoxy paint. Error bars are the representative standard deviation of each sample set considering of 3-5 samples.

V. Conclusion

The works presented in this study aimed at pioneering the study of adhesive properties of isocyanate-free polyurethane materials. These PHU were synthesized from di- (PPOBC380 and -640) and tri- (TMPTC) cyclic carbonates and commercially available diamines (EDR-148 and CBMA). The polymers thus obtained were structurally characterized by infrared and a qualitative characterization of crosslinking degree was performed by the measurement of swelling index and gel content. Moreover, the materials were also characterized by TGA, DSC, durometer, dynamometer, DMA and finally their adhesive properties were studied on three different supports: wood, aluminum and glass. All properties of these PHU materials were compared with reference polyurethanes with analogous structures, synthesized with poly(propylene oxide) triol and HDI or CBMI. On aluminum, PHUs exhibited similar adhesion properties than PUs; whereas on wood, the adhesion properties of PHUs were outstandingly higher that the ones of PUs. Moreover, these PHUs exhibited interesting cohesive failure mechanism on wood and bended the aluminum plate throughout shear bonding. Concerning the glass support, we observe glass break before the bonding rupture of PHUs. As a conclusion, PHU materials exhibit excellent adhesive properties compared to classical PU on different support, which could make them promising candidates for binders and bonding applications. The adhesive properties of isocyanate-free PHUs had never been observed and reported in the literature. Only the process of crosslinking at high temperature could limit the development of this technology. Therefore, it would be interesting to use an alternative technology to synthesize hybrid non-isocyanate polyurethane (HNIPU) at room temperature from prepolymers with dangling [73] or main [74] chain carbamate and check their adhesive properties.

VI. Acknowledgement

This study was supported by ANR project CYRRENAS. The authors thank Huntsman for supplying EDR-148 and Dr. Marine Blain for fruitful discussion. The authors thank also Marjorie Pereira-Bayart and Aurélien Wiegand, research technicians at Bostik, for their help for the characterization of the mechanical and adhesive properties of PU and PHU materials.

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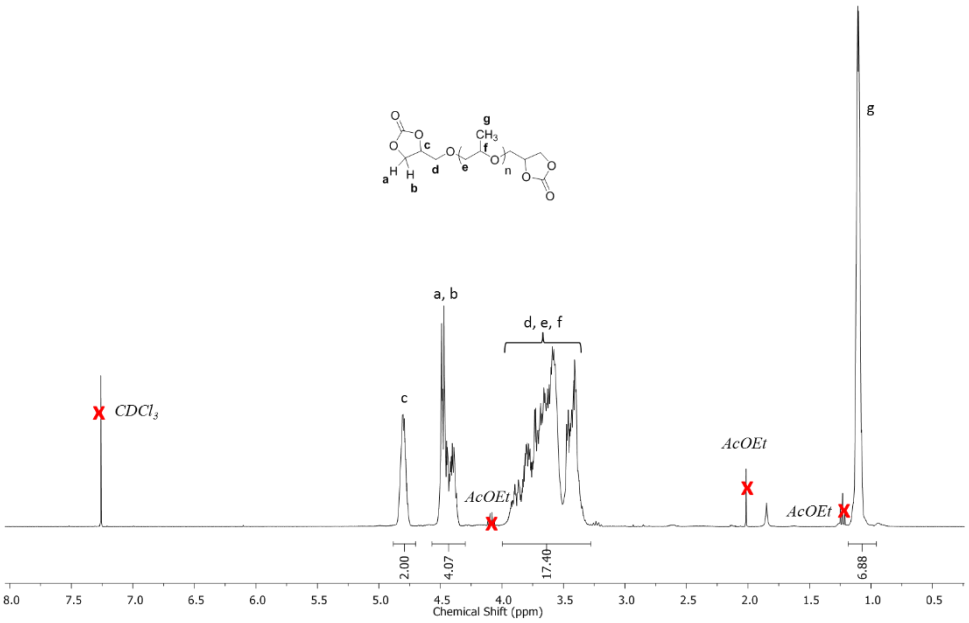
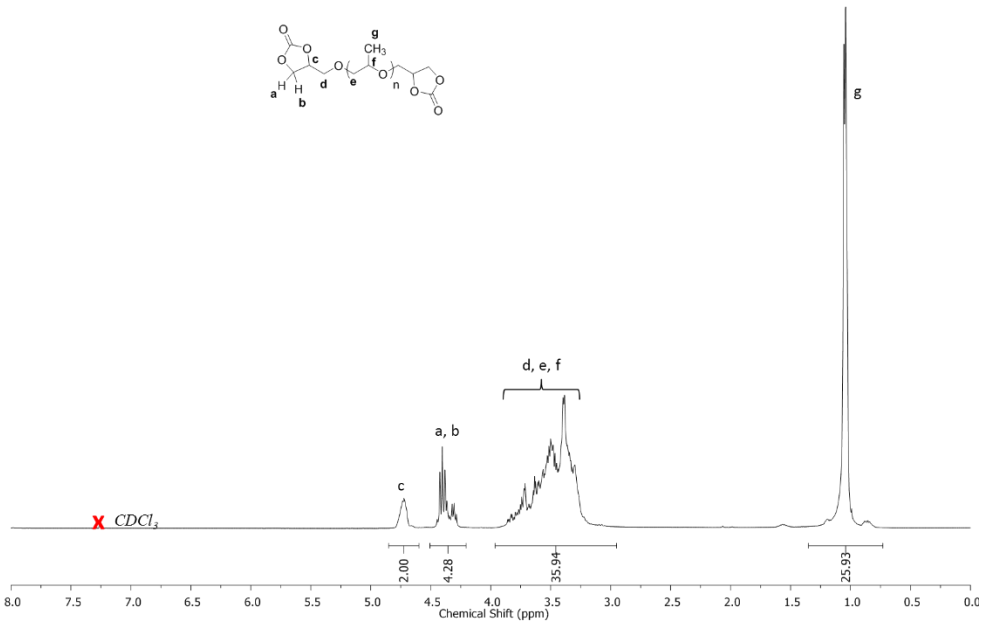
VIII. Supporting Informations

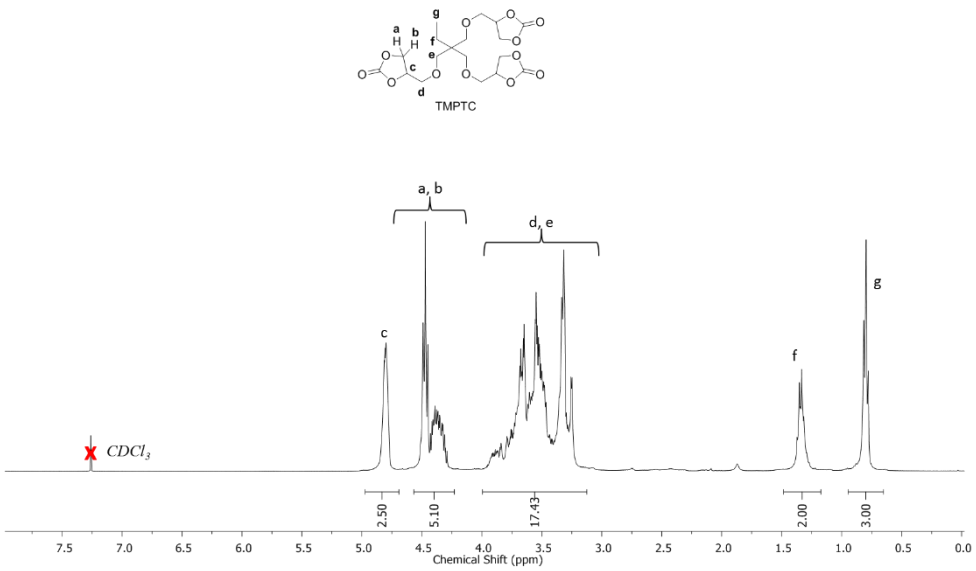
VIII.1 ^{1}H NMR spectra of raw materials



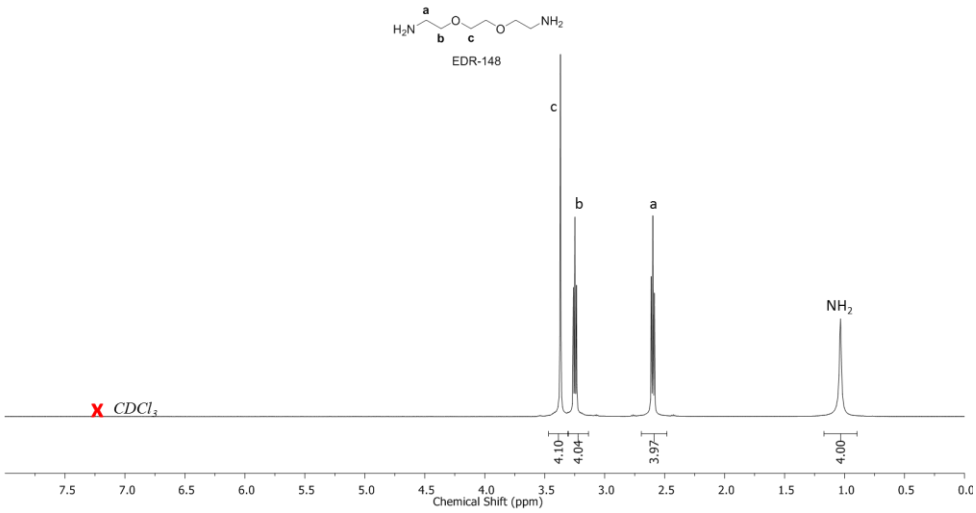
SI - Figure III-1: ^{1}H NMR Spectrum of PPOBC380 in $CDCl_3$



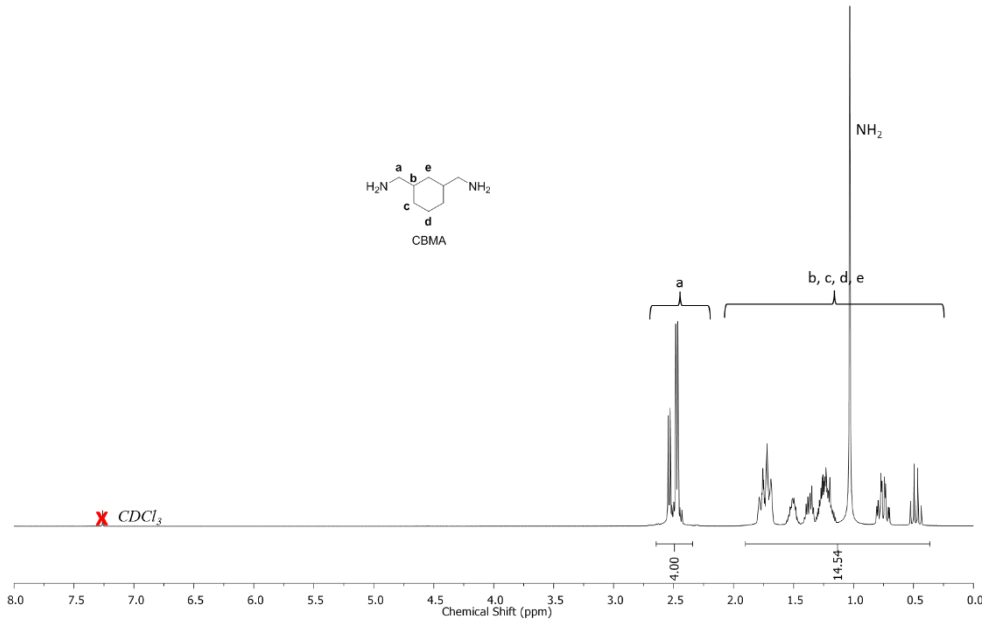
SI - Figure III-2: ^{1}H NMR spectrum of PPOBC640 in $CDCl_3$



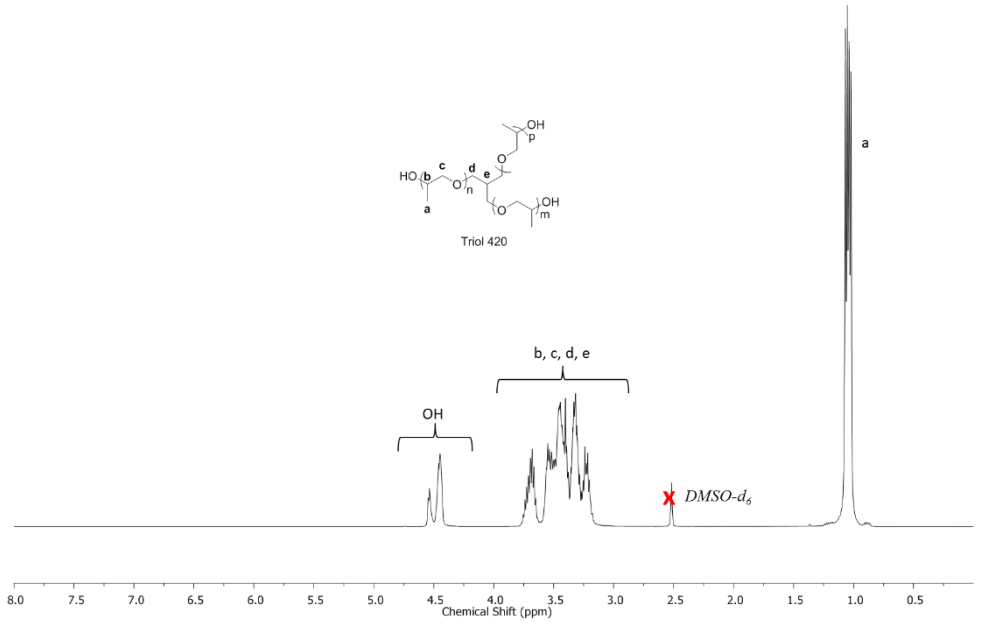
SI - Figure III-3: ^{1}H NMR spectrum of TMPTC in $CDCl_3$



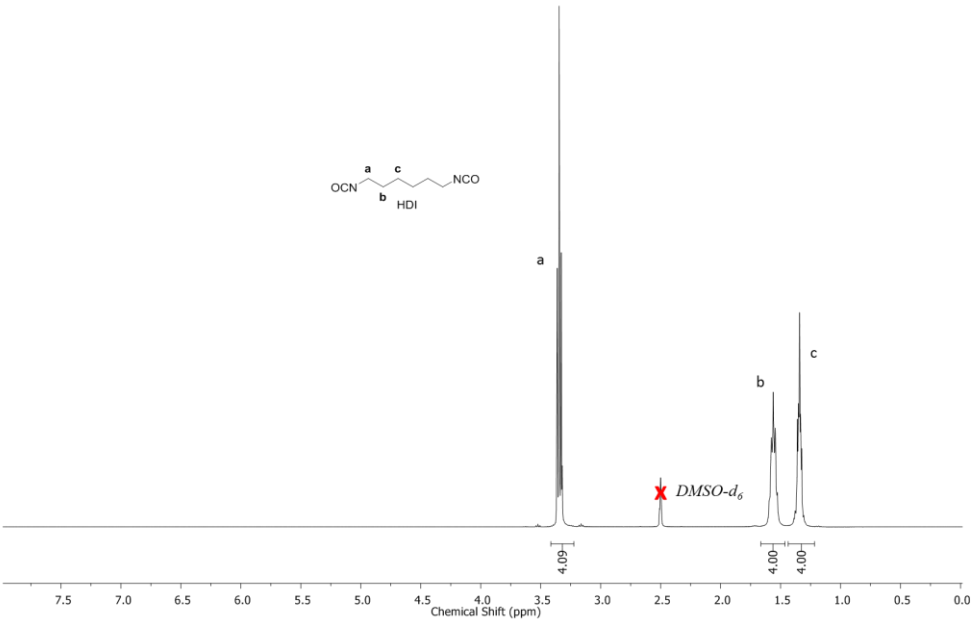
SI - Figure III-4: ^{1}H NMR spectrum of EDR-148 in $CDCl_3$



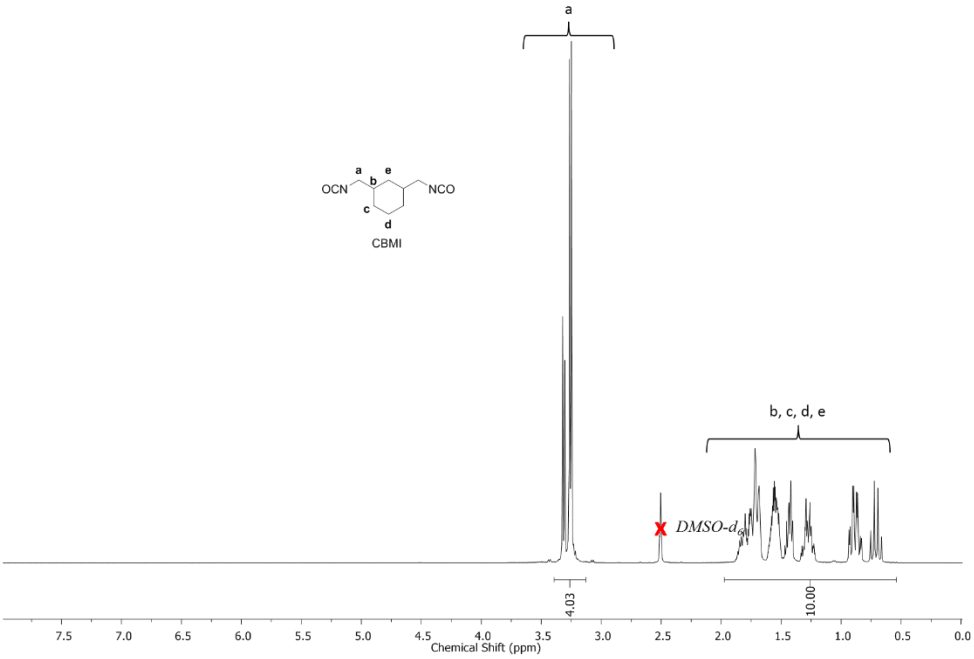
SI - Figure III-5: ^{1}H NMR spectrum of CBMA in $CDCl_3$



SI - Figure III-6: ^{1}H NMR spectrum of Triol 420 in DMSO-d_6

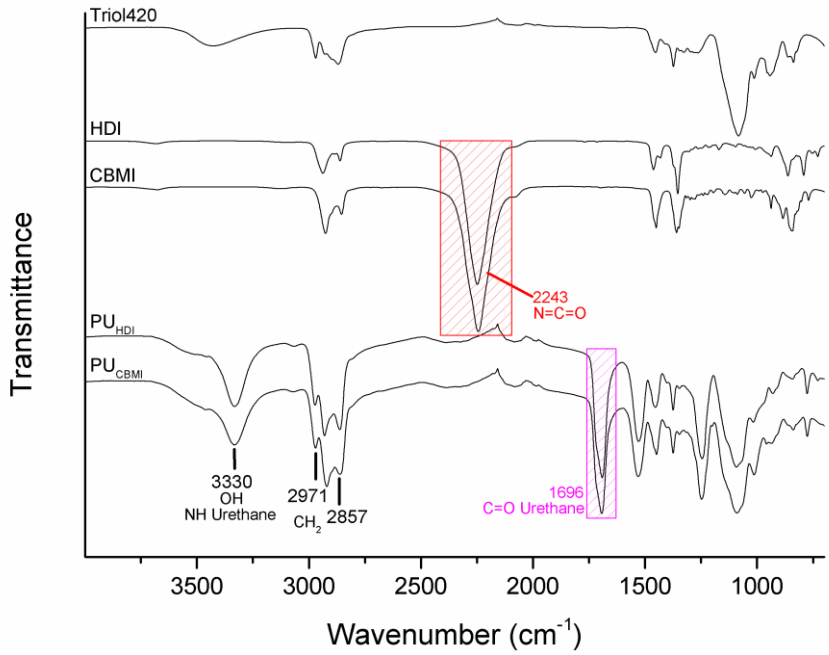


SI - Figure III-7: ^{1}H NMR spectrum of HDI in DMSO-d_6



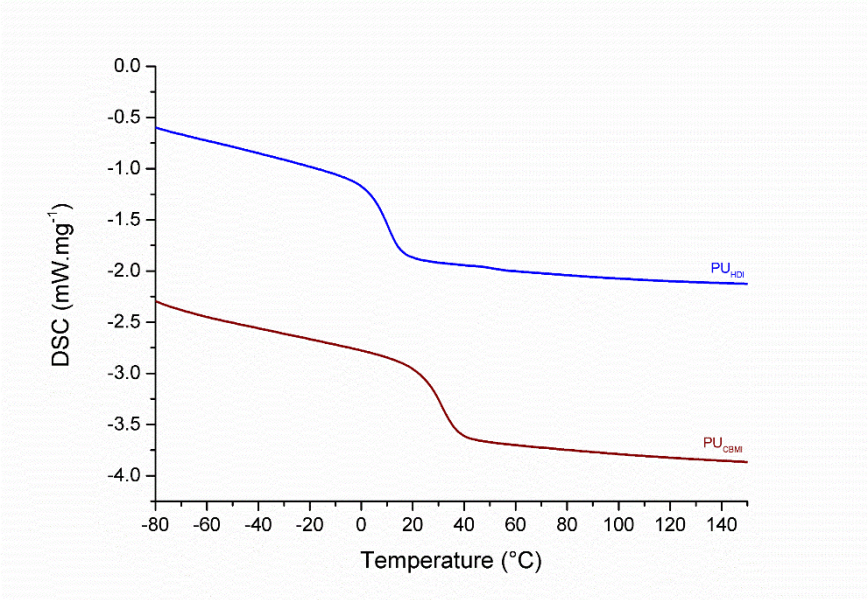
SI - Figure III-8: ^{1}H NMR spectrum of CBMI in DMSO-d_6

VIII.2 Infrared Spectra

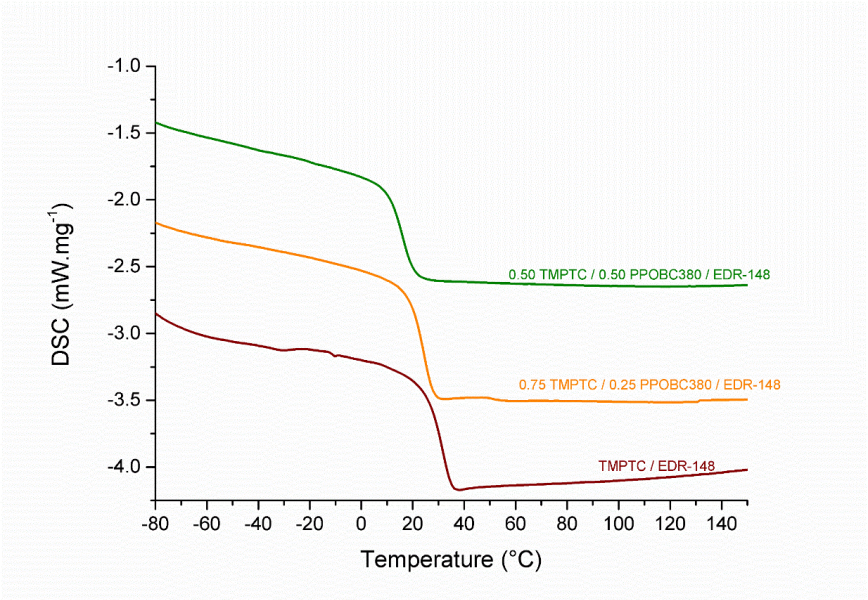


SI - Figure III-9: Overlay of infrared spectra of Triol 420, HDI, CBMI and PU materials

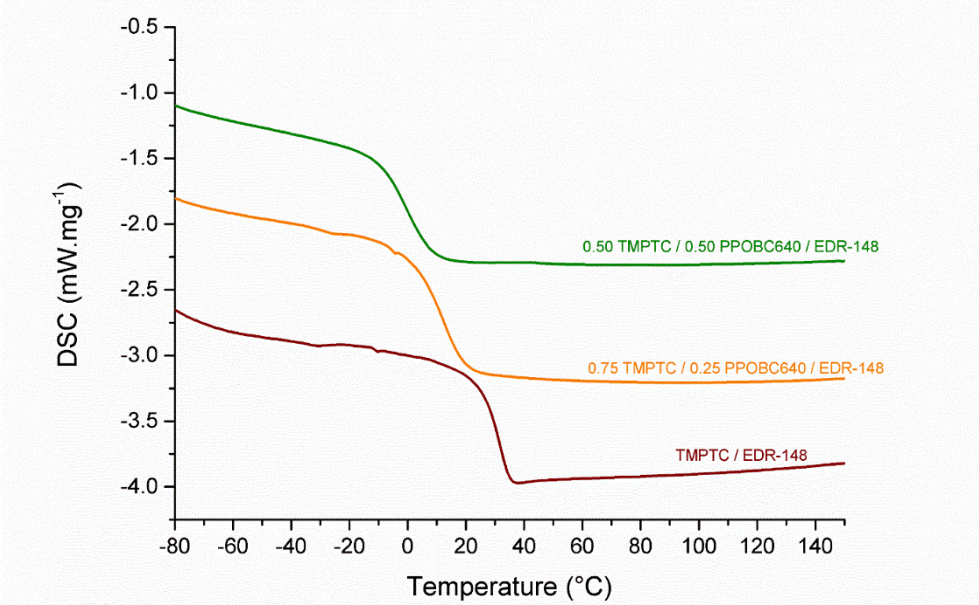
VIII.3 Tg measured by DSC on the second heating ramp for PU and PHU materials



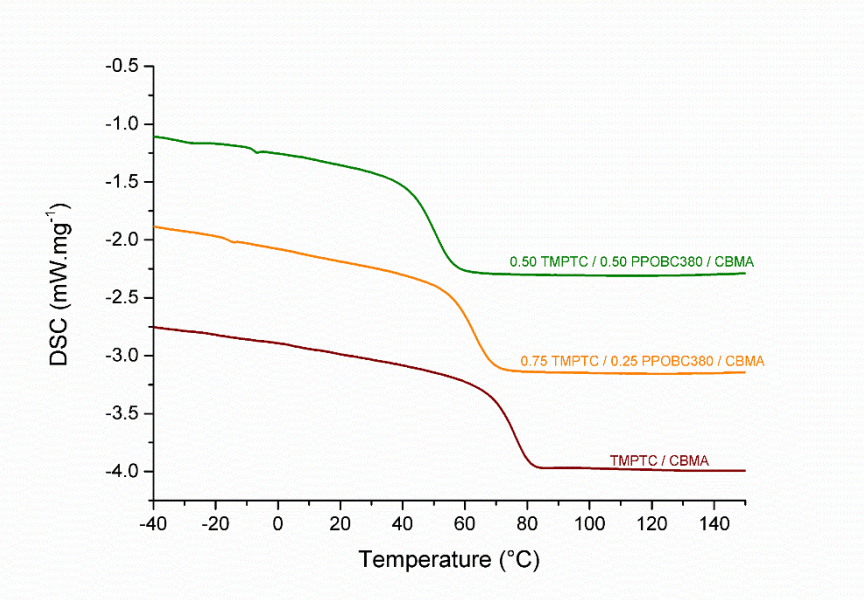
SI - Figure III-10: DSC curves of PU materials



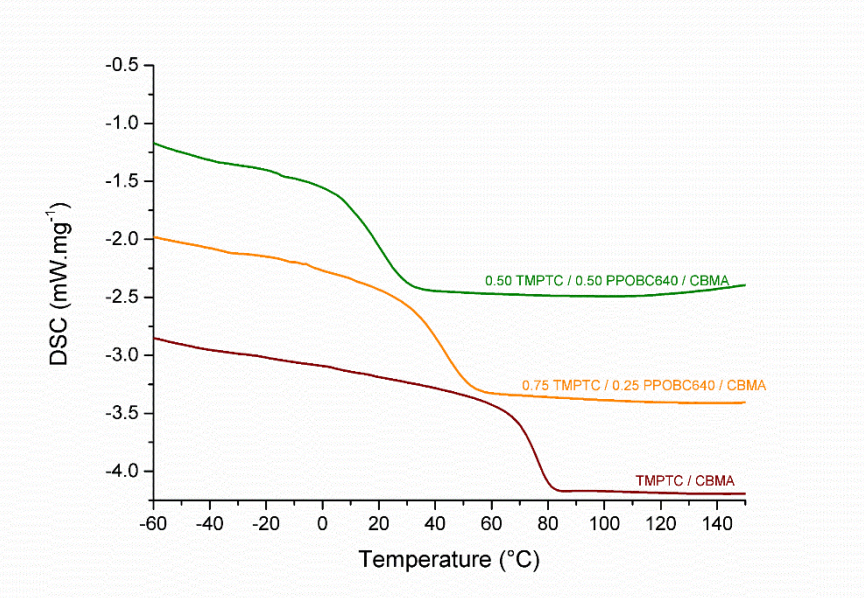
SI - Figure III-11: DSC curves of PHU materials synthesized with TMPTC, PPOBC380 and EDR-148



SI - Figure III-12: DSC curves of PHU materials synthesized with TMPTC, PPOBC640 and EDR-148

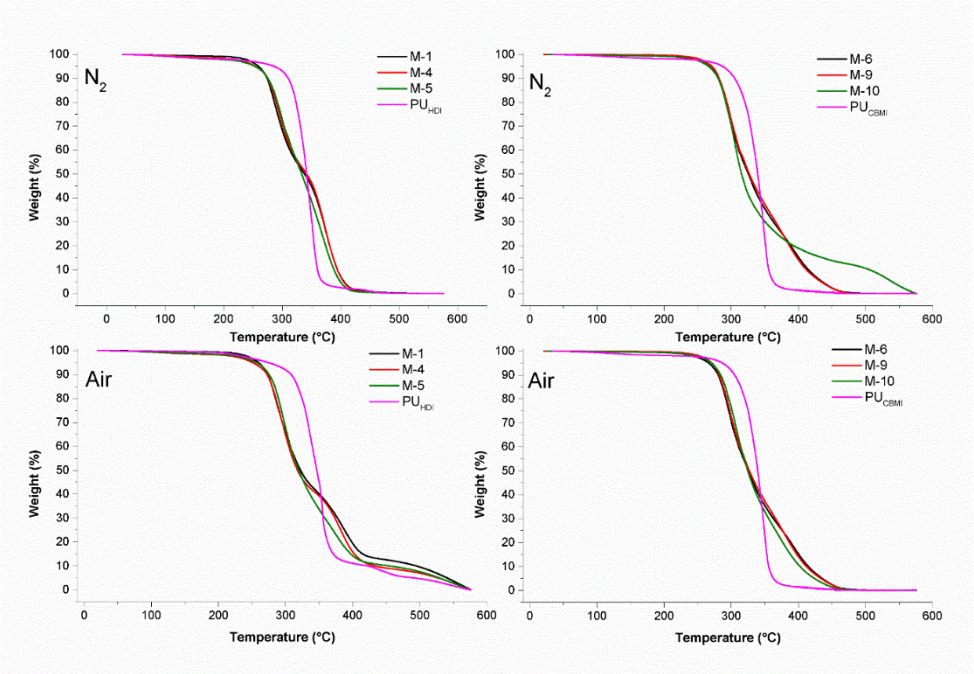


SI - Figure III-13: DSC curves of PHU materials synthesized with TMPTC, PPOBC380 and CBMA



SI - Figure III-14: DSC curves of PHU materials synthesized with TMPTC, PPOBC640 and CBMA

VIII.4 Thermal stability measured by TGA for PU and PHU materials



SI - Figure III-15: TGA curves of PU and PHU materials under N_2 and Air

Conclusion Partie 1

Cette étude a permis de mettre en évidence, pour les polymères PHUs, des propriétés thermiques, mécaniques, thermomécaniques et d'adhésion analogues ou supérieures à celles des matériaux PUs classiques issus de la voie alcool / isocyanate. Cela est dû à la création de groupements hydroxy lors de l'aminolyse des carbonates cycliques. Ces derniers permettent de créer davantage de liaisons hydrogène dans les matériaux PHUs leur conférant des propriétés extrêmement intéressantes aux matériaux PHUs, notamment concernant leurs propriétés d'adhésion.

Néanmoins, ces liaisons hydrogène contraignent de formuler les matériaux PHUs à chaud et constituent un frein à leur développement industriel. Par conséquent tous les domaines d'application des adhésifs ne peuvent pas être couverts en utilisant un tel procédé de synthèse.

Etant donné l'apport bénéfique des motifs hydroxyuréthane dans les propriétés des matériaux PHUs, il serait intéressant d'utiliser ces motifs dans des matrices réactives à température ambiante afin d'élargir les domaines d'application de tels adhésifs. Cette nouvelle approche a été décrite par Figovsky *et al.* et présentée dans le chapitre I en utilisant des HUMs possédant des groupements amine réactifs en combinaison avec des composés époxydés. Une autre approche, développée dans ces travaux de thèse et présentée dans le chapitre I et également détaillée dans le chapitre IV de ce manuscrit, consiste à utiliser des pré-polymères amino-téléchéliques contenant des groupements hydroxyuréthanes. Ces derniers sont réticulés par des matrices époxydées.

Partie 2 - Formulations et caractérisations de mousses PHUs

D'après le chapitre I, les mousses PUs représentent deux tiers de la production totale des matériaux PUs à travers le monde. Cependant, en 2015, aucun travail dans la littérature ne rapportait leur synthèse sans l'utilisation de produits dangereux. C'est dans ce contexte que nous nous sommes intéressés à la synthèse de mousses à partir de la technologie carbonate cyclique / amine.

Cette seconde partie de ce chapitre est donc consacrée à la formulation de mousses PHUs. Ce travail, extrêmement novateur, est présenté sous forme de deux articles scientifiques publiés dans *European Polymer Journal* en 2015 et 2016. Ces travaux ont été réalisés en collaboration avec le Professeur Dariusz Bogdal de l'université de Cracovie en Pologne ainsi que l'entreprise COP Chimie spécialisée dans la conception de matériaux pour des applications dans le domaine médical tels que les appareils orthopédiques externes (prothèses et orthèses).

Le premier article présente la formulation de mousses PHUs et leurs caractérisations. Ces mousses, dites de première génération, sont formulées en température à partir de composés polyfonctionnels, de catalyseur (TBD) et d'agent moussant.

Le second article présente la formulation de ces mêmes mousses PHUs, dites de seconde génération, à température ambiante.

A New Way of Creating Cellular Polyurethane Materials: PHU foams

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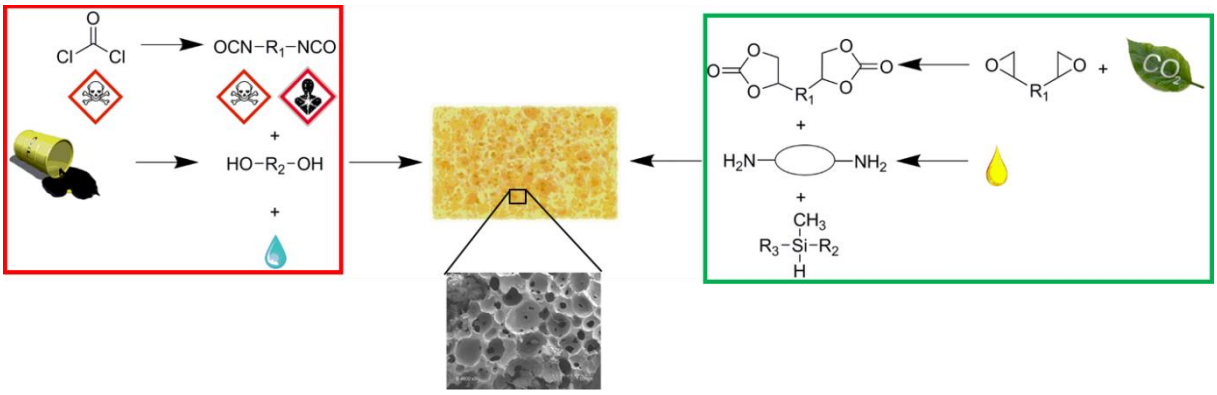
I. Abstract

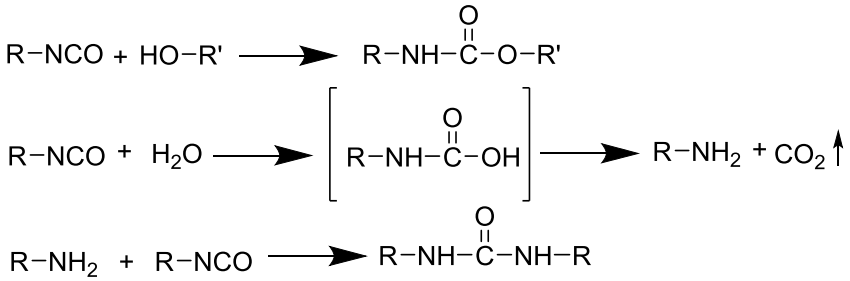
This article describes, for the first time, the synthesis of polyurethane foams from the reaction between cyclic carbonates and diamines to yield NonIsocyanate PolyUrethane (NIPU) foams. A poly(methylhydrogenosiloxane) was used as blowing agent to foam the NIPU by reaction with diamines. The raw materials were characterized in order to determine reaction stoichiometry. PHU foams were characterized by scanning electron microscopy and by measurement of their swelling index and apparent density. The mechanical compression and the recovery of these PHU foams were analyzed by dynamic mechanical analyses at room temperature. The foams exhibited glass transition temperature between -18 °C and 19 °C and a thermal stability above 300 °C.



II. Introduction

The development of polyurethanes (PUs) began in 1947 at I.G. Farbenindutrie where Bayer with coworkers discovered the addition polymerization reaction between diisocyanates and diols. Since their discovery, the demand in PUs has continued to increase and it will attain in 2016 a production of 18 million tons[1, 2] of which 75% are foams. With a market share of 7% of total demand, the PUs are ranked fifth in the world production of plastics. Among the wide range of PU applications, the PU foams represent the two-thirds of the global PU market[3]. Basically, PU foams are classified into two distinct groups, rigid and flexible foams, depending on their mechanical properties and cross-linking densities[4, 5]. The flexible foams are used in many diverse applications such as automotive, bedding and furniture industry. This is explained by their exceptional characteristics such as sound insulation, energy and shock absorption, consumer comfort and protection from impact. These characteristics result from a specific open cell structure of flexible foams[4-7].

PUs are important versatile polymers varying from thermoplastics to thermosets[8], obtained by step growth polymerization between diisocyanate or polyisocyanate and hydroxyl terminated oligomer (polyol) having at least two reactive hydrogen atoms. However, polyol / isocyanate (gelling) and isocyanate / water (blowing) reactions are competing reactions[9] (Scheme III-1). The reaction between polyol and isocyanate forms urethane linkages, while reaction between isocyanate and water yields amine and carbon dioxide allowing for foaming in the preparation of PU foams. Amines thus formed continuous to react with isocyanate to train urea linkages. However, some catalysts need to be used in order to control and balance properly gelling and blowing reactions. Since the first syntheses of PUs, many metal complexes were used for the gelling reaction. Among them, there were lead compounds before the 50s', replaced later by mercury complex[10-14]. Tin compound derivatives quickly became among the most used catalysts in order to favor gelling reaction[15-18]. Nowadays, there is used mostly a mixture of organometallics with amine catalysts. The best known example in the world of PU foams is dibutyltin dilaurate (DBTDL) / 1,4-diazobicyclo-[2.2.2]-octane (DABCO) association[19]. Catalysts used in the PU foams preparation cause environmental pollution when they are released to atmosphere. However, some companies introduce non-volatile catalysts, which do not create toxic vapours. The water was the first blowing agent used for the formation of polyurethane foams but other foaming agent was described in the literature.



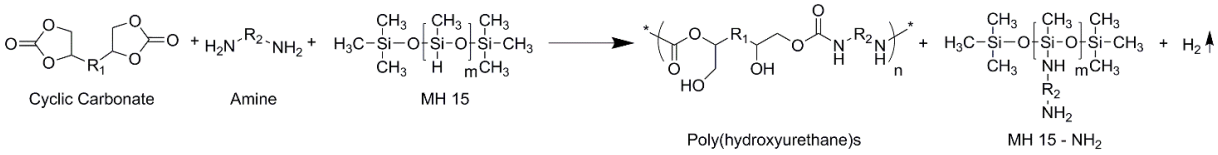
Scheme III-1: Isocyanate reactions with hydroxyl compounds, wate and amine

The main environmental issue of PU materials concerns the use of isocyanate raw materials. In fact, these compounds are harmful for human and environment. Methylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), the most widely used isocyanates in PU industry, are classified as CMR (Carcinogen, Mutagen and Reprotoxic)[20].

Some of us already reported on the synthesis of vegetable oil-based PU flexible foams using TDI[21, 22]. In order to design isocyanate-free materials, an interesting alternative is the use of nonisocyanate polyurethane (NIPU) by reaction between cyclic carbonate and polyfunctional amines[23]. Recently, Thebault *et al.*[24, 25] were prepared non-isocyanate polyurethane by carbonating hydrolysable tannin and reacting it with a primary amine. The cyclic carbonate / amine reaction, already studied in the past by Whelan *et al.* and Mikheev *et al.*[26, 27], avoids the use of isocyanates and diamines and permits the formation of poly(hydroxyurethane)s (PHUs) with hydroxyl groups. This method was tremendously studied and has recently attracted much attention, particularly by Endo *et al.*[23, 28-31] and Figovsky *et al.*[32, 33]. The main problem concerning NIPU synthesis relates to the low reactivity of carbonate / amine reaction. Many studies in the literature have been conducted to design NIPU materials from reactive cyclic-carbonates bearing electro-withdrawing substituent [23, 30, 34-43] or by using six-, seven-membered or thio- cyclic carbonate[31, 41, 44-46].

In order to improve the kinetics of the carbonate / amine reaction, much research has been devoted to develop novel catalysts. Blain *et al.*[47] and Lambeth *et al.*[48] showed that the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and cyclohexylphenyl thiourea are the best catalysts for carbonate / amine reaction. However, the reaction between carbonate and amine does not yield any gas, therefore cannot lead to PHU foam as easily as in the case of PUs. Moreover, to the best of our knowledge, no literature has been published on the preparation of PHU foams, therefore, we aspired to synthesize the first PHU foams as an original work.

We chose five-membered cyclic carbonates since their synthesis does not require any phosgene derivative as in the case of six- or seven-membered cyclic carbonates. PHU foams were obtained by step growth polymerization of two types of five-membered cyclic carbonates, trimethylolpropane tris-carbonate (TMPTC) and polypropylene oxide bis-carbonate (PPOBC640), in combination with aliphatic amines. The development of PHU foams is a challenge which lies in the coordination of gelling reaction (carbonate/amine reaction) and foaming reaction. We used Momentive MH 15 as blowing agent which was already reported in epoxy foams preparation[49]. MH 15 is a poly(methylhydrogenosiloxane) which reacts with amines, releasing dihydrogen (Scheme III-2) which allows to expand the NIPU materials. The synthesis of various PHU foams from cyclic carbonate / amine reaction with MH 15 as blowing agent is summarized in general Scheme III-2.



Scheme III-2: General scheme of formation of PHU foams by reaction wetween cyclic carbonate, amine and MH 15

III. Experimental Section

Materials

Poly(propylene oxide) bis-carbonate (PPOBC640, SP-1P-0-004) and trimethylolpropane tris-carbonate (TMPTC, SP-3-00-003) were purchased from Specific Polymers. Acetic anhydride, 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) and tetrahydrofuran (THF) were purchased from Sigma Aldrich. Jeffamine EDR-148 was obtained from Hunstman and Priamine 1073 was obtained from Croda. Poly(methylhydrogenosiloxane) Momentive MH 15 was obtained from Momentive.

Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^{1}H NMR spectroscopy using a Bruker Avance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: 10 mg of product for ^{1}H experiment in 0.5 mL of $CDCl_3$.

Size Exclusion Chromatography

Size exclusion chromatography (SEC) analyses were carried out with a Varian PL-GPC-50 chromatography apparatus equipped with a RI detector. Two PL GeL Mixed-E columns and one PLgel 3µm-100A thermostated at 35 °C were used with an eluent flow of 1 mL/min. Columns were calibrated with polystyrene (PS) standards. SEC analyses were performed for Priamine 1073 deactivated in THF with a small amount of toluene as flow rate marker.

Dynamic Mechanical Analyses

Creep mode

Dynamic mechanical analyses (DMA) were carried out using a Metravib DMA 25 with Dynatest 6.8. The mechanical compressions of the samples were measured using 20 x 20 x 10 mm^3 foam samples in the creep mode with tension holders at room temperature. The measurements were repeated three times. The static displacement was fixed to -6 mm with time of loading of 1 s, a maximum strength of -10 N and an application time of 120 s.

Relaxation mode

The resilience of foams was measured using above mentioned DMA (Metravib DMA 25) with Dynatest 6.8 for the same foam samples. Samples were first compressed to 50% of their original thickness during 600 s with maximum strength equal to -10N and the time of loading was 1s. Then the time for the recovery of the shape was measured during 300s. Measurements were repeated three times for the same samples.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of 10 °C/min. Approximately 10 mg of sample was placed in an aluminum pan and heated from room temperature to 500 °C under nitrogen atmosphere (60 $mL.min^{-1}$).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. 10-15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at 20 °C/min in the range between -100 and 100 °C to observe the glass transition temperature at the second ramp. All the reported temperatures are on set values.

Titration of the cyclic carbonate by ^{1}H NMR

A specified amount of cyclic-carbonate (around 10 mg) and a standard (toluene, around 6 mg) were weighed into an NMR tube. Once the ^{1}H NMR acquisition was completed, the characteristic peaks of carbonate a (4.90 ppm) and CH_3 (2.49 ppm) of toluene were integrated (Figure III-16). The integration of CH_3 of toluene was fixed to 300. The carbonate equivalent weigth (CEW) of PPOBC640 and TMPTC were calculated according to Equation III-10, where I_a an integration of peak a, $m_{standard}$ - mass of toluene introduced into the NMR tube, I_{CH3} - integration of peak CH_3 of toluene, $M_{standard}$ - molar mass of toluene and $m_{cyclic\ carbonate}$ - mass of PPOBC640 or TMPTC introduced into NMR tube. The CEW values for each carbonate were obtained in triplicate determinations.

Equation III-10

$$CEW = 3\frac{I_a \times m_{standard}}{I_{CH3} \times M_{standard} \times m_{cyclocarbonate}}$$

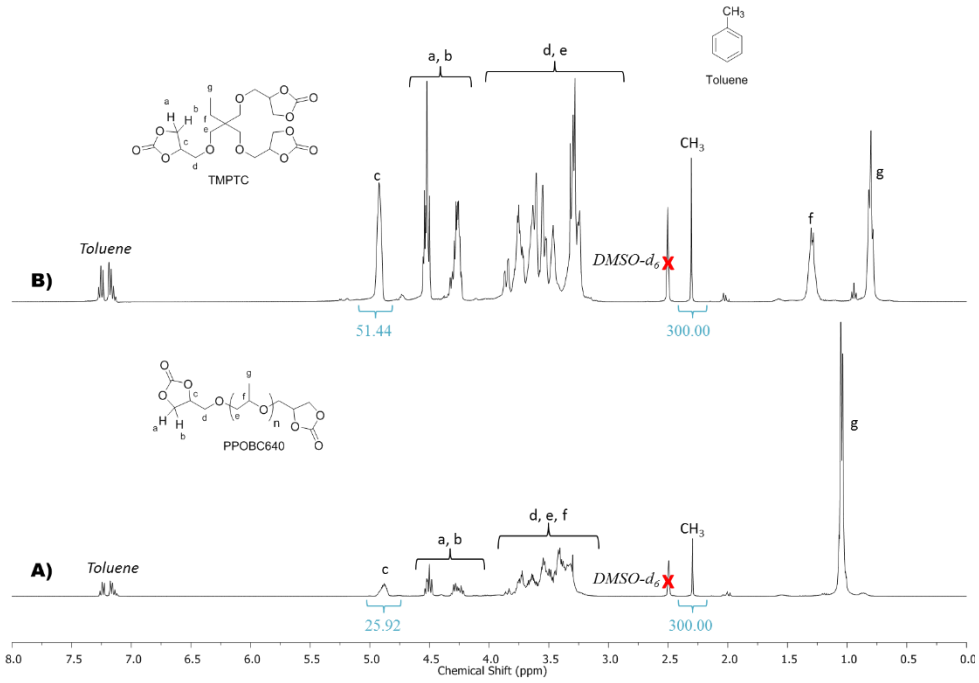


Figure III-16: ^{1}H NMR spectra of (A) PPOBC640 with toluene and (B) TMPTC with toulene

Synthesis of PHU foams

The formulations of PHU foams were calculated from 1 equivalent of carbonate (PPOBC640 or TMPTC), 1.05 equivalent of amine (Jeffamine EDR-148 or Priamine 1073), 0.05 equivalent of MH 15 compared to the amine and 0.05 equivalent of TBD in relation to the carbonate.

First, the five-membered cyclic carbonate (PPOBC640 or/and TMPTC) and the TBD were placed in the silicone mold and stirred mechanically for 3 min. Then, the amine (Jeffamine

EDR-148 or Priamine 1073) was added and the mixture was, once again, stirred mechanically for around 3 min. Once the homogenous mixture was obtained, the blowing agent, MH 15, was added and the mixture was stirred for 2 min. The obtained foamed mixtures were heated at 80 °C for 12 h and 120 °C for 4 h.

Deactivation of Priamine 1073

Stoichiometric amounts of acetic anhydride and Priamine 1073 were placed together in a round bottom flask, assuming the molecular weight of the amine equal to 600 $g.mol^{-1}$. The reaction was continuously stirred for 7 h at 60 °C.

Swelling Index

Three samples (30mg each) were separately put into 30 mL THF for 24 h. The swelling index, SI, is given by Equation III-11, where m_0 is initial mass of tab and m_1 is mass of tab after swelling in solvent.

Equation III-11 $$SI=\frac{m_1-m_0}{m_0}\times 100$$

Apparent density

The PHU foams were cut into samples in the cuboid shape. Their dimensions were measured using caliper and the apparent density, ρ_a, was calculated from Equation III-12, where m express the mass of the foams samples in kg and V is volume of the samples in m^{-3}.

Equation III-12 $$\rho_a = \frac{m}{V}$$

IV. Results and Discussion

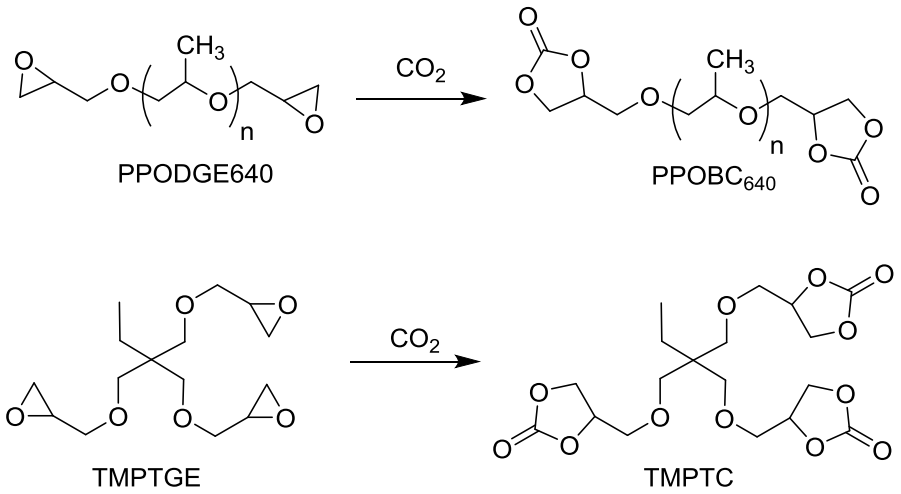
IV.1 Characterization of reactants

IV.1.1 Cyclic carbonate

Specific Polymers company synthesized two five-membered cyclic carbonates by carbonation of poly(propylene oxide) diglycidyl ether and trimethylolpropane triglycidyl ether to obtain respectively poly(propylene oxide) bis-carbonate (PPOBC640) and trimethylolpropane tris-carbonate (TMPTC) (Scheme III-3). The carbonate equivalent weigth (CEW) of these products were determined by ^1H NMR titration. The real molar masses were obtained from Equation III-13 using calculated CEW values and functionalities of carbonates, $f_{carbonate}$, i.e. 2 for PPOBC640 and 3 for TMPTC. The determination of real molar masses of carbonates was

necessary to calculate the quantities of amines, blowing agent and catalyst to introduce in the PHU foam formulations.

Equation III-13 $$M_{carbonate}=\frac{f_{carbonate}}{CEW}$$



Scheme III-3: Carbonation of PPODGE640 and TMPTGE

IV.1.2 Amine

In order to apply the alternative NIPU for design of new foams, two amines were used in combination with PPOBC640 and TMPTC. The first amine was Jeffamine EDR-148 from Hunstman. The ^{1}H NMR of Jeffamine EDR-148 (Figure III-17) confirms the di-functionality of this amine. Indeed, three signals for a, b and c protons present on the ^{1}H NMR spectrum are integrated respectively for 4, 4.02 and 4.04 protons. In addition, protons corresponding to amine function (NH_2) integrate for 3.84 protons. Therefore, this amine contains two primary amine groups in gamma position of ethylene glycol. Thus, the oxygen atoms in gamma position relative to amine group give a high reactivity to the amine[50]. The molar mass of Jeffamine EDR-148 equal to 148 $g.mol^{-1}$, was given owing to technical data sheet of Huntsman.

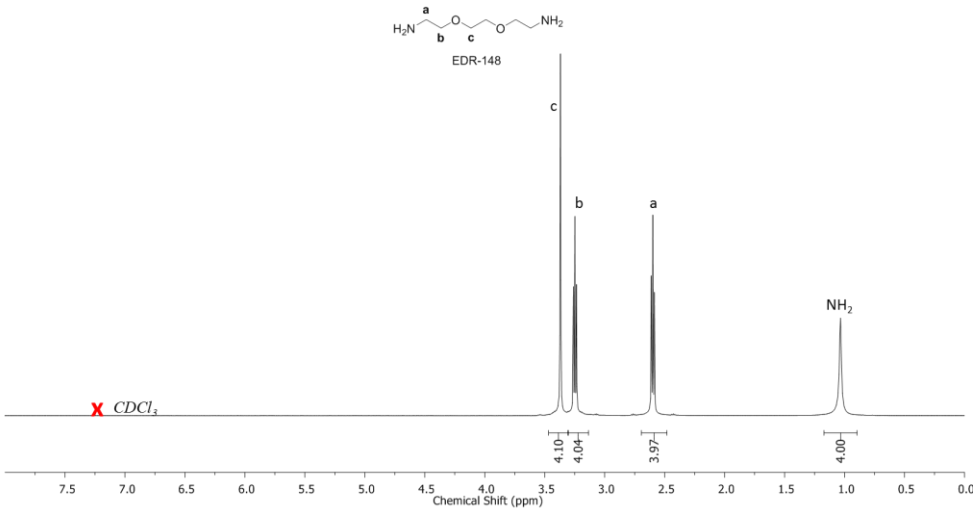


Figure III-17: [1]H NMR spectrum of Jeffamine EDR-148

The second amine used in the foam formulations was Priamine 1073 from Croda Company. This amine is a di-functional derivative of C_{18} fatty acids resulting from dimerization or/and trimerization process. Consequently, it contains 100% renewable carbon. This structure could bring flexibility to the NIPUs. In order to characterize the Priamine 1073 and to check its functionality, a SEC analysis was performed, after deactivation of amine by an acetalization reaction with acetic anhydride. The distribution of molar masses shown in the SEC chromatogram (Figure III-18) displays two distinctly separated peaks for the molar masses of the species present in the product. The two peaks correspond to two polyamines of different functionalities. The first peak (1) around 900 g.mol^{-1}, corresponds to the di-functional amine derived from a dimerization process of C_{18} fatty acid. The second peak (2) which is twice the molar mass of the first peak (1800 g.mol^{-1}), corresponds to a trimerization of C_{18} fatty acid and gives a tri-functional amine. However, the SEC trace gave noticeably wider peak for the molar mass related to the di-functional amine compared to tri-functional amine. This characterization proves that Priamine 1073 is mainly a di-functional amine.

In order to formulate PHU foams from cyclic carbonate and Priamine 1073, the molar mass of amine was determined from AHEW (Amine Hydrogen Equivalent Weight) value given by Croda: 139 g.eq^{-1} [51]. This value is the ratio of molar mass (M) to the number of active hydrogens. Therefore, the molar mass is AHEW multiplied by the number of active hydrogens equal to 4 for this amine. As a result, the molar mass of Priamine 1073 is 556 g.mol^{-1}.

Equation III-14 $$AHEW = \frac{M}{Number\ of\ active\ hydrogens}$$

$$M = AHEW \times \text{Number of active hydrogens}$$

where: M - Molar Mass, AHEW - Amine Hydrogen Equivalent Weight

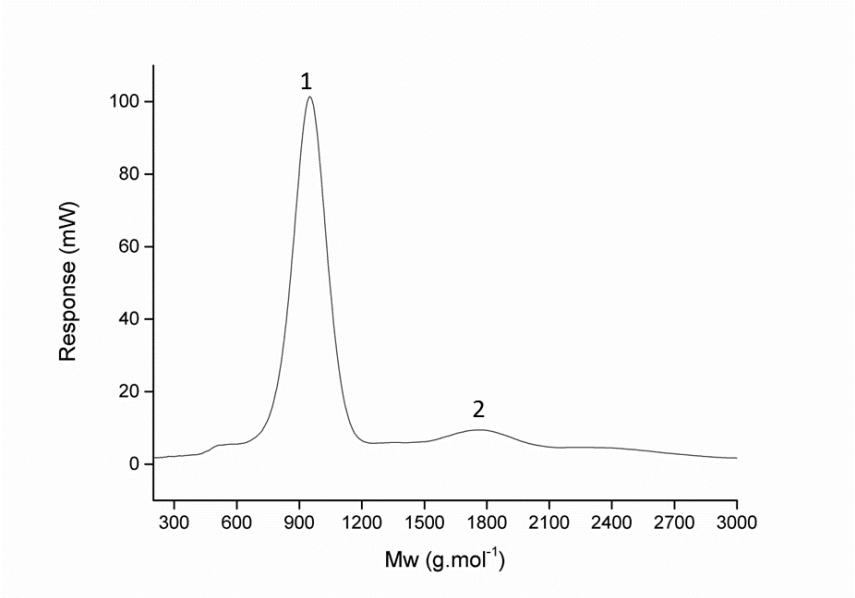


Figure III-18: SEC chromatogram of deactivated Priamine 1073

IV.1.3 Blowing Agent: MH 15

The blowing agent, MH 15 from Momentive company, is a polymethylhydrogensiloxane (Scheme III-2). It contains SiH groups capable of reacting with compounds bearing amine. In this study, MH 15 reacts with equimolar amount of amine releasing the dihydrogen. In order to calculate the molar mass of this blowing agent, two procedures were established. The first procedure consisted of calculating the theoretical molar mass from data given by Momentive while in the second procedure the real molar mass was determined by ^{1}H NMR.

The release of gas was responsible for the expansion of materials to get PHU foams. According to the technical data sheet of Momentive MH 15, 1 gram of MH 15 which react with amine releases 340 ml of dihydrogen. This data allows for determining the number of repetition units of CH_4SiO denoted as n (Equation III-15), and, therefore, the theoretical molar mass of MH 15. Solution of this equation enabled to determine the number of repetition of SiH group, n, being equal to 28 and the theoretical molar mass of 1843 $g.mol^{-1}$.

Equation III-15

$$V_{gas\ released} = \frac{r\,n}{M_{C6H18OSi2} + nM_{CH4SiO}}$$

where r=22 400 mL.mol^{-1} , $M_{C6H18OSi2}$=162.38 g.mol^{-1} , M_{CH4SiO}=60.02 g.mol^{-1} and $V_{gas\ released}$ = 340 mL.g^{-1}

To compare this theoretical molar mass with real molar mass, ^{1}H NMR of product was performed (Figure III-19). In the spectrum, integration of the characteristic peak of CH_3 end chain, 0.14 ppm, denoted as a, was fixed at 18 protons. Therefore, the protons c, 4.74 ppm, characteristic for SiH in unity of repetition CH_4SiO are integrated for 32.42 protons.

Consequently, the number of repetition of CH_4SiO pattern determined by ^{1}H NMR, n, is 32. Accordingly, the real molar mass of MH 15 is 2083 g·mol^{-1}. For the formulations of PHU foams, only the real mass of MH 15 was used.

The summary of the characterization of reactants is given in Table III-5.

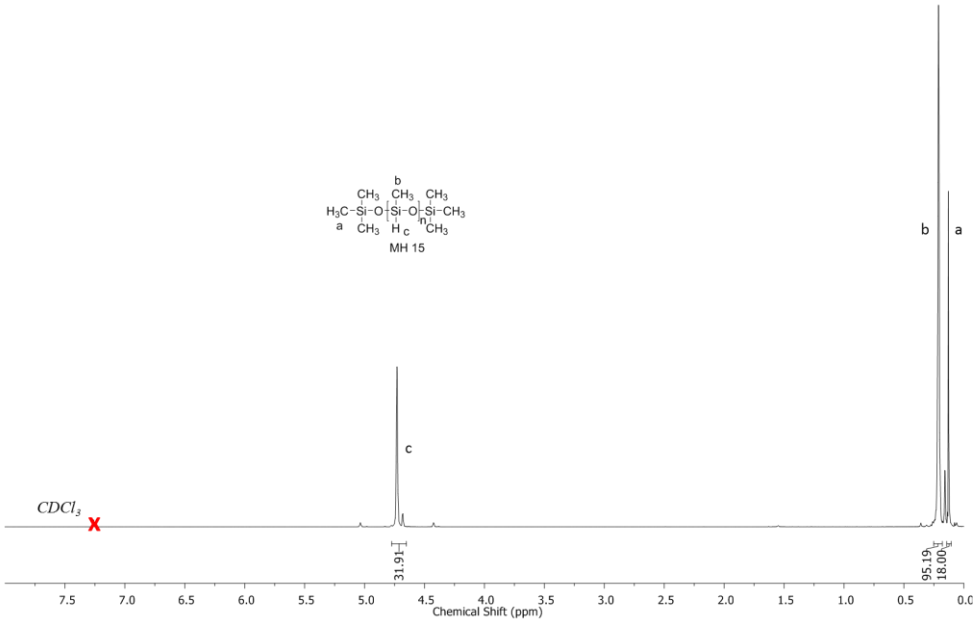


Figure III-19: ^{1}NMR spectrum of blowing agent MH 15 in $CDCl_3$

Table III-5: Characterization of substrates

Reactants	CEW (meq.g^{-1})	AHEW[2] (g·eq^{-1})	Functionality carbonate or amine	Number of active hydrogens	M (g·mol^{-1})
PPO-Bis-C_5	2.76	-	2	-	725[3]
TMP-Tri-C_5	5.28	-	3	-	568[3]
Jeffamine EDR-148	-	37	2	2	148[4]
Priamine 1073	-	139	2	2	556[5]
MH 15	-	-	-	-	1843[6a] 2083[6b]

[1]: Carbonate equivalent weigth determined by ^{1}H NMR titration with standard: toluene
[2]: AHEW (Amine Hydrogen Equivalent Weight) determined by Huntsman for Jeffamine EDR-148 and Croda for Priamine 1073
[3]: Molar mass of PPO-Bis-C_5 and TMP-Tri-C_5 determined from Equation III-13
[4]: Molar mass of Jeffamine EDR-148 from data provided by Huntsman
[5]: Molar mass of Priamine 1073 determined from Equation III-14
[6]: Theoretical and real molar mass of MH 15 determined by a) theoretical data of Momentive or b) ^{1}H NMR

IV.2 Formulation and characterization of PHU foams

IV.2.1 Preparation of PHU foams

In this study, five PHU foams were synthesized: one with TMPTC and Jeffamine EDR-148, two with TMPTC and PPOBC640 in combination with Jeffamine EDR-148 and, finally, two with TMPTC and PPOBC640 in combination with Priamine 1073. The properties of PHU foams were affected by the differences in the functionalities of the cyclic-carbonates as well as the structures of the carbonates and amines. These foams were prepared by using well-established formulations based on molar equivalent of reactants (Table III-6, Figure III-20). In the first formulation (1), TMPTC was used in combination with Jeffamine EDR-148. The functionality of this carbonate is equal to 3, therefore, this TMPTC brings rigidity to system by crosslinking with diamine. On the contrary, the formulations 2 and 3, with respectively 0.5 and 0.3 equivalents of PPOBC640 in combination with 0.5 and 0.7 equivalents of TMPTC and Jeffamine EDR-148 could lead to a lower rigidity. The long carbon backbone of PPOBC640 decreased the rigidity to system of carbonate/amine. The formulations 4 and 5 used the Priamine 1073. This amine has a long carbon backbone which, as PPOBC640, could increase the flexibility of PHU foams.

Table III-6: PHU foam formulations in molar equivalent

Reactants	1	2	3	4	5
PPOBC640	-	0.5	0.3	0.5	0.3
TMPTC	1	0.5	0.7	0.5	0.7
EDR-148	1.05	1.05	1.05	-	-
Priamine 1073	-	-	-	1.05	1.05
MH 15[1]	0.05	0.05	0.05	0.05	0.05
TBD[2]	0.05	0.05	0.05	0.05	0.05

[1]: Quantities in equivalent of MH 15 introduced in the foam formulations compare to amine
[2]: Quantities in equivalent of TBD introduced in the foam formulations relative to carbonate

The main disadvantage of the alternative PHU foams is the low reactivity of carbonate / amine reaction. In order to increase this reactivity, a catalyst was used in the formulations. A lot of catalysts were reported in the literature, but the best were thiourea (1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea) and TBD[47, 48]. However, only TBD is a commercial product, therefore we chose it. Moreover, the results of Blain *et al.*[47] showed that the optimal amount of TBD introduced into the formulation was 5% compare to carbonate to obtain the same catalytic activity of thiourea.

In the case of blowing reaction, MH 15 was used in the carbonate / amine / TBD formulation providing the foaming of the material by releasing di-hydrogen during the reaction between amine and blowing agent. Stefani *et al.*[49] showed that the blowing agent influences the apparent density of the foam. Therefore in our study, the same quantities of MH 15 equal to 5% equivalent with respect to amine, were used in the foam formulations. The amount of amine used is adjusted (1.05 equivalent) to compensate for the amount of polysiloxane in the system to be in a stoichiometric amount of cyclic carbonate and amine. The differences between the structures of PHU foams were characterized by the measurement of the apparent density, scanning electron microscopy (SEM) and dynamic mechanical analysis (DMA). Then, the degree of cross-linking was analyzed by measurement of swelling index. Finally, thermal properties of PHU foams were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

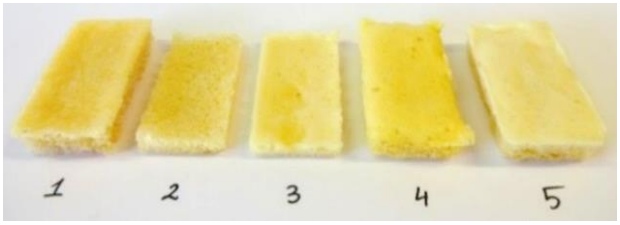


Figure III-20: Picture of different PHU foams

IV.2.2 Structural characterization of PHU foams

IV.2.2.1 Density of PHU foams

Generally, at the macroscopic scale, the cellular materials are described by their relative density ρ_r defined as the ratio of apparent density of bulk cellular material ρ_a to the density of the solid material of which the foam is made ρ_s (Equation III-16). In the case of polyurethane foams, the reference solid density ρ_s is 1150 kg.m^{-3} [52]. Above $\rho_r = 0.3$, the material goes from a cell structure to a solid containing isolated pores[53]. In the case of polymeric materials, $\rho_r <$ 0.3.

Flexible foams are used for insulation, packaging and shock absorption and possess relative density values between 0.05 and 0.2. Apparent density values of low density flexible foams varies in the range 10-80 kg.m^{-3}, whereas, high density flexible foams exhibit apparent density of about 100-900 kg.m^{-3} [54]. In order to determine the apparent density values of PHU foams, the foams samples were cut into geometric shapes (cuboid) and their dimensions were measured with caliper (Figure III-21) to calculate the volume. With the mass of the samples, we were able to determine apparent density values of PHU foams.

Equation III-16 $$\rho_r = \frac{\rho_a}{\rho_s}$$

Apparent density of PHU foams varies in the range 194-295 kg.m^{-3} (Table III-7), therefore they can be classified as high density foams. First of all, these results show that the use of only tri-functional cyclic carbonate increases the apparent density of foams. In fact, for the same amine (Jeffamine EDR-148), the density of 1 is 295 kg.m^{-3} whereas the densities of 2 and 3 are respectively 248 and 242 kg.m^{-3}. The increase in apparent density is related to the degree of cross-linking of the foam. On the other hand, the comparison of the apparent densities between 2 and 4, or, 3 and 5 shows that the long carbon chain of Priamine 1073 decreases the apparent density of the foams. The PHU foams can be considered for use as integral foams to make moulded parts with cellular core and relative dense decorative skin.

The potential applications are related to their cushion and shock adsorption abilities and include furniture, automobile and packaging.

Figure III-21: Picture of measuring of volume of PHU foam

IV.2.2.2 Morphological characterization of PHU foams

The PHU foams were analyzed by scanning electron microscopy (SEM) in order to determine their morphology relative to used raw materials (Figure III-22). The first picture (1) shows a network with a higher apparent density than the other foams. Indeed, foam (1) was prepared from only TMPTC whereas the other four were prepared from mixture of PPOBC640 and TMPTC in various ratios (0.5 or 0.7 TMPTC and 0.5 or 0.3 PPOBC640). The TMPTC plays the role of cross-linking agent and increases the apparent density of foam. On the contrary, PPOBC640 provides flexibility to materials by its aliphatic chain and provides more uniform cellular structure with smaller cells ((1) respectively compared to (2) and (3)). Moreover, two different amines were used to prepare PHU foams: Jeffamine EDR-148 and Priamine 1073. The second one, has in its chemical structure a long aliphatic chain, which, as the PPOBC640, provides flexibility to the materials and increases the sizes of cells of PHU foams ((4) and (5) respectively compared to (2) and (3)). All these characteristics are closely related and checked by determination of apparent density calculated previously. Finally, all the pictures show interconnected cells and thus open porosity of PHU foams.

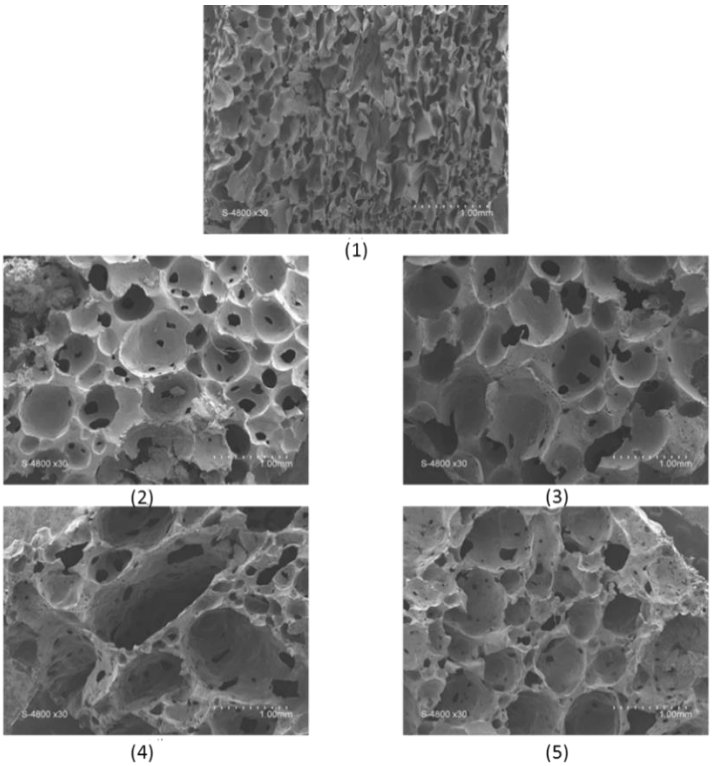


Figure III-22: Pictures of SEM micrographs of PHU foams

IV.2.3 Mechanical characterization of PHU foams

The mechanical properties of the PHU foams were analyzed by dynamic mechanical analysis (DMA). Two tests were made for flexible foams: the first corresponded to the behavior of the foam subjected to a stress in monotone tension exceeding the region of linear elasticity and the second showed the time of recovery of the flexible foams. For this purpose, the foams were cut into cuboid shapes of 20x20x10 mm and analyzed with tension holders at room temperature. Measurements were realized three times for the same samples.

The first experiment shows the same behavior of the PHU foams in monotone tension. Indeed, the five curves presented by the Figure III-23 can be divided into three regions corresponding to different mechanisms. The first region, of the lower strain (between 0 and 10-15% for 1, 2 and 3; and 5% for 4 and 5), is the linear elasticity. This domain is due to the strain for bending of the edge of the foam. The second region of these curves is characterized by a plateau. Physically, this part corresponds to the collapse of foam caused by the compressibility of the cells. Finally, the last region is the densification of the foam: when the stress is important, the opposite cells walls are crushed and they have formed a compressed material itself. However, only the values of stress to the different threshold depend on the type of studied foam. In fact, the foam 1 presents a more important stress for to deform the foam

compare to other foams. This foam was prepared with only tri-carbonate (TMPTC) which provides rigidity to the foam through more crosslinking of PHU foam. The foam 2 and 3 as 4 and 5 present a lower stress on the strain because PPOBC640 used in the formulations provided flexibility to foams. Finally, the structure of amine influences also the stress-strain curves. The long aliphatic chain of the Priamine 1073 which gives the flexibility for the foams 4 and 5 thus reduces their stress to strain compare to foams 2 and 3.

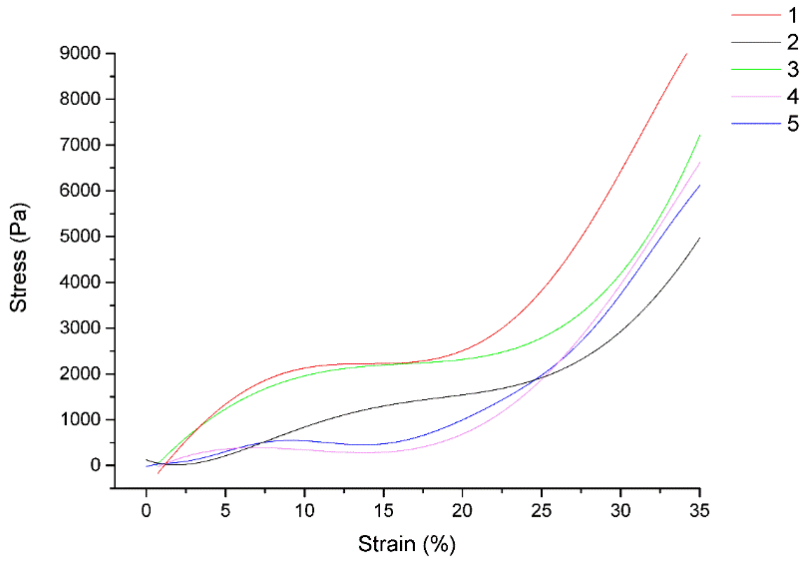


Figure III-23: Tension of the PHU foams at room temperature in DMA with tension holders

The second experiment shows the recovery of the PHU foams. For this reason, all the foams were compressed at 50% of strain during ten minutes and the time of recovery of these foams was saved (Figure III-24). All the curves of recovery foams overlays indicating that time back to the initial state is the same regardless of the formulation used to form the PHU foams.

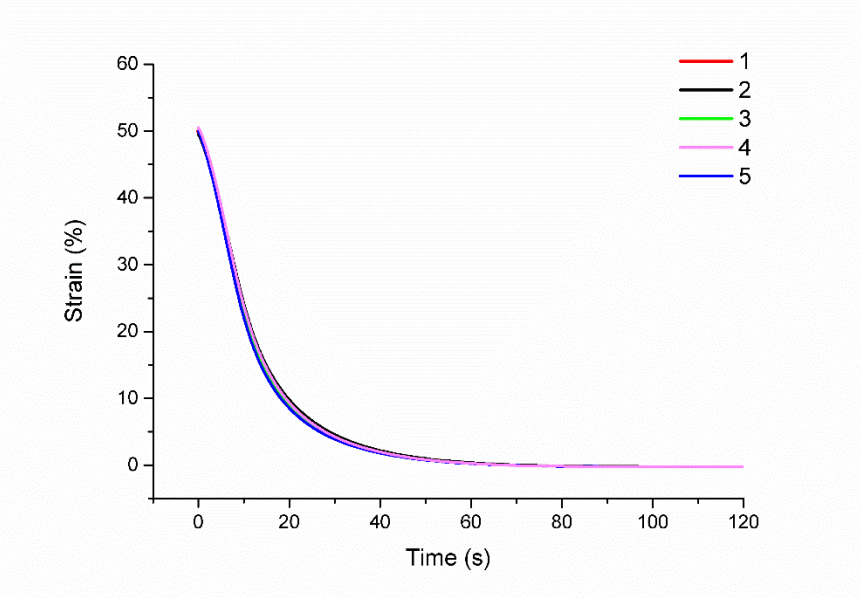


Figure III-24: Recovery of the PHU foams at room temperature investigated usind DMA with tension holders

IV.2.4 Degree of cross-linking characterization of PHU foams

In order to compare the degree of crosslinking of the different PHU foams, the swelling indices were measured. Three samples of known mass (m_0) of PHU foams were immersed in 30 mL of THF during 24h, and then reweighed to get the wet mass (m_1). The swelling index was calculated from Equation III-11. The results are summarized in Table III-7. The lowest swelling index and the highest index gel content correspond to the optimum cross-linking of polymer. 1 gives a lower swelling index compare to other formulations. This result is due to the use of only tri-functional cyclic carbonate (TMPTC) which brings more cross-linking PHU foam. All other PHU foams have swelling indices higher than 1. This arises from the use of difunctional cyclic carbonate (PPOBC640) besides TMPTC. This PPOBC640 gives flexibility to the foams through carbon backbone and, therefore, a higher swelling index because of the decrease of crosslinking of materials allowing the solvent to penetrate into the material more easily. This is confirmed by comparing the formulation 2 and 3, and, 4 and 5. In fact, the formulations 2 and 4 include 0.5 equivalent of PPOBC640 while the formulations 3 and 5 involve 0.3 equivalent of this cyclic carbonate. Furthermore, the swelling index of 4 and 5 are higher than 2 and 3. This is due to the long carbon backbone of the Priamine 1073 which brings, as PPOBC640 compare to TMPTC, the flexibility to the materials.

All these characterizations of morphology of the foams allow relating following formulations used. Indeed, the use of crosslinking agent (TMPTC) in the formulation imply the decrease the swelling index and the increase the apparent density and the stress at strain. The SEM

pictures show a denser network and smaller porosity. On the contrary, the use of long aliphatic chain (PPOBC640 and Priamine 1073) gives foams with a higher swelling index but lower apparent density and stress at strain. The MEB pictures show a lower apparent density of the foams and larger pore size.

IV.2.5 Thermal characterization of PHU foams

First, thermal properties were measured by DSC. Two dynamic temperature ramps were performed between -100 and 100 °C at 20 °C·min^{-1} under nitrogen flow. Results of DSC measurements are shown in Table III-7. The glass transition temperature values Tg obtained for foams of 1, 2, 3, 4, 5 formulations are equal to 19, -12, -2, -18 and -13 °C, respectively. Tg of foam 1 is higher than others, because of the higher cross-linking resulting from containing only tri-functional carbonates which cross-linked the material. Moreover, the PPOBC640 and Priamine 1073 contain long carbon backbones which could bring flexibility to materials and, therefore, decrease the Tg of foams from 2, 3, 4, 5 formulations.

TGA analyses were performed for all PHU foams in order to determine thermal stability of synthesized networks under nitrogen. Table III-7 gives the temperature at 30% of degradation and the char contents at 500 °C. The thermal stability of the PHU foams 1, 2 and 3 are similar with $Td_{30\%}$ around 320 °C. The thermal stability values of PHU foams 4 and 5 are higher, with a Td 30% equal to 360 °C, due to the absence of ether hinges in the Priamine 1073, by comparison to Jeffamine EDR-148, which increases the thermal resistance.

Table III-7: Apparent density, relative density, swelling index and thermal characterization of PHU foam

Foam formulations	ρ_a (kg·m^{-3})	ρ_r	Swelling Index (%)	Td 30% (°C)	Char at 500°C (%)	Tg (°C)
1	295	0.257	42	310	8	19
2	248	0.216	153	320	14	-12
3	242	0.210	147	314	6	-2
4	197	0.171	236	366	24	-18
5	194	0.169	211	352	14	-13

V. Conclusion

Nowadays, the alternative NIPU (Non Isocyanate PolyUrethane) constitutes a significant opportunity to replace isocyanate in the formulation of PU materials. This study reports, for the first time, the synthesis of PU foams without isocyanate. PHU foams were prepared from carbonate i.e. poly(propylene oxide) bis carbonate and trimethylolpropane tri carbonate and two amines. To ensure the reaction expansion, the same quantities of blowing agent (MH 15) were used in the foam formulations. The blowing reaction proceeded between amine and SiH groups of MH 15 by releasing of dihydrogen. NIPUs foams were then studied by characterizing the structure (apparent density, SEM, DMA), the degree of crosslinking (swelling index) and thermal properties (TGA and DSC). All these characterizations showed that the synthesized foams were high apparent density flexible foams and their structure and thermal properties depend on degree of crosslinking provided by the difference in functionality of cyclic carbonate and the structure of amine.

VI. Acknowledgement

This study was supported by ANR project CYRRENAS. S.D. acknowledges support by European Union through the European Social Found within “Cracow University of Technology development program – top quality teaching for the prospective Polish engineers; University of the 21st century” project (contract no. UDA-POKL.04.01.01-00-029/10-00). The authors also thank Specific Polymers for the synthesis of cyclic carbonates (PPOBC640 and TMPTC), Momentive for the blowing agent MH 15, Huntsman for Jeffamine EDR-148 and CRODA for Priamine 1073. The authors thank Emilie Darroman for fruitful discussion.

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Room temperature flexible isocyanate-free polyurethane foams

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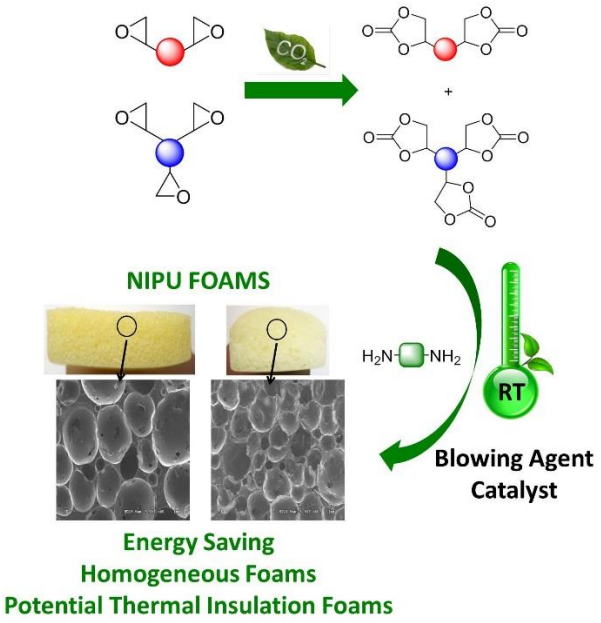
I. Abstract

We report the synthesis of sustainable isocyanate-free polyurethane foams. For the first time, polyhydroxyurethane (PHU) foams were synthesized at room temperature by high conversion step growth polymerization of cyclic carbonates and diamines. Trimethylolpropane tris-carbonate and polypropylene oxide bis-carbonate were copolymerized with EDR-148 diamine with thiourea as catalyst. A poly(methylhydrogenosiloxane) was used as blowing agent to foam the NIPU by reaction with diamines. PHU foams were characterized by scanning electron microscopy and by measurement of their swelling index and apparent density. The mechanical compression and the recovery of these PHU foams were analyzed by dynamic mechanical analyses at room temperature. The thermal insulating capacities and thermal degradation mechanism were determined.



II. Introduction

In 1947, Otto Bayer and coworkers[1] at I.G. Farben Industry discovered the synthesis of polyurethanes (PU) from reaction between diisocyanates and polyols. Owing to the facile variation of these two components, PU were readily tailored for diversified applications ranging from flexible foams for bed mattresses and automotive seats, to rigid foams for thermal insulation, scratch- and corrosion-resistant coatings, elastomer fibers for textiles and components of adhesives and sealants[2-4]. All these applications explain the high demand in PU since their discovery. Hence the global production of PU is currently 16kt/y and could attain in 2016[5] 18 kt/y of which 75% are foams. However, nowadays, a large quantity of chemical substances are suspected to be responsible of negative effects on environment and human health[6, 7]. In this context, the European regulation REACH, is seriously considering the effects of the synthesis of polyurethanes[8]. Indeed, most of diisocyanates are very harmful compounds. Prolonged exposure to them presents dramatic health risks such as asthma, dermatitis, conjunctives and acute poisoning[6], and they are produced from the even more toxic phosgene. In conjunction with these serious health concerns, the environmental regulations limit or banish the use of some isocyanates[9]. The two most widely used isocyanates in PU industry, ethylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as CMR (Carcinogen, Mutagen and Reprotoxic).

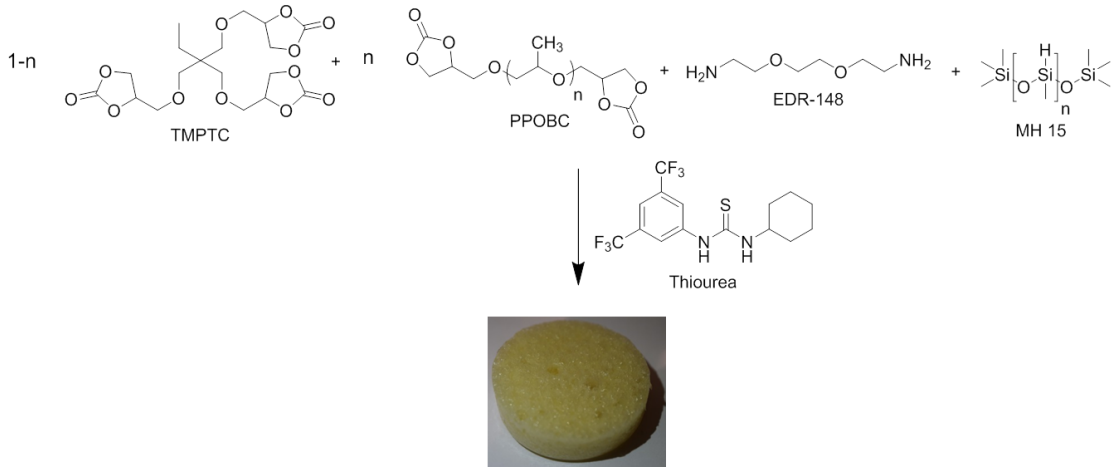
In order to design a PU material without isocyanate, the synthesis of non-isocyanate polyurethane (NIPU) by reaction between a bicyclic carbonate monomer and a diamine represents one of the most promising alternatives to the conventional synthesis of PU[10-33]. The resulting materials are called polyhydroxyurethane (PHU), since they contain also primary or secondary hydroxyl groups hanging off the macromolecular chain. However, the main problem of this technology is the low reactivity of carbonate/amine reaction compared to alcohol/isocyanate. In order to remedy this drawback, many studies in the literature have been conducted to design NIPU materials from more reactive cyclic carbonates, bearing electro-withdrawing substituent[20, 22, 30, 32, 34-42] or by using six-, seven-, eight-membered or thio-cyclic carbonate[29, 33, 40, 43-45]. But, the preparation of these compounds involves phosgene or its derivatives for six or seven-membered carbonates or carbon disulfides for thiocarbonates, which remain harmful reactants[29, 33, 40, 43, 44, 46]. Another method to increase the kinetics of the carbonate/amine reaction consists to use a catalyst. Blain *et al.*[47] and Lambeth *et al.*[48] showed that 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) and cyclohexylphenyl thiourea are the best catalysts for carbonate/amine reaction. However,

despite numerous studies dedicated to enhance the reactivity of carbonate/amine reaction, actually, the preparation of the NIPU materials with total conversion of carbonate at room temperature has never been reported.

Yet, the preparation of classic polyurethane foam is carried out at room temperature, adding water to the polyol/isocyanate mixture. The reaction between isocyanate and water yields amine and carbon dioxide that allows foaming[49]. As the gelling reaction (polyol/isocyanate), the foaming reaction takes place at room temperature. In contrast, concerning the formation of PHU, the reaction between cyclic carbonate and amine does not produce any blowing agent. Various polymer foams are already synthesized via polymerization reactions that do not produce any blowing agent, therefore additives should be added to the reactive formulation. Thus, in the case of epoxy polymers, several methods can be used to obtain epoxy foams. Indeed, epoxy-amine system can be blown by decomposition of azodicarbonamide[50] or sodium bicarbonate[51, 52] mixed either with epoxy or curing agent. Another method consists to use the thermoreversible reaction between amine and CO_2. This reaction gives a carbonated amine salt which decomposes at 90-100 °C and yields amine and releases CO_2. Ren *et al.*[53] obtained epoxy foams with carbonated amine salt with epoxy. At high temperature, the salt decomposes and the amine thus formed reacts with epoxy. Moreover, some systems can be physically blown by gas issued from boiling of monomers[54] or heating of volatile liquids incorporated into the formulation[55, 56]. However, all these methods of blowing reaction are performed at rather high temperature. Therefore this is a real challenge to propose the synthesis of PHU foams at room temperature.

Right now, only a handful of works reported the synthesis of non-isocyanate polyurethane foams in the literature. In 2015, our team published for the first time the synthesis of PHU foams using reaction between amine and polysiloxane in order to release H_2 as blowing agent.[57]. However these formulations were carried out at high temperature (80-120 °C). Very recently, Grinard *et al.*[58] reported on the synthesis of low density and low thermal conductivity PHU foams using supercritical carbon dioxide foaming technology. However, this synthesis is made under high CO_2 pressure (100 - 300 bars) and at high temperature (80 - 100 °C). Finally, Figovsky *et al.* [59-61] have developed hybrid systems called HNIPU to form foams. This technique consists to use epoxy monomers, acrylic monomers, cyclic carbonates and amines as raw materials and hydrofluorocarbons, hydrochlorofluorocarbons, alkylhydrogenosiloxane and also hydrocarbons as blowing agents.

The development of PHU foams at room temperature is really a challenge that could path the way to the development of sustainable routes to replace PU foams. However, the issue lies in the coordination of both gelling (carbonate/amine reaction) and foaming reaction. To the best of our knowledge, the preparation of PHU foams at room temperature was never reported in literature; therefore, we aspired to synthesize the first PHU foams at room temperature as an original work. Moreover, very little characterizations of PHU foams are described in the literature. Therefore, we based this study on our previous work[57] and chose three five-membered cyclic carbonates (trimethylolpropane tris-carbonate (TMPTC) and polypropylene oxide bis-carbonate of different length (PPOBC)) able to react with aliphatic amine (EDR-148). The catalyst (Thiourea) was used to increase the kinetics of carbonate/amine reaction at room temperature. The synthesis of various PHU foams by reaction between cyclic carbonate monomers and diamine with MH 15 blowing agent is summarized in Scheme III-4.



Scheme III-4: Formation of PHU foam by reaction between cyclic carbonate, di-amine, MH 15 and catalyzed with thiourea

III. Experimental Section

Materials

Poly(propylene oxide) diglycidyl ether ($\overline{M_n}$≈380 g.mol^{-1} PPO-DGE-380 and $\overline{M_n}$≈640 g.mol^{-1} PPODGE-640), trimethylolpropane triglycidyl ether (TMPTGE), cyclohexamine, 3,5-bis(trifluoromethyl)phenyl isothiocyanate, lithium bromide (LiBr), dimethylformamide (DMF), ethyl acetate, tetrahydrofurane (THF) and toluene were purchased from Sigma Aldrich. EDR-148 was obtained from Huntsman. Poly(methylhydrogenosiloxane) (MH 15) was obtained from Momentive. Deuterated solvents ($CDCl_3$ and DMSO-d_6) were purchased from Eurisotop (Saint-Aubin, France).

Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy using a Bruker Advance 400 MHz spectrometer equipped with a QNP z-gradient probe at room temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: around 10 mg of product for ^{1}H, ^{13}C and ^{19}F experiment in around 0.5 mL of $CDCl_3$ or DMSO-d_6.

Fourier Transform Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Nicolet 210 Fourier transform infrared spectroscopy (FTIR) spectrometer. The characteristic IR absorptions mentioned in the text were strong bands are reported in cm^{-1}.

Scanning Electron Microscopy

The morphology and the internal structure of the foams were investigated in parallel surface to the rise direction of PHU foam by scanning electron microscopy (SEM). A Hitachi S-2600N was used to obtain images of foams.

Dynamic Mechanical Analyses

Dynamic Mechanical Analyses (DMA) were carried out on Metravib DMA 25 with Dynatest 6.8 software. Uniaxial stretching of foam samples (10 x 15 x 12 mm^3) was performed while heating at a rate of 3 °C.min^{-1} from -100 °C to 150 °C, keeping frequency at 1 Hz.

Crosslinking density (ν) was calculated on the basis of the relation between average molecular weight of effective networks chains (Mc) and density of the polymer (ρ) (Equation III-17).

Equation III-17 $$\nu = \frac{\rho}{M_c}$$

From rubber elasticity theory[62, 63], the uniaxial stretching were studied on the rubbery plateau at Tα+50, and at very small deformations. Under these hypotheses, the crosslinking density ($\nu_{E'}$), can be obtained from Equation III-18 and Equation III-19, where R is gas constant and T is temperature in K [64].

Equation III-18 $$E' = \frac{3\rho RT}{M_c}$$

Equation III-19 $$\nu'_E = \frac{E'_{at\ T\alpha+50}}{3RT_{\alpha+50}}$$

The mechanical compressions of the samples were measured at room temperature using 10 x 15 x 12 mm^3 foam samples in the creep mode with compression holders. The static force was

fixed to 20N with application time of 100s, a maximum displacement of 30-35% of strain and the time charging of 1s. Then, the time of recovery of foams was measured during 200s.

Thermogravimetric Analyses

TG/IR analysis was performed on a Perkin Elmer Pyris I at a heating rate of 10 °C/min. Approximately 10 mg of sample was placed in an aluminum pan and heated from room temperature to 500 °C under nitrogen atmosphere (60 mL.min^{-1}). TGA was coupled with an FTIR IFS66 Brujer Optics, in order to detect the evolved gases. The FTIR measurements were carried out in the range of 4000-400 cm^{-1}, with 8 scans and spectral resolution of 1 cm^{-1}.

TGA/MS analysis was carried out using a STA-449 Jupiter thermal analyzer coupled with quadrupole QMS 403 S Aëolos® mass spectrometer. The ion source was a 100 eV electron impact ion source. Around 10 mg of sample was placed in aluminum pan and heated from room temperature to 500 °C under argon atmosphere (60 mL.min^{-1}).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. 10-15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at 20 °C.min^{-1} in the range between -80 and 100 °C to observe the glass transition temperature at the second ramp. All the reported temperatures are on set values.

Thermal Conductivity measurement

The thermal conductivity measurements were executed with a Hot Disk TPS 2500 S unit using the transient plane source TPS method. For this method, a thin disk-shaped sensor was used. The TPS-sensor was sandwiched between two identical samples to have uniform heat dissipation from both sides of the sensor during the measurements. Measurements were performed in open atmosphere at room temperature. A 2.001 mm diameter Ni TPS-element with Kapton insulation was used.

General procedure for syntheses of cyclic-carbonates: PPOBC380, PPOBC640 and TMPTC

In a round-bottom flask (500 mL), poly(propylene oxide) diglycidyl ether (PPODGE-380 or -640) or trimethylolpropane diglycidyl ether (TMPTGE) (1 eq, 100 g) and LiBr (5 mol%) were dissolved in DMF (150 mL). The solution was introduced onto a reactor and the atmosphere

was replaced with CO_2 (P=15 bar). The solution was then allowed to stand at 80 °C with continuous stirring for 36 h. DMF was removed by distillation under vacuum (70 °C, P= 10 mbar). The pure product (PPOBC380 and PPOBC640) was obtained quantitatively as brown oil with a 76% yield.

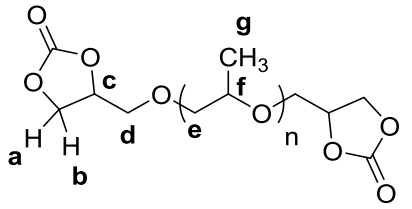


Figure III-25: PPOBC380 and -640 idealized structure

^{1}H NMR PPOBC380 (400 MHz, $CDCl_3$, ppm) (SI - Figure III-16): δ: 1.06 (m, 7H, H_g); 3.24-3.90 (m, 18H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

^{1}H NMR PPOBC640 (400 MHz, $CDCl_3$, ppm) (SI - Figure III-17): δ: 1.06 (m, 23H, H_g); 3.24-3.90 (m, 32H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

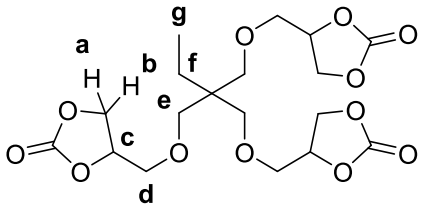


Figure III-26: TMPTC idealized structure

^{1}H NMR TMPTC (400 MHz, $CDCl_3$, ppm) (SI - Figure III-18): δ: 0.81 (t, 3H, H_g); 1.34 (m, 2H, H_f); 3.20-4.00 (m, 12H, H_d, H_e); 4.25-4.60 (m, 6H, H_a, H_b); 4.82 (m, 3H, H_c).

Titration of the cyclic carbonate by ^{1}H NMR

A specified amount of cyclic carbonate (TMPTC, PPOBC380 or -640) (around 50 mg) and a standard solution of DMSO with toluene (around 60 mg of toluene dissolved in 10 mL of DMSO-d_6) were weighted into an NMR tube. Once the ^{1}H NMR acquisition was completed, characteristics peaks of carbonate a, b and c (4.51, 4.29 and 4.92 ppm respectively) and CH_3 (2.32 ppm) of toluene were integrated. The integration of CH_3 of toluene was fixed to 300. Carbonate equivalent weight (CEW) of TMPTC, PPOBC380 and -640 were calculated according to Equation III-20, where m_{C5} – mass of cyclic carbonate introduced into the NMR tube, $n_{function\ of\ carbonate}$ – molar amount of function carbonate in cyclic carbonate, I_a, I_b, I_c – integrations of characteristics peaks a, b and c of carbonate, $n_{toluene}$ – molar amount of toluene

introduced in standard solution, I_{CH3} – integration of peak CH_3 of toluene. The CEW values for each cyclic carbonate were obtained in triplicate determinations.

Equation III-20 $$CEW = \frac{m_{C5}}{n_{function\ of\ carbonate}} = \frac{m_{C5} \times I_{CH3}}{(I_a + I_b + I_c) \times n_{toluene}}$$

Synthesis of 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (Thiourea)

Thiourea was synthesized according to the literature procedure[65]: at room temperature, cyclohexylamine (0.534 g, 5.39 mmol) was added dropwise to a stirred solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (1.500 g, 5.53 mmol) in THF (10 ml). After stirring for 4 h at room temperature, the solvent was evaporated. The white residue was recrystallized from chloroform to give thiourea as a white powder with a 88% yield.

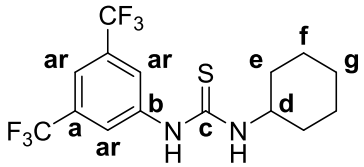


Figure III-27: Thiourea structure

^{1}H NMR (400 MHz, DMSO-d_6, ppm) (SI - Figure III-21): δ: 9.81 (br. s, 1H, NH), 8.24 (s, 2H, H_{ar}), 7.69 (s, 1H, H_{ar}), 4.11 (br. s, 1H, H_d), 1.93-1.16 (m, 10H, H_e, H_f, H_g).

^{13}C NMR (100 MHz, DMSO-d_6, ppm) (SI - Figure III-22): δ: 179.19 (C_c), 142.04 (C_b), 127.33 (C_{ar}), 124.62 (Ca), 121.91 (CF_3), 115.81 (C_{ar}), 52.28 (C_d), 31.59 (C_e), 25.1 (C_f), 24.4 (C_g)

^{19}F NMR (376 MHz, DMSO-d_6, ppm) (SI - Figure III-23): δ: -63.5 (s, CF_3).

Synthesis of PHU foams

First, the cyclic carbonate compounds (TMPTC and/or PPOBC380 or -640) and the thiourea were stirred mechanically for 3 min in silicone mold. Then, the blowing agent, MH 15, was added and the mixture was stirred for 3 min. Once the homogenous mixture was obtained, EDR-148 was added and the mixture was stirred for 2 min then the mixture was poured into a polypropylene beaker. The obtained foamed mixture was left for three days at room temperature. Typically, the PHU foams were prepared from around 3.2 and 4.5g of reactants and gave samples of 35 mm of diameter and 12-18 mm of height.

Swelling Index and Gel Content

Swelling Index: three samples (30mg each) were separately put into 30 ml THF for 24 h. The swelling index, SI, is given by Equation III-21, where m_0 is initial mass of tab and m_1 is mass of tab after swelling in solvent.

Equation III-21 $$SI=\frac{m_1-m_0}{m_0}\times 100$$

Gel content: After SI measurement, the three tabs are dried in a ventilated oven at 50 °C during 24 h. The gel content GC is given by following Equation III-22, where m_0 is initial mass of tab and m_2 is mass of tab after drying.

Equation III-22 $$GC = \frac{m_2}{m_0} \times 100$$

Apparent density

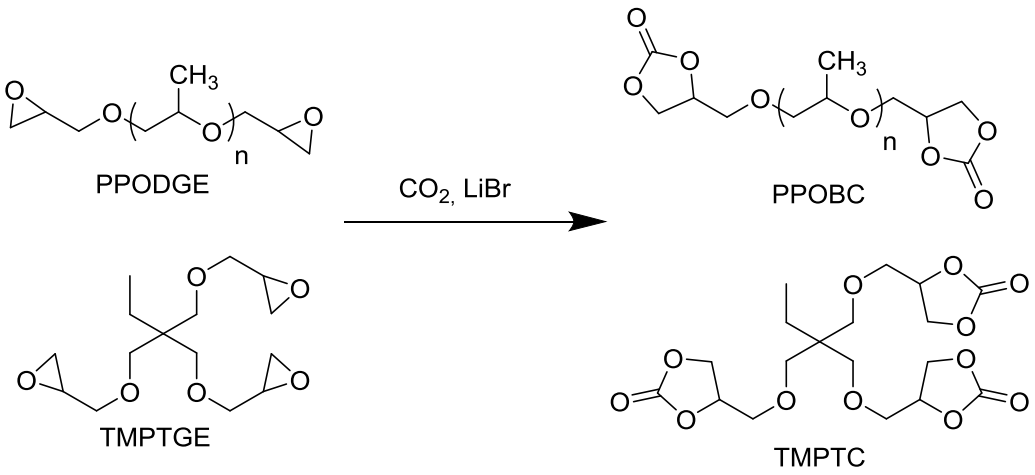
The PHU foams were cut into samples in the cuboid shape. Their dimensions were measured using caliper and the apparent density, ρ_a, was calculated from Equation III-23, where m express the mass of the foams samples in kg and V is volume of the samples in m^3.

Equation III-23 $$\rho_a = \frac{m}{V}$$

IV. Results and Discussion

IV.1 Synthesis and characterization of raw materials

Before the synthesis of the PHU foams, the synthesis and characterization of the cyclic carbonates was achieved. Three five-membered cyclic carbonates were synthesized by carbonation of poly(propylene oxide) diglycidyl ether (PPODGE-380, $\bar{M}n$≈380 $g.mol^{-1}$ and PPODGE-640, $\bar{M}n$≈640 $g.mol^{-1}$) and trimethylolpropane triglycidyl ether (TMPTGE) in presence of lithium bromide. We respectively obtained poly(propylene oxide) biscarbonate (PPOBC380 and -640) and trimethylolpropane triscarbonate (TMPTC) (Scheme III-5).



Scheme III-5: Carbonation of PPODGE and TMP-TGE

Moreover, the degree of polymerization of PPOBC380 and -640 was calculated according to ^{1}H NMR (SI - Figure III-16 and SI - Figure III-17) analysis and Equation III-24 (I_g, I_c - Integration of characteristic protons g or c) and the real molar masses were determined (Table III-8).

Equation III-24 $$n = \frac{\frac{I_g}{3}}{\frac{I_c}{2}}$$

The precursor of TMPTC, TMP-TGE, is synthesized by epoxidation of trimethylolpropane in two steps. The first step consists in the formation of TMP alcoholate ammonium salt by solubilization of TMP in a large excess of epichlorohydrin in presence of an ammonium phase transfer catalyst. The alcoholate then reacts with epichlorohydrin, yielding chlorinated intermediates. Although epichlorohydrin is obtained from biobased compounds (glycerin) [66, 67], it remains dangerous and harmful compound to humans. In a second step, the crude mixture is treated with NaOH solution to form oxirane rings from chlorinated intermediates. Upon NaOH treatment, some chlorinated intermediates remain under chlorinated form which explains that the functionality of TMP-TGE is lower than 3. Consequently, as TMPTC is obtained by carbonation of TMPTGE, its functionality is also lower than 3. The ^{1}H NMR spectrum (SI - Figure III-18) of TMPTC reveals a carbonate functionality of 2.6. The carbonate equivalent weights (CEW) of carbonate monomers were determined by ^{1}H NMR titration with standard solution (DMSO-d_6 with few milligram of toluene). CEW, functionalities and molar masses of five-membered cyclic carbonates were summarized in Table III-8.

For the synthesis of NIPU, EDR-148 from Huntsman Company was used in combination with PPOBC380 or -640 and TMPTC. The phenomenon of carbonation of amines with CO_2 of air is well known[68, 69]. Therefore the diamine has been previously distilled under vacuum at 120 °C and stored under inert gas (Argon). ^{1}H NMR analysis of EDR-148 (SI - Figure III-19) confirms the purity and the di-functionality of this amine. Indeed, the integrations of the three signals for a, b and c protons correspond respectively to 4.0, 4.1 and 4.1 protons. In addition, the integration of protons corresponding to amine function (NH_2) corresponds to 4.0 protons. This amine contains an oxygen atom in beta position of each primary amine group. Webster *et al.*[70] reported the high reactivity towards carbonates of such amines with oxygen atoms in beta position. In order to formulate PHU foams from cyclic carbonate and EDR-148, the Amine Hydrogen Equivalent Weight (AHEW) of diamine was calculated from Equation III-25 where M is the molar mass of EDR-148 and nb active H is the number of active hydrogen of the amine (2 in the case of cyclic carbonate / amine reaction).

Equation III-25 $$AHEW = \frac{M}{nb\ active\ H}$$

Finally, to trigger expansion of NIPU, a blowing agent was used in the formulations: MH 15 from Momentive Company (Scheme III-4). This foaming agent was previously characterized in our previous study[57] (^{1}H NMR in SI - Figure III-20). The molar masses are summarized in Table III-8.

Table III-8: Characteristics of reactants

Reactants	CEW ($g.eq^{-1}$)	AHEW ($g.eq^{-1}$)	Carbonate or amine functions	M ($g.mol^{-1}$)
PPOBC380	235	-	2	352[1]
PPOBC640	350	-	2	661[1]
TMPTC	183	-	2.6	476[2]
EDR-148	-	74	2	148
Thiourea	-	-	-	370
MH 15	-	-	-	2083[3]

[1]: Molar mass calculated by ^{1}H NMR
[2]: Molar mass calculated from M=CEW x Carbonate function
[3]: Molar mass calculated by Cornille *et al.*[57]

IV.2 Formulation and characterization of PHU foams

IV.2.1 Synthesis of PHU foams

In this study, eleven PHU foams were synthesized at room temperature from TMPTC, PPOBC380 and PPOBC640 carbonate monomers and EDR-148 diamine. Thiourea was used as catalyst and MH 15 as blowing agent. This last compound reacts with amines, releasing H_2

which allows the foaming of synthesized NIPU[57, 71]. In this study, we used 2% and 5% molar equivalent of MH 15. The amount of amine used is adjusted (1.02 and 1.05 equivalent) to compensate the amount of polysiloxane in the system and keep a stoichiometric amount of cyclic carbonate and amine. The main drawback of NIPU technology remains the low reactivity of reaction between cyclic carbonate and amine. In order to improve the kinetics of the carbonate/amine reaction, two catalysts were identified[47]: 1,5,7-triazabicyclo [4.4.0]dec-5-ene(TBD) and 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (Thiourea). In our previous works[57], we have synthesized the first PHU foams from cyclic carbonates and amines by using TBD catalyst which is a commercial catalyst. However, this catalyst is not soluble in cyclic carbonate or amine at room temperature, therefore, in this new study, we used thiourea for formulations at room temperature. From Blain *et al.*[47] after 10 minutes of reaction, the thiourea is a more efficient catalyst than TBD when the catalyst load is kept below 1 mol%. In this study, all the PHU foams were synthesized with 1 mol% of thiourea relative to cyclic carbonate. The catalyst was previously synthesized by reaction between cyclohexylamine and 3,5-bis(trifluoromethyl)phenyl isothiocyanate. The activation mode of the carbonate by thiourea can be explained by the creation of two hydrogen bonds with the oxygen of the carbonyl function in a 6-membered ring reaction of the thiourea, making cyclic carbonate more reactive in cyclic carbonate / amine reaction [47].

The presence of crosslinking carbonate (TMPTC) was crucial to obtain homogenous foams. Moreover, the long aliphatic carbon backbone of PPOBC380 and -640 confers flexibility to foams. Therefore, PPOBC640 brings more flexibility to the foam that PPOBC380. These foams were prepared by using formulations based on molar equivalent of reactants (Table III-9).

The difference between the structures of PHU foams were characterized by scanning electron microscopy (SEM), measurement of the apparent density and dynamic mechanical analysis (DMA). Then, the degree of cross-linking was characterized by measurement of swelling index. Finally, thermal and thermo-mechanical properties of PHU foams were determined by differential scanning calorimetry (DSC), DMA, thermogravimetric analysis (TGA) and measurement of thermal conductivity and diffusivity. All characteristics were compared to commercial PU foam commercialized by COP-Chimie Company under brand name Viscomousse and synthesized from polyol and isocyanate. This PU foam is used for the development of corset of foam-bed in the medical domain for treatment of bedsore. In order to determine the industrial composition of this PU foam, infrared spectrum was recorded (SI -

Figure III-24). This spectrum shows characteristic bands of N-H (3298 cm^{-1}), aromatic C-H (3100 cm^{-1}), CH_2 (2970-2868 cm^{-1}), C=O urethane (1724 cm^{-1}), C=C (1510 cm^{-1}), C-N (1224 cm^{-1}) and C-O-C (1090 cm^{-1}) stretching. These bands prove that PU foam had been formulated with unsaturated polyol containing ether bond such as polyol issued of fatty acid and isocyanate containing aromatic ring such as TDI or MDI.

Table III-9: PHU foams formulation in molar equivalent

	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8	F-9	F-10	F-11
PPOBC380	-	-	0.3	0.2	0.1	-	-	-	-	-	-
PPOBC640	-	-	-	-	-	0.3	0.3	0.2	0.2	0.1	0.1
TMPTC	1	1	0.7	0.8	0.9	0.7	0.7	0.8	0.8	0.9	0.9
EDR-148	1.05	1.02	1.02	1.02	1.02	1.05	1.02	1.05	1.02	1.05	1.02
Thiourea[a]	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MH 15[b]	0.05	0.02	0.02	0.02	0.02	0.05	0.02	0.05	0.02	0.05	0.02

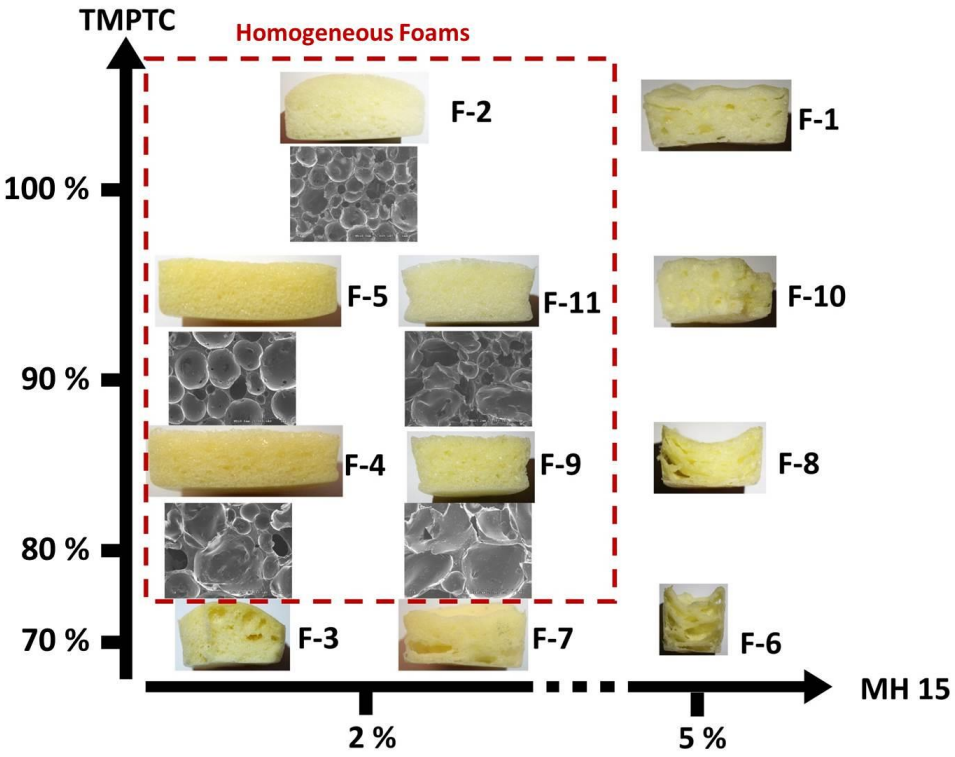
[a]: Quantities in molar equivalent of Thiourea introduced in the foam formulations compare to cyclic carbonate.
[b]: Quantities in molar equivalent of MH 15 introduced in the foam formulations relative to amine.

IV.2.2 Structural characterization of PHU foams

First of all, PHU foams were visually characterized to compare homogeneity according to ratio of carbonate monomers and blowing agent amount. Hence, the PHU foams obtained at room temperature are more homogeneous than our first PHU foams previously obtained at high temperature[57]. Cells exhibit more regular shapes and sizes. Moreover, the PHU foam pictures in Scheme III-6 showed that the foams with 5% of MH 15 are less homogeneous that the foams with only 2%. Indeed, the PHU foams formulated with 0.8 or 0.7 TMPTC/ 0.2 or 0.3 PPOBC and 5% MH 15 present variable pore sizes. Moreover, during crosslinking, these foams collapsed. This can be explained by the excessive amount of H_2 released during blowing reaction. Foams are not sufficiently crosslinked and the exterior cell walls have collapsed (Scheme III-6: F-6 and F-8). However, when the TMPTC amount increases (TMPTC, 0.9TMPTC/0.1PPO-Bis-C_5), the PHU foams don't collapse. The cross-linker allows maintaining the expanding cell walls but the size pores are still inhomogeneous. In order to obtain homogeneous foams, a compromise between blowing and crosslinking reaction must be found. Therefore, MH 15 amount was decreased at 2% in following formulations (F-2, F-3, F-4, F-5, F-7, F-9, F-11). From pictures, PHU foams obtained present uniform size pores for F-2, F-4, F-5, F-9 and F-11. However, more the PPOBC amount increases, more the foam is inhomogeneous (F-3 and F-7). PHU foams synthesized from 0.7 TMPTC and 0.3 PPOBC380 or -640 have varying pore sizes. This can be due to poor mixing between raw materials in the formulation of the foam. Scheme III-6 and SI - Figure III-27 - SI - Figure III-32 display the morphologies and cell sizes of the different homogeneous foams observed in SEM.

Later in this study, only homogenous foams (F-2, F-4, F-5, F-9 and F-11) were characterized. Microscopic examination of the resulting internal structure reveals that all homogeneous foams contain interpenetrated cells, with similar shapes. The SEM picture of foam formulated with only TMPTC, shows a network with smaller cells (0.71-0.92 µm) than other foams. The TMPTC plays the role of cross-linking agent, increases the density of foam and decreases the pore size. On the contrary, PPOBC used in PHU foam formulations, provides flexibility to materials by its aliphatic chain and increases the pore size.

We also determined apparent density (ρ_a) of PHU foams. Apparent density of our PHU foams varies between 195 and 382 kg.m^{-3} (Table III-10) whereas apparent density of the reference PU foam is 96 kg.m^{-3}. The increase in apparent density of PHU foams is related to the degree of cross-linking of the foam. In fact, the density of PHU foam F-2 formulated with 100% TMPTC is 303 kg.m^{-3} whereas the densities of PHU foams synthesized with 10 and 20% of PPOBC640 are respectively 273 and 271 kg.m^{-3}. On the other hand, the comparison of the apparent densities between foams prepared from PPOBC380 or -640 shows that the long backbone chain of PPO slightly decreases the density of the foams. This trend is related to the pore size.



Scheme III-6: PHU foam samples and SEM pictures

Finally, infrared spectroscopy analysis was performed to check complete conversion of carbonate groups of TMPTC and PPOBC380 and -640 with amine group of EDR-148. Figure III-28 gives the overlaying infrared spectra of cyclic carbonate and PHU foams. The spectra of all PHU foams are similar. On the PHU foams spectra, we observe the disappearance of the bands at 1793 cm^{-1} characteristic of carbonate group C=O bond stretching and the appearance of the characteristic band at 1693 cm^{-1} corresponding to elongation of urethane C=O bond. Moreover, a broad band appears between 3150 and 3620 cm^{-1}, characteristic of NH of urethane groups and hydroxyl groups from the ring opening of cyclic carbonate by amine. Finally, on PHU foams spectra, we observe the total disappearance of bands at 1612 cm^{-1} corresponding to NH_2 of EDR-148 and at 2161 cm^{-1} corresponding to elongation of Si-H of MH 15. These results prove, for the first time in NIPU materials, the total conversion of cyclic carbonate monomers by aminolysis at room temperature. This quantitative reaction at room temperature is both due to the efficiency of thiourea catalyst and the blowing reaction. Indeed, in order to determine the influence of blowing reaction on conversion, a NIPU material, without blowing agent, was formulated with TMPTC, EDR-148 and 1% of thiourea. The mixture gave a material which remained sticky, indicating the presence of unreacted species in the material. An infrared spectra of polymer was recorded (SI - Figure III-25) and showed the presence of a band at 1791 cm^{-1} characteristic of carbonate C=O bond elongation. Thus the blowing reaction allows a fine stirring of cyclic carbonate / amine mixture that could break the hydrogen bonds created between hydroxyl and urethane groups which generally block the system carbonate/amine. Moreover, to test the influence of catalyst, one PHU foam was formulated (TMPTC, EDR-148, 2% MH 15) without thiourea. The mixture did not give a material but a highly viscous liquid, demonstrating the efficiency of the catalyst for carbonate/amine reaction. So only use of both thiourea catalyst and foaming allows to reach quantitative conversion of carbonate/amine polymerization at room temperature. This result is of paramount importance since it path the way for the first time to the complete synthesis of NIPU at room temperature. Finally, to complete this study, the exothermic reaction to produce F-2 was recorded during 30 minutes (SI - Figure III-26). This test shows an increase of the temperature of around 10 °C during the crosslink and blowing reaction.

In addition, the measurement of Swelling Index (SI) and Gel Content (GC) of PHU foams were performed. These results gave information on crosslinking degree of materials. Indeed, lowest SI and highest GC correspond to the optimum crosslinking of polymer. PHU foams F-2 formulated with 100% TMPTC gives a lower SI than other foams. This result is due to the

only use of a carbonate with a functionality higher than 2 which increases cross-linking of polymer. The use of PPOBC for F-4, F-5, F-9 and F-11 increases the SI of these foams. Indeed, PPOBC decreases the crosslinking of polymers, allowing the solvent to penetrate easily into material. Concerning gel contents, all foams exhibited high insoluble contents (91-95%), which indicates a high cross-linking of urethane networks and confirms the conversion results by infrared analysis.

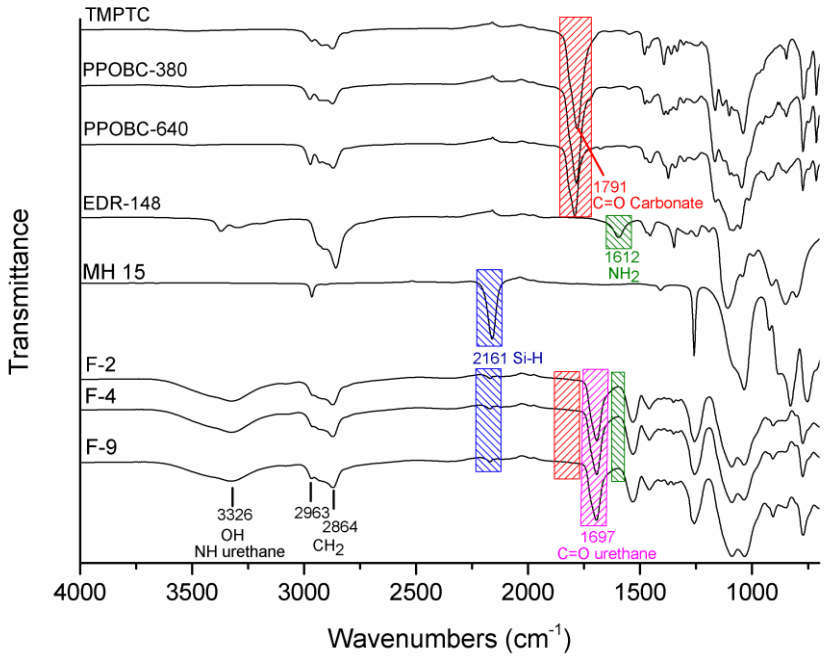


Figure III-28: Overlay of infrared spectra of raw materials and PHU foams

Table III-10: Main characteristic values of homogeneous PHU foams synthesized from cyclic carbonate, EDR-148, Thiourea and 2% MH 15

Foam	Composition	ρ_a (kg.m^{-3})	SI[1] (%)	GC[2] (%)	Tg (°C)	Tα (°C)	E'[3] (10^5 Pa)	ν_e[4] (mol.m^{-3})
Ref	-	96	977	92	0	31	0.78	9
F-2	TMPTC	303	96	92	10	37	5.52	62
F-5	0.9TMPTC/ 0.1PPOBC380	301	118	91	11	27	6.47	74
F-4	0.8TMPTC/ 0.2PPOBC380	295	123	91	7	26	8.85	102
F-11	0.9TMPTC/ 0.1PPOBC640	273	153	95	8	30	3.17	36
F-9	0.8TMPTC/ 0.2PPOBC640	271	162	94	0	21	1.40	16

[1]: Swelling Index; [2]: Gel Content; [3]: E' at Tα+50 °C; [4]: Crosslink density

IV.2.3 Mechanical characterization of PHU foams

Dynamic mechanical analysis of NIPU and PU foams was carried out to determine their mechanical properties. For this purpose, two tests were performed: the first one corresponds to the study of behavior of foams subjected to a stress in monotone tension (Figure III-29) and the second one concerns the time of recovery of NIPU and PU foams after compression at 30% of strain in parallel direction to the foam growth direction (Figure III-30). Prior to analysis, the foams were cut into cuboid shapes of average 11 x 13 x 14 mm and analyzed with compression holders at room temperature.

The first experiment shows the same behavior of foams in monotone compression. Indeed, curves of 4 PHU foams presented in Figure III-29 can be divided into three regions corresponding to different steps. The first region (between 0 and 7% of strain) corresponds to the strain for edge bending of the foam. This region is called linear elasticity. The second corresponds to the collapse of foam caused by the compression of the cells (between 7 and 24%). A third region is remarkable by a significant increasing of the stress for a lower strain. Physically, this part corresponds to the densification of the materials when the cells are completely compressed. This region is not visible for the foams with small density such as reference PU foam and PHU foam formulated with PPOBC640 (F-4 and F-9) because these foams are not enough compressed. Only the values of stress to the different threshold depend on the type of studied foam and consequently of their density. In fact, the higher is the density of the foam, the higher is the stress to be applied to compress the foam. This explains that the PHU foam formulated with 100% of TMPTC requires the highest stress to be compressed. Moreover, the foam formulations including PPOBC640 present a lower stress on the strain compared to foams prepared with PPOBC380 because the longer aliphatic chain of PPOBC640 enhances the flexibility of foams, reduces their density and thus their stress to strain.

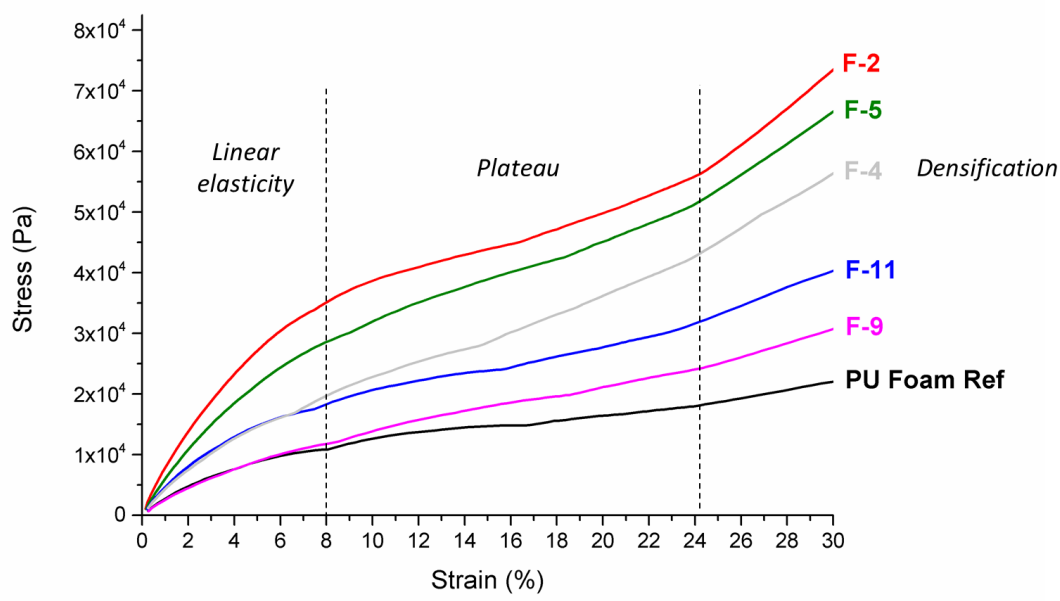


Figure III-29: Tension of the foams at room temperature measured by DMA with tension holders

In order to investigate the recovery of foams to initial state, the materials were compressed at 30% of strain and the time of recovery of foams was recorded (Figure III-30). From this graph, all the curves of foam recovery are almost overlaid which indicates that time to come back to the initial state is the same, regardless of the formulation. Indeed, the apparent density and consequently the crosslinking rate should influence the recovery time of these foams. However, the sensibility of DMA does not allow differentiating the recovery time owing to density: the stresses of strain (30%) of all foams are close (2.0-7.5x10^4 Pa).

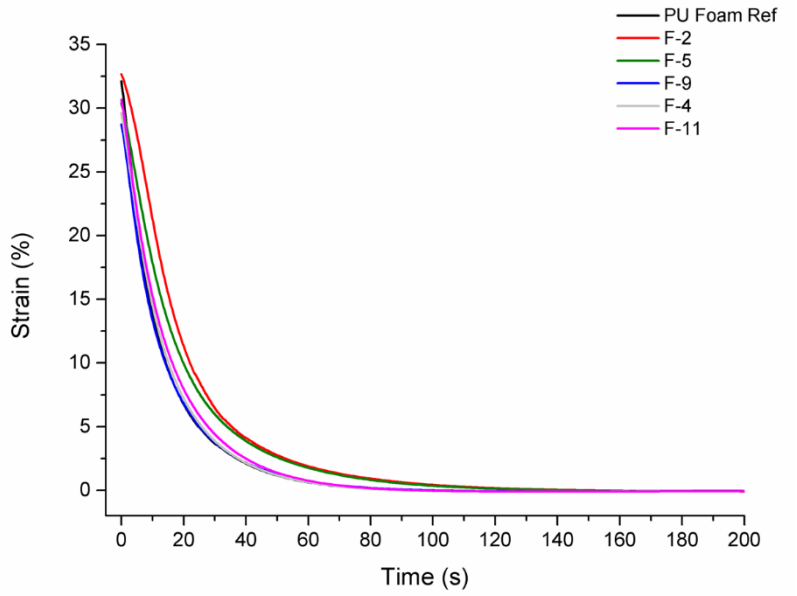
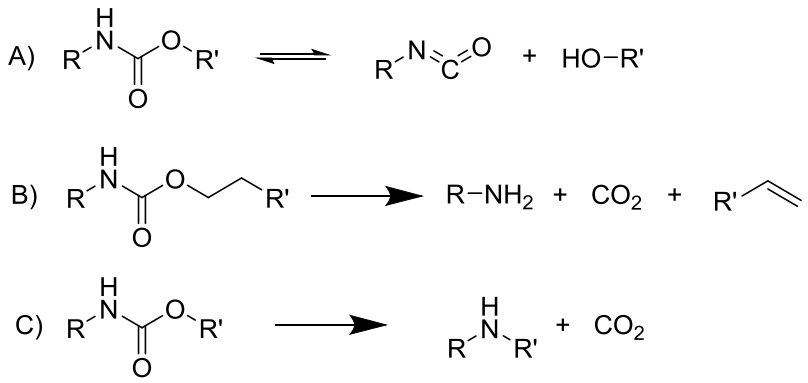


Figure III-30: Recovery of the PU and PHU foams at room temperature studied by DMA with tension holders

IV.2.4 Thermal characterization of PHU foams

First, thermal properties were measured by differential scanning calorimetry. Two dynamic temperature ramps were performed between -80 °C and 100 °C at 20 °C.min^{-1} under nitrogen flow. Results of DSC measurements are shown in Table III-10. With increasing contents of TMPTC cross-linker, Tg values slightly increase for foams prepared with 80, 90 and 100% TMPTC. The addition of cross-linker increased the rigidity of the final material. This evolution, visible at macroscopic scale, is confirmed by stress-strain curves obtained by DMA. Moreover, the structure of PPOBC influences the rigidity and thus the Tg of PHU foams. In fact, the higher is the molar mass of PPO (molar mass of 640 compared to 380 g.mol^{-1}), the lower are the Tg value and the rigidity of material.

Thermal stability was also characterized by thermogravimetric analysis (TGA) under inert gas (Ar): the results are summarized in Table III-11 and the curves are shown in Figure III-31. All the PHU foams showed a good thermal stability with a decomposition starting at 200 °C. The thermal stability of these NIPU is similar to other NIPU materials reported in literature [20, 72]. However, thermal decomposition of PU foam reference started at 250 °C indicating a higher thermal stability. It may be explained, in the case of NIPU materials, by the weakening of bond between carbonyl carbon and oxygen in urethane group due to the influence of OH-group [73]. In our case, a decomposition in two (PU Foam Ref and F-2) or three steps (F-4 and F-9) is observed. Conventional PU materials present also a two or three-step degradation mechanism[74]. The first degradation process concerns the thermal decomposition of hard segments (urethane functions) that yields alcohol and isocyanate (Scheme III-7-A), primary amine and terminal olefin group (Scheme III-7-B) and lastly secondary amine (Scheme III-7-C) with CO_2 elimination [75]. The second and third processes take place above 300 °C and correspond to the scission of ether linkage and decomposition of soft segments (R, R'). The second and third steps of decomposition are much slower and depend on the soft segment structures and its three-dimensional arrangement. The presence of oxygen does not influence the decomposition rate of polyurethane to diisocyanates and polyols, although it affects the breakage of the polymer chains[76].



Scheme III-7: Mechanism of decomposition of urethane bonds: first step at low temperature (200-300 °C)

Table III-11: Main degradation temperatures of PHU foams synthesized with cyclic carbonate, EDR-148, Thiourea and 2% MH 15 compared to PU foam

Foam	Composition	1st degradation		2nd degradation		3th degradation	
		%deg	T_{max} (°C)	%deg	T_{max} (°C)	%deg	T_{max} (°C)
Ref	-	65	352	35	400	-	-
F-2	TMPTC	41	306	59	373	-	-
F-4	0.8TMPTC/ 0.2PPOBC380	42	300	17	380	41	416
F-9	0.8TMPTC/ 0.2PPOBC640	49	305	12	380	39	416

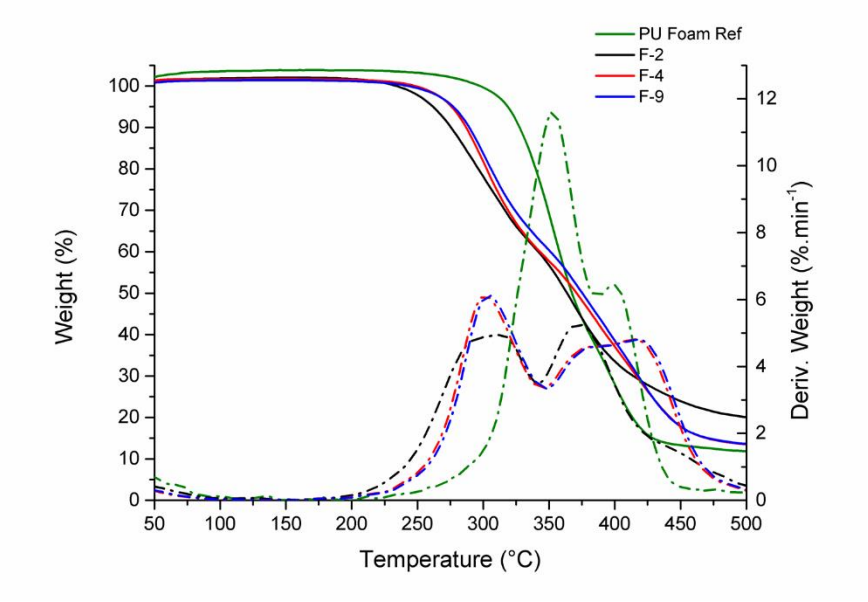


Figure III-31: TGA (solid line) and DTGA (dotted line) curves of NIPU under air

In order to determine the species released during thermal decomposition, infrared spectroscopy (TGA/IR) and mass spectrometry (TGA/MS) were performed on degradation products during TGA analysis of foams under inert gas (N_2). Figure III-32 and Figure III-33 (SI - Figure III-33 and SI - Figure III-34) show the infrared spectra respectively obtained during thermal decomposition of PU foam reference and PHU foam prepared with 80% of

TMPTC and 20% of PPOBC640 (F-9). On these spectra, we observe the appearance of an intense band around 2300 cm^{-1} around 370 °C for PU foam and around 300 °C for PHU foam. This band could correspond to elongation of N=C=O groups, suggesting a dissociation into alcohol and isocyanate. However, since this band is observed at second and third steps of degradation, it should correspond to release of CO_2. The TGA/MS analysis allowed to confirm the exact composition of volatile molecule. Figure III-34 shows the mass spectra at DTG_{max} for PU foam and PHU foam F-9. First of all, this analysis confirms the generation of CO_2 (m/z 44) during the degradation of foams. Hence, the intense band around 2300 cm^{-1} on the infrared spectra of both foams is attributed to CO_2. This production of CO_2 decreases from the second degradation step. Figure III-35 shows the evolution of CO_2 released during the degradation of PU and PHU foams from 50 to 500 °C. The maximum of CO_2 production corresponds to the same temperature of first DTG_{max}. The intensity of CO_2 production peak of PHU foams is higher than for PU foam. The production of CO_2 comes from thermal decomposition of urethane groups, therefore this analysis suggests that PHU foam contains a higher content of urethane groups in macromolecular chain than PU foams. Finally, from MS-spectra, olefin (m/z 28) and H_2O (m/z 18) are generated from the thermal degradation. Very small amount of HCN (m/z 27) and HNCO (m/z 43) from decomposition of isocyanate (first step of decomposition of urethane group Scheme III-7-A) are detected but with low intensity. They have not been shown in Figure III-34 to make it more readable. To conclude, the TGA/IR and TGA/MS analyses show that thermal decomposition mechanisms of NIPU and PU are similar.

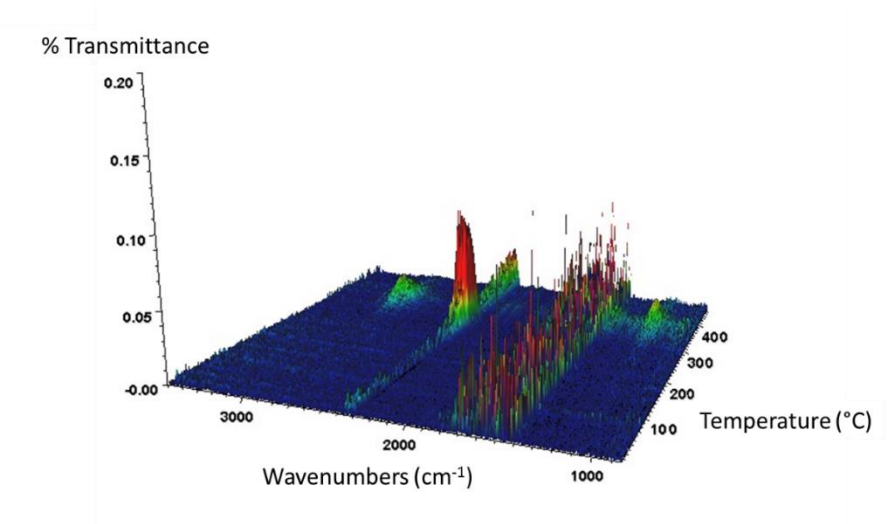


Figure III-32: Infrared spectra of thermal decomposition of PU foam reference

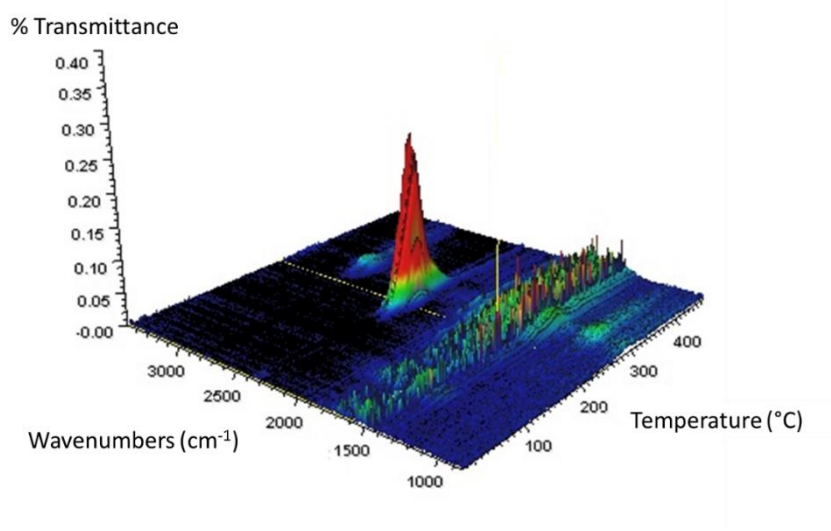


Figure III-33: Infrared spectra of thermal decomposition of PHU foam prepared with 80% of TMPTC, 20% of PPOBC640 EDR-148, Thiourea and 2% of MH 15

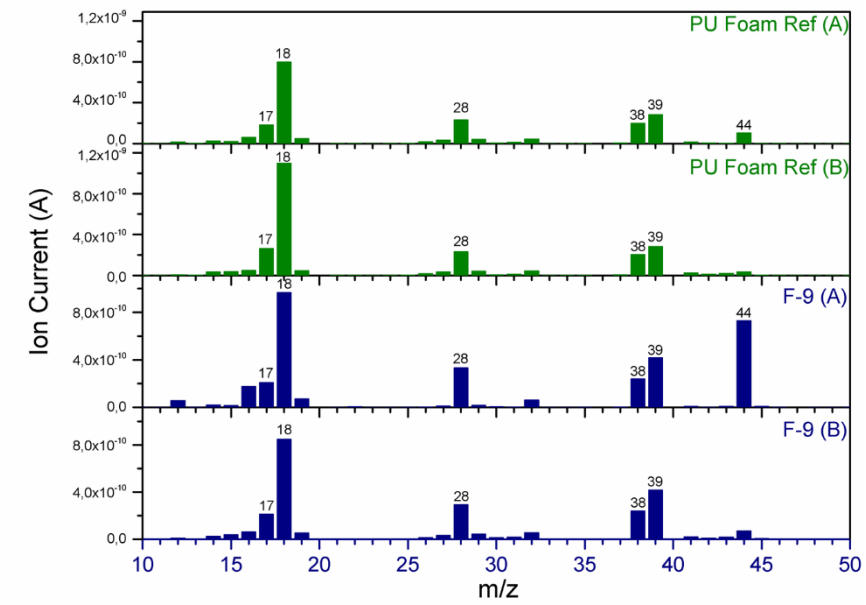


Figure III-34: MS-spectra of degradation products from PU and PHU foam (F-9) at DTGmax: (A) 1st step and (B) 2nd step

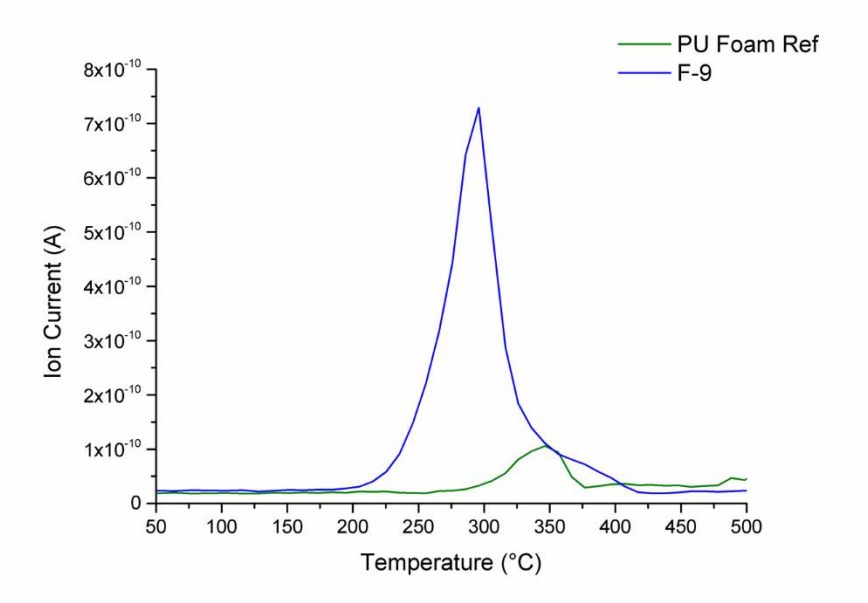


Figure III-35: MS ion current intensity curves of m/z 44 (CO_2)

Furthermore, thermal conductivity (λ) and diffusivity (D) of PHU foams were evaluated and compared to PU foam reference (Table III-12). These thermal characteristics represent the thermal insulating capacity of materials. All the PHU foams exhibit thermal conductivity values between 100 and 115 $mW.m^{-1}.K^{-1}$, which are close to the value of thermal insulation of plywood (110 $mW.m^{-1}.K^{-1}$). We observed that the PHU foams formulated with 100% TMPTC or 20% of PPOBC380 had a lower thermal conductivity whereas the foams prepared with 10 or 20% of PPOBC640 had a higher thermal conductivity. This result is related to density and therefore pore size [77]: materials with smaller cell sizes have a higher number of pores than other foams, therefore, the thermal radiation through the cells is reduced. Hence, the thermal conductivity of PHU foams of Grignard *et al.* [78] are lower (50-65 $mW.m^{-1}K^{-1}$) but the cell size of their foams is lower (3-11 μm) and cells are closed. Although the PU foam is not realistic reference as an insulation material, it is exhibits a lower thermal conductivity of 67.1 $mW.m^{-1}.K^{-1}$ despite its lower density than PHU foams. However, PHU foams exhibit interesting potentially thermal insulating capacities related to their thermal diffusivities (D). Indeed the thermal diffusivity is a physical quantity which characterizes the ability of a material to transmit a temperature signal from one point to another. Thermal diffusivities are similar for all PHU foams (0.11-0.15 $mm^2.s^{-1}$), lower than the one of PU foam reference (0.93 $mm^2.s^{-1}$). Indeed, the temperature in the PHU foams spreads more slowly than in PU foam reference. This agrees with the fact that the thermal diffusivity decreases when density increases[79].

Table III-12: Size cell, thermal conductivity and diffusivity of homogeneous PHU foams

Foam	Composition	Cell sizes (µm)	λ^1 ($mW.m^{-1}K^{-1}$)	D^2 ($mm^2.s^{-1}$)
Ref	-	350-850	67.1	0.92
F-2	TMPTC	400-700	100.4	0.15
F-5	0.9TMPTC/0.1PPOBC380	140-970	101.3	0.15
F-4	0.8TMPTC/0.2PPOBC380	470-1000	100.4	0.11
F-11	0.9TMPTC/0.1PPOBC640	310-1300	108.9	0.12
F-9	0.8TMPTC/0.2PPOBC640	430-1300	115.5	0.11

[1]: Thermal conductivity; [2]: Thermal diffusivity

IV.2.5 Thermo-mechanical characterization of PHU foams

Finally, the thermo-mechanical properties of the foams were investigated using DMA. Figure III-36 (SI - Figure III-35 - SI - Figure III-40) shows storage modulus E' and loss factor tan δ as a function of temperature for NIPU and PU foams. The transition from vitreous to elastic domain corresponds to the α transition relaxation, associated to the glass transition temperature, when the chains in the amorphous region begin to coordinate large scale motions. Temperature Tα of the α transition were determined at the maximum of the tan δ curves (Table III-10). Tα values follow the same trend than Tg determined by DSC in function of TMPTC amounts. The tan δ peak form reflects homogeneity of material: a symmetrical and narrow tan δ peak reveals a homogenous material[80]. Consequently, tan δ peak of PHU foams reveals more homogenous materials than PU foam reference. Usually, the crosslinking density ($\nu_{E'}$ determined from Equation III-19) of carbonate networks increases with the content of cross-linker (TMPTC). Hence, crosslinking density of PHU foams formulated with 100% TMPTC are respectively 1.7 and 3.9 times higher than crosslinking densities of PHU foams formulated with 10 and 20% of PPOBC640. Indeed, the structure of TMPTC presents a carbonate functionality of 2.6, which decreases the distance between urethane groups in the material, and increases the crosslinking density. This phenomenon was not observed for PHU foams prepared with 10 and 20% of PPOBC380.

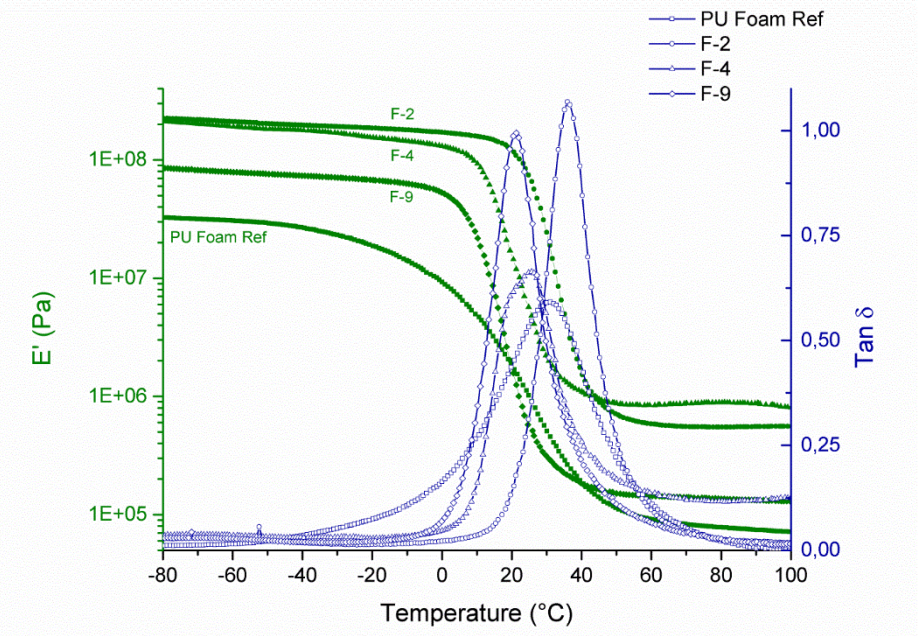


Figure III-36: DMA of PU and PHU foams

V. Conclusion

Isocyanate free polyurethane foams were successfully synthesized for the first time at room temperature by step growth polymerization of three types of five-membered cyclic carbonates (TMPTC, PPOBC380 and PPOBC640) in combination with aliphatic amine (EDR-148), Thiourea catalyst and MH 15 blowing agent. The total conversion of carbonate groups was determined by FTIR spectroscopy. These crosslinked polymer foams presented an interpenetrated-cell structure with different sizes of pores, depending on the carbonate structure and the blowing agent content. Homogeneous pore sizes were obtained with low contents of both blowing agent and PPOBC. Thermal conductivity values were slightly increased compared to a classical PU foam but the potential thermal insulation ability of PHU foams are promising due to a low thermal diffusivity. Finally, the presence of hydroxyurethane groups slightly reduced the thermal stability. Hence improvement of thermal and mechanical properties could be proposed by the modification of chemical structure of carbonate soft segments. Finally, this study allowed to demonstrate the ability to synthesize NIPU at room temperature, with quantitative conversion and for foam application, which corresponds to the major application of PU. Therefore, these NIPU path the way to a sustainable route to replace PU foams.

VI. Acknowledgement

The authors thank Momentive for supplying the blowing agent MH 15 and Huntsman for supplying EDR-148. The authors thank also Marine Blain, PhD student in our group, for the synthesis of Thiourea and Anthony Bilot, Research Engineer at Institute Charles Gerhardt, for SEM, conductivity and diffusivity characterizations. Finally, authors thank Dr Claire Longuet, Research Engineer at Ecole des Mines d'Alès and Joël Couve, Research Engineer at Institute Charles Gerhardt for the characterization of PHU foams by ATG-IR and ATG-MS.

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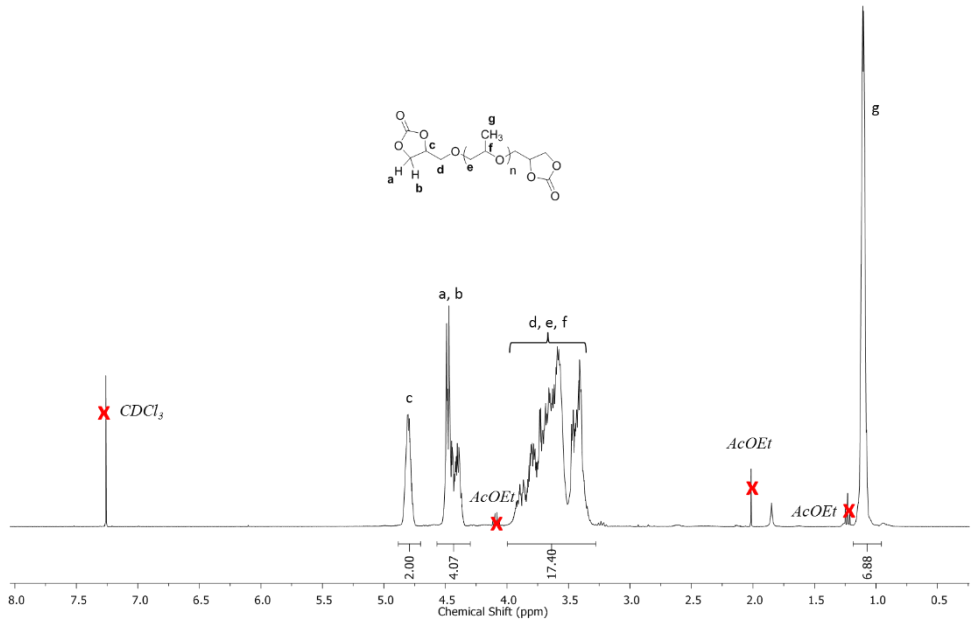
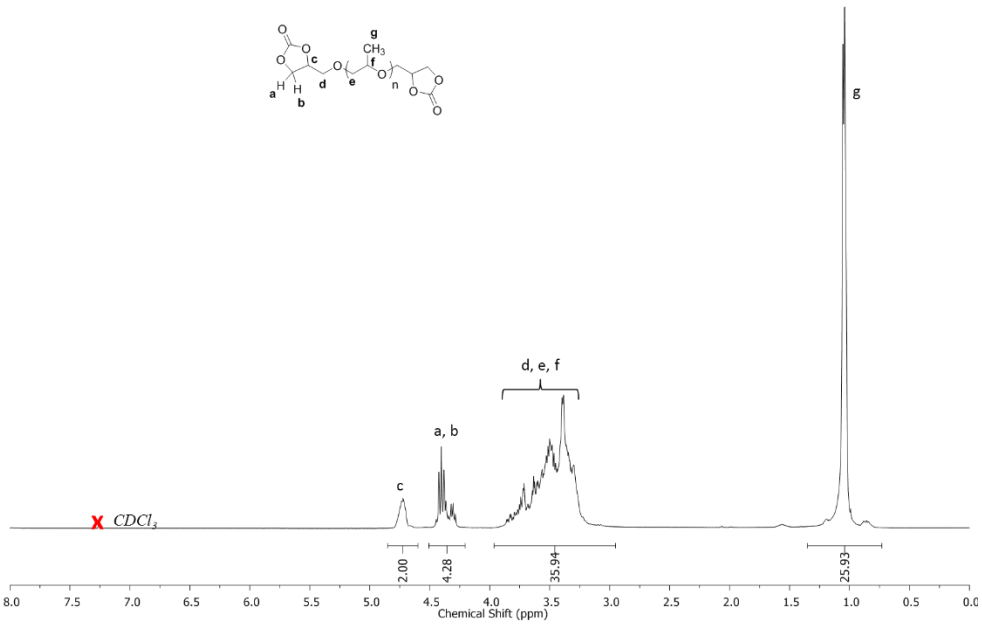
VIII. Supporting Informations

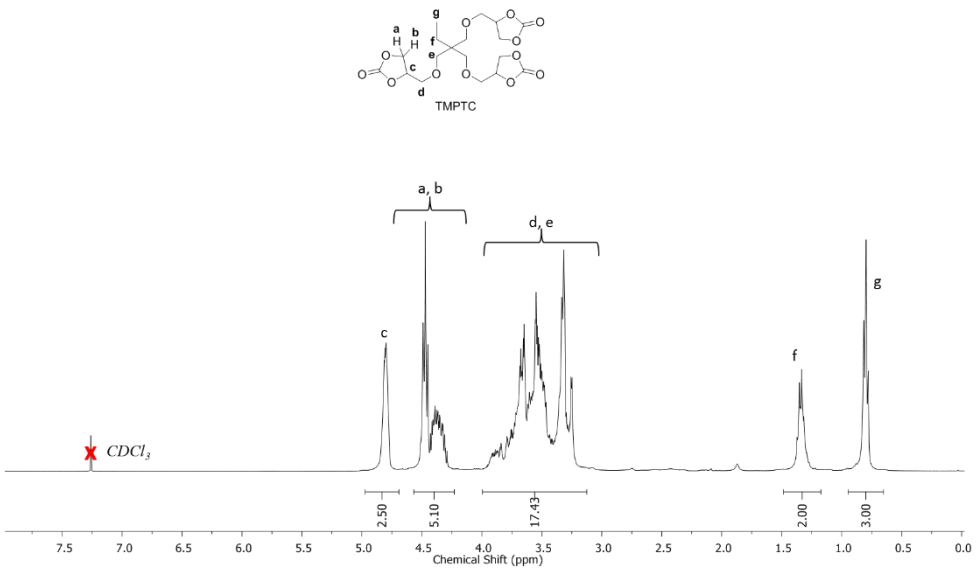
VIII.1 ^{1}H NMR spectra of raw materials



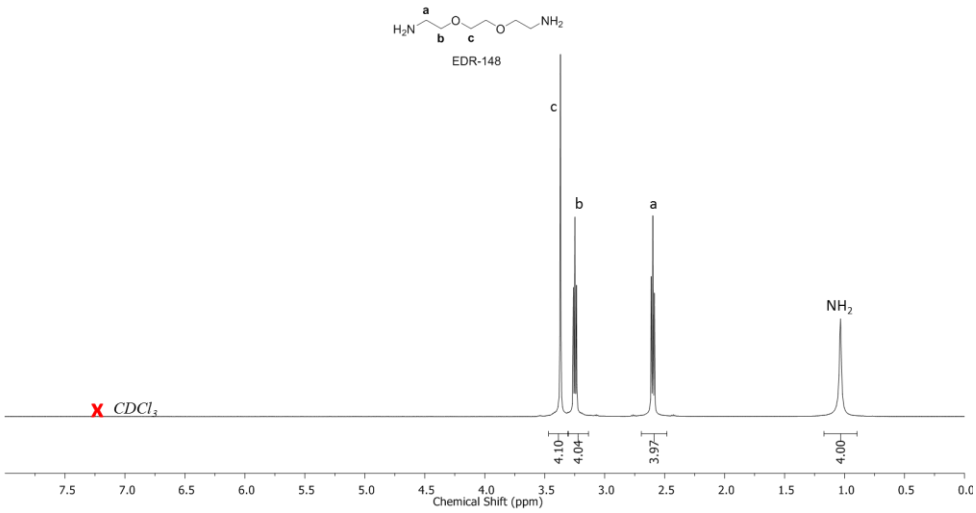
SI - Figure III-16: ^{1}H NMR spectrum of PPOBC380 in $CDCl_3$



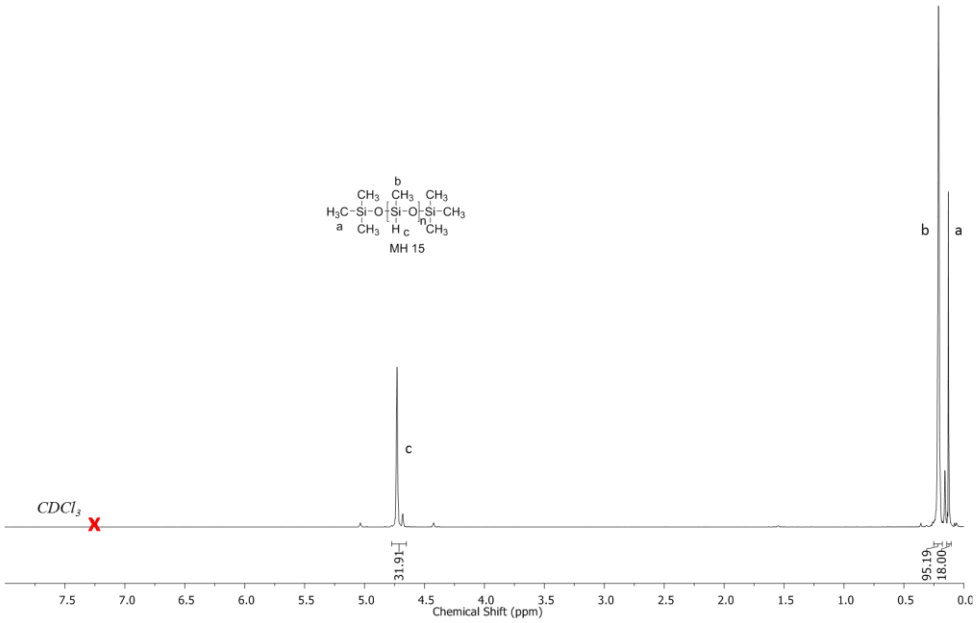
SI - Figure III-17 : ^{1}NMR spectrum of PPOBC640 in $CDCl_3$



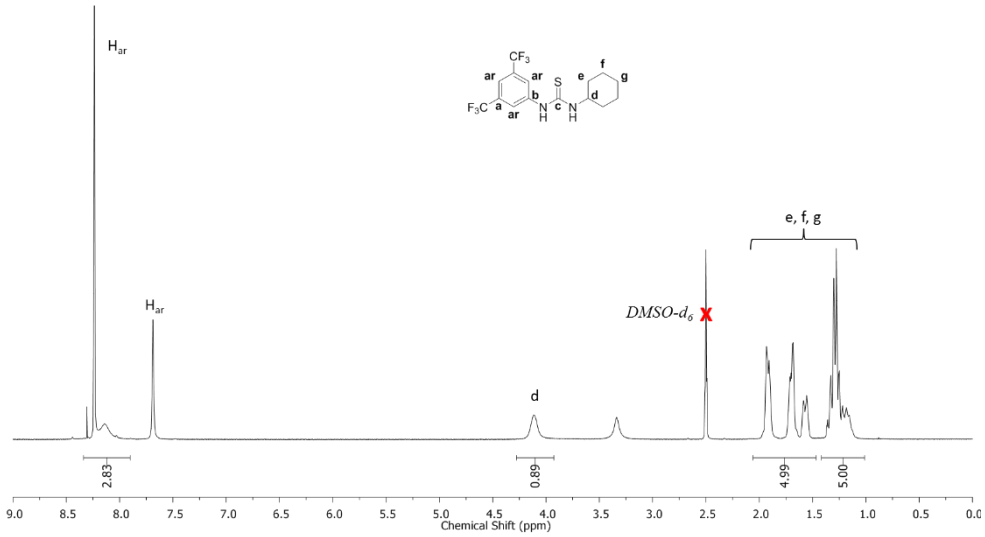
SI - Figure III-18: ^{1}H NMR spectrum of TMPTC in $CDCl_3$



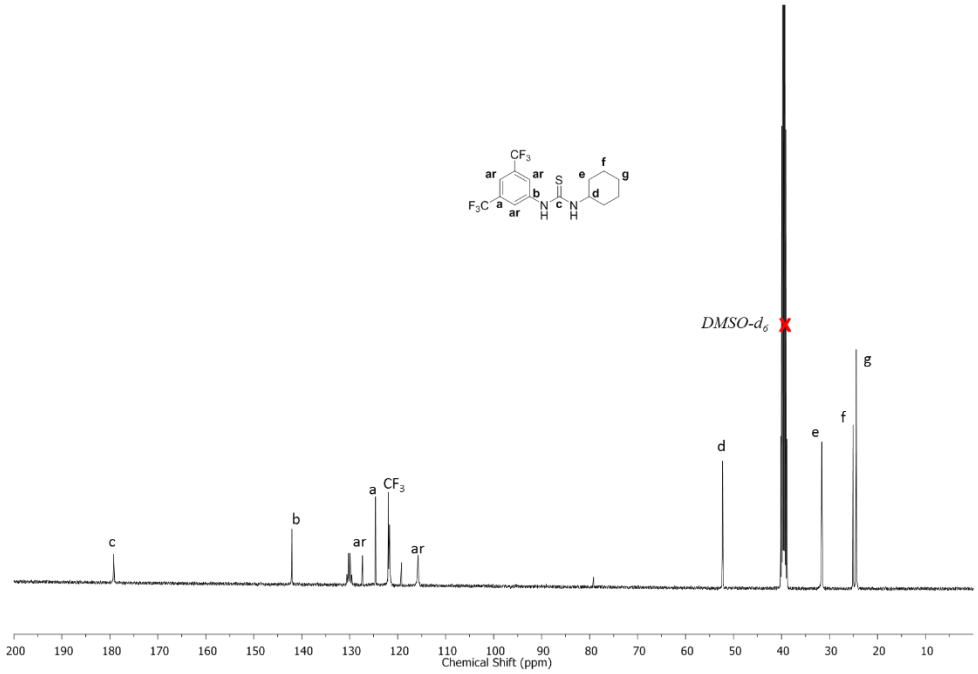
SI - Figure III-19: ^{1}H NMR spectrum of EDR-148 in $CDCl_3$



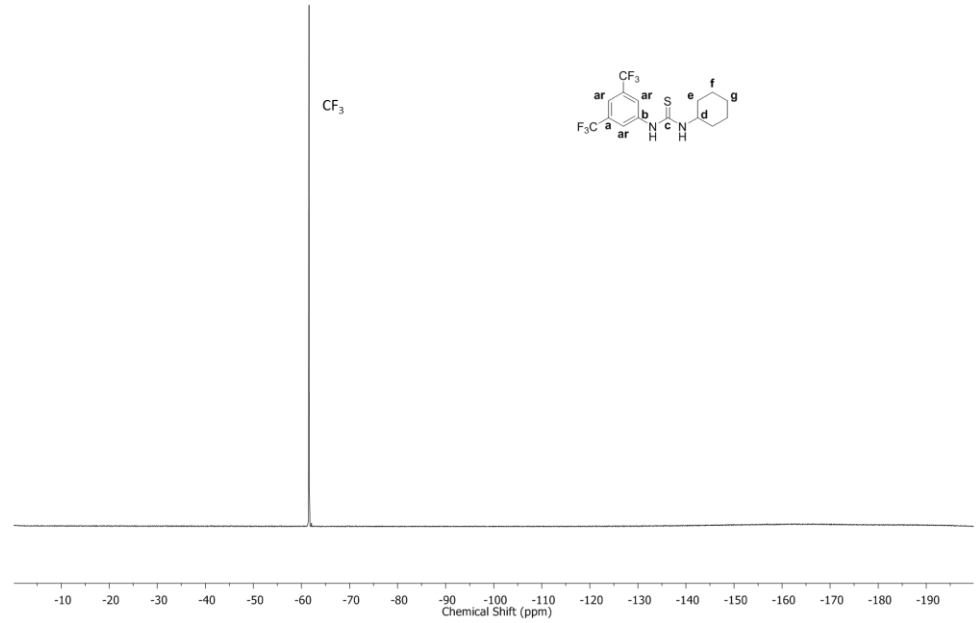
SI - Figure III-20 : ^{1}H NMR spectrum of MH 15 in $CDCl_3$



SI - Figure III-21 : ^{1}H NMR spectrum of Thiourea in DMSO-d_6

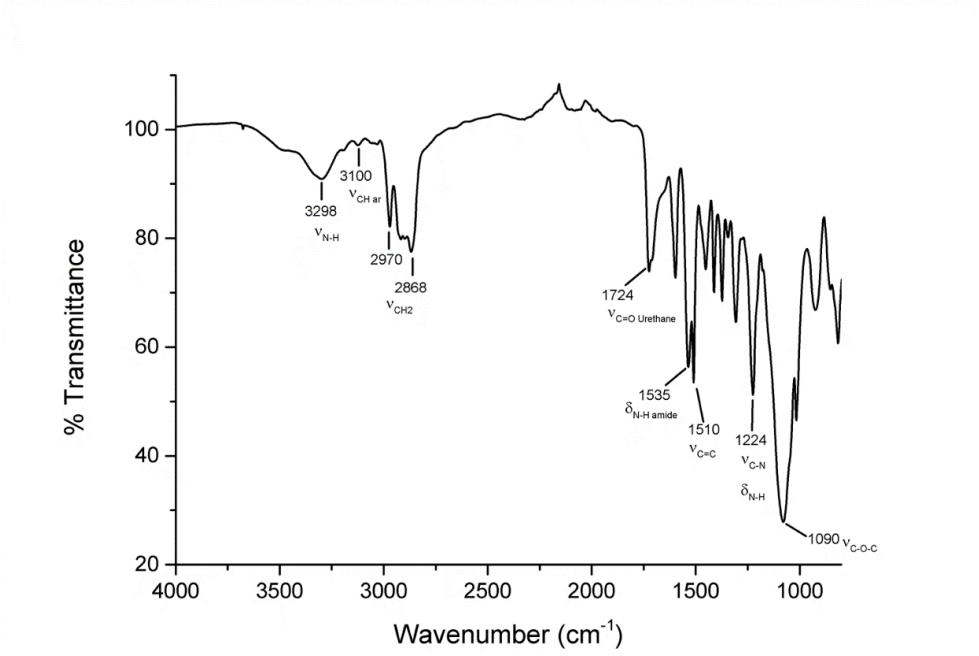


SI - Figure III-22 : ^{13}C NMR spectrum of Thiourea in DMSO-d_6

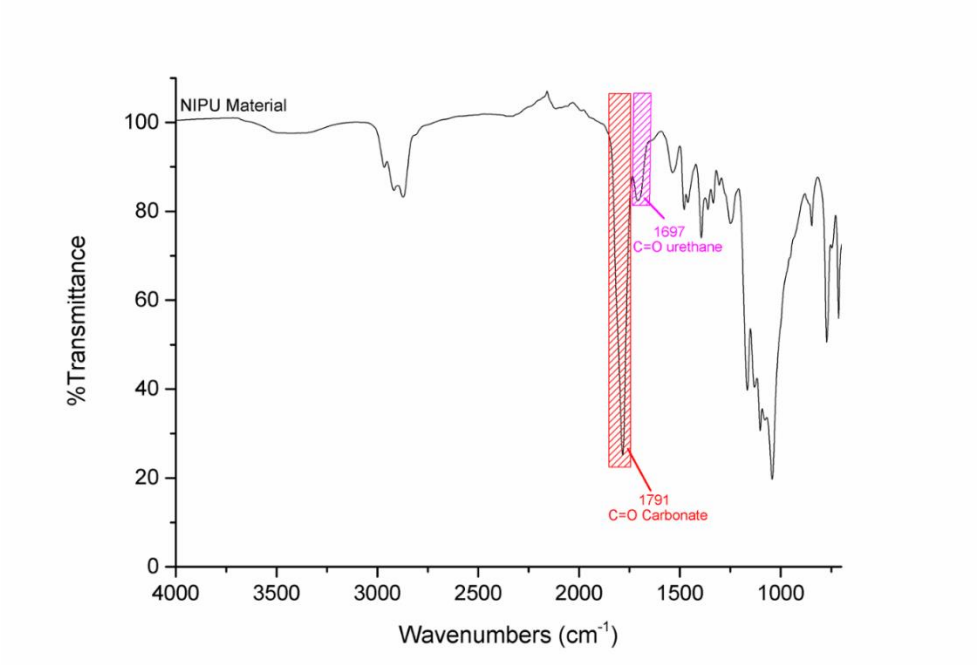


SI - Figure III-23: ^{9}F NMR Spectra of Thiourea in DMSO-d_6

VIII.2 Infrared spectra

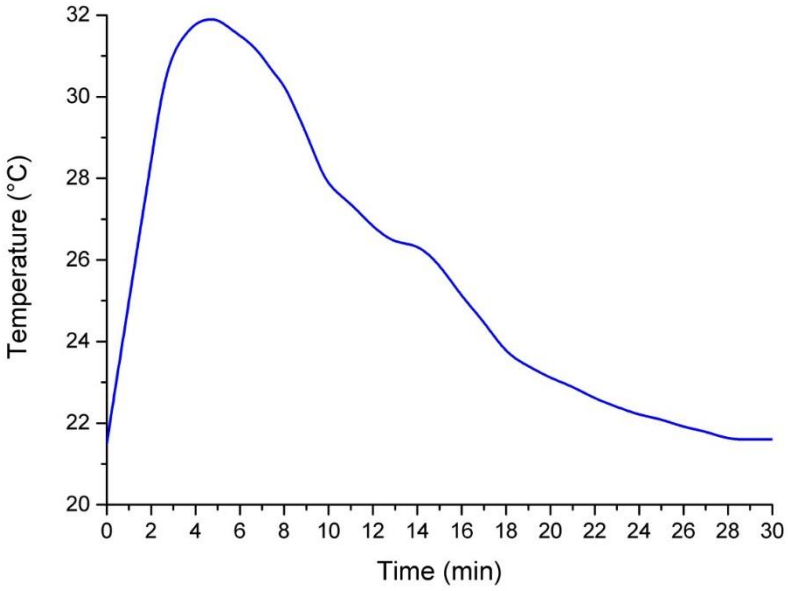


SI - Figure III-24 : Infrared spectrum of PU foam reference



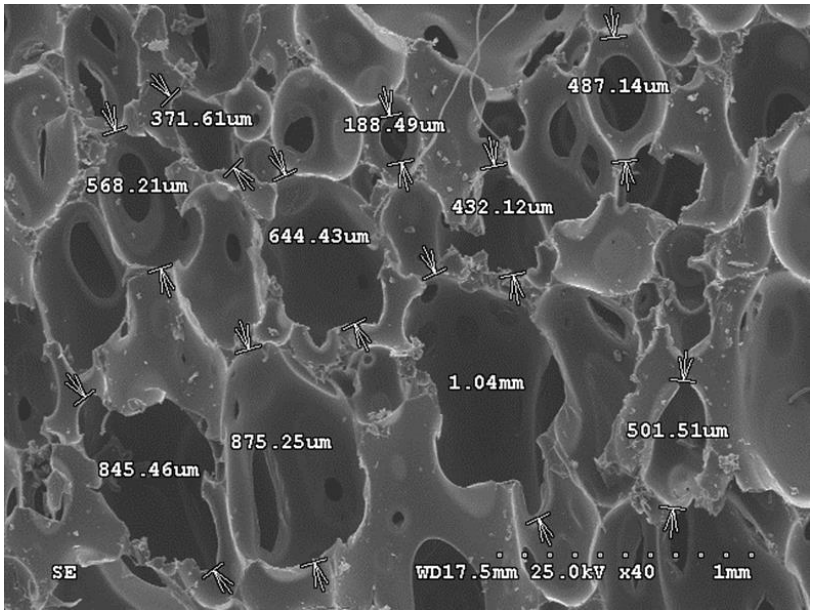
SI - Figure III-25: Infrared spectrum of NIPU material without blowing agent in same condition than the syntheses of PHU foams

VIII.3 Exothermic of reaction to produce PHU foam

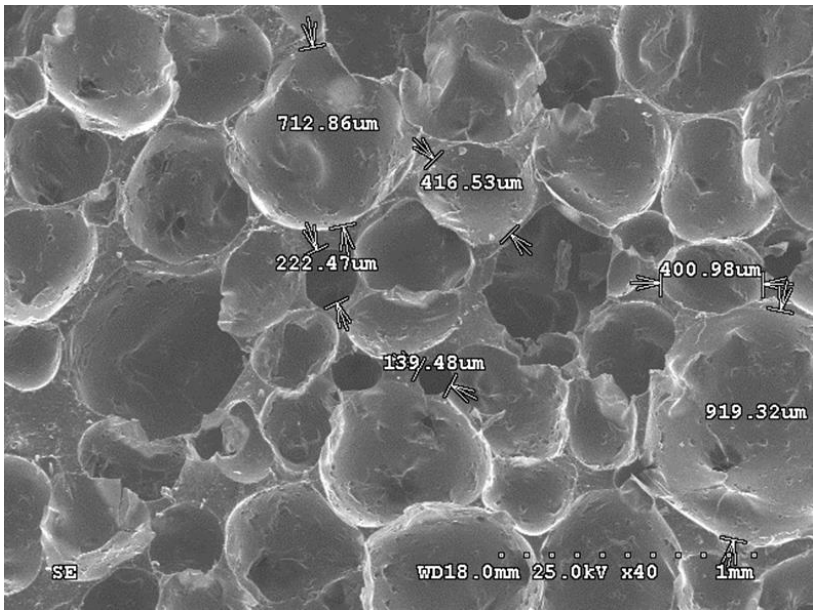


SI - Figure III-26: Exothermic of the reaction to produce F-2

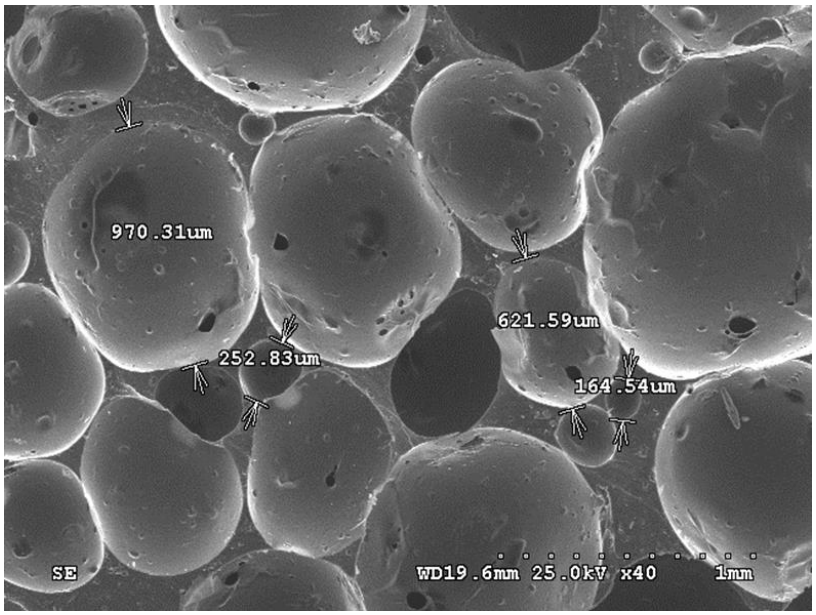
VIII.4 Scanning electron microscopy pictures of foams



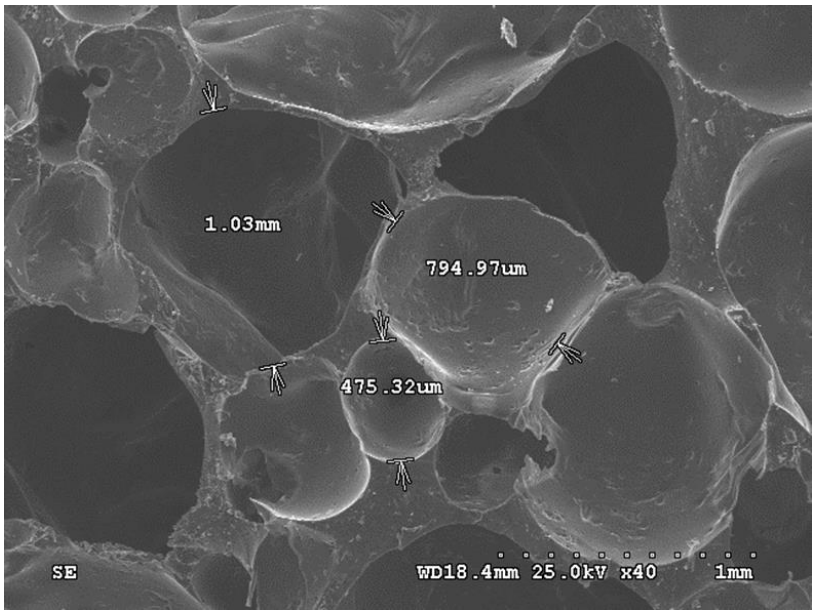
SI - Figure III-27: SEM micrograph of PU foam reference



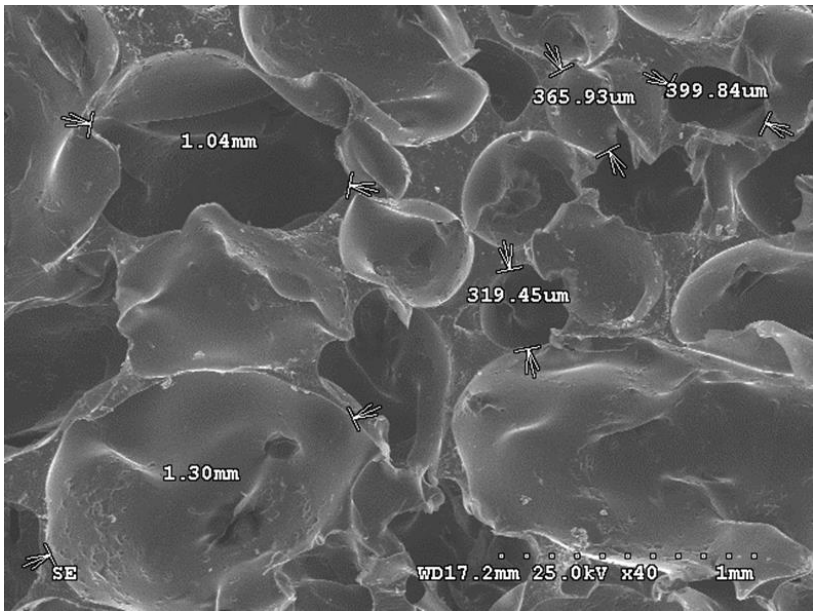
SI - Figure III-28 : SEM micrographs of PHU foam synthesized with 1.00 TMPTC / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



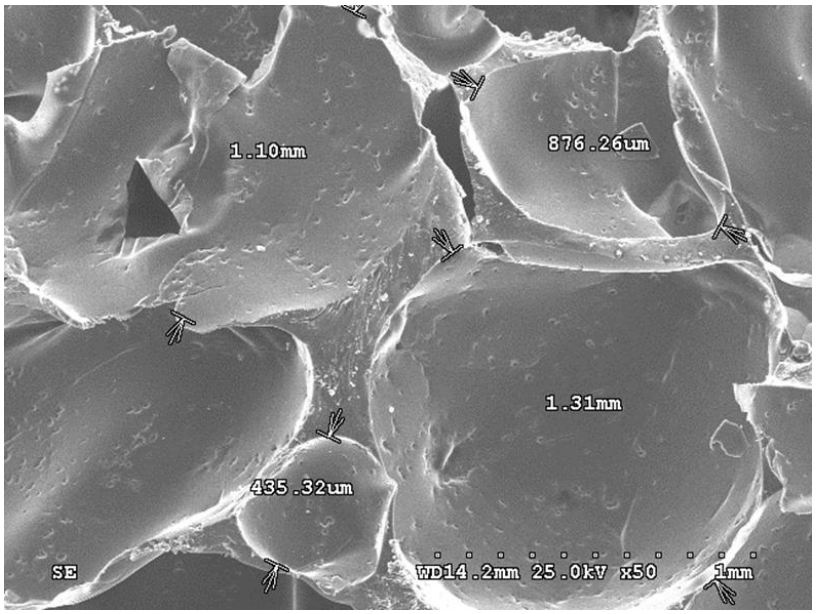
SI - Figure III-29 : SEM micrograph of PHU foam synthesized with 0.90 TMPTC / 0.10 PPOBC380 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



SI - Figure III-30: SEM micrographs of PHU foam synthesized with 0.80 TMPTC / 0.20 PPOBC380 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

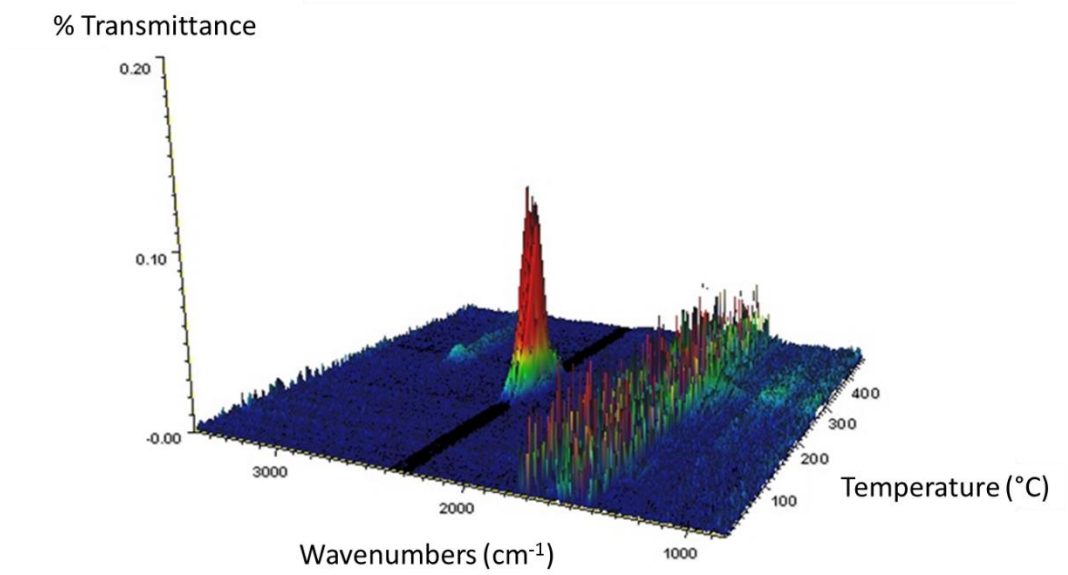


SI - Figure III-31: SEM micrograph of PHU foam synthesized with 0.90 TMPTC / 0.10 PPOBC640 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

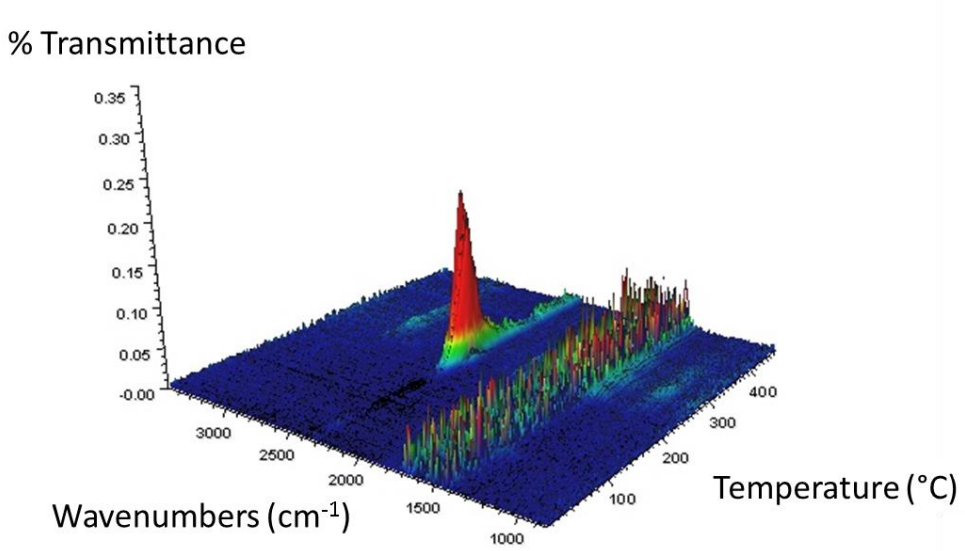


SI - Figure III-32 : SEM micrograph of PHU foam synthesized with 0.80 TMPTC / 0.20 PPOBC640 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

VIII.5 Infrared spectra of thermal decomposition during TGA of foams

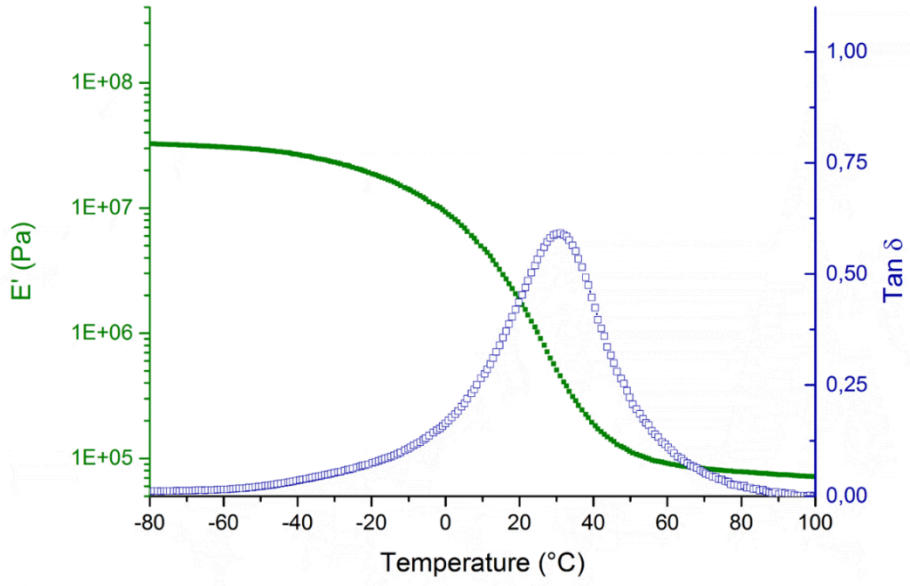


SI - Figure III-33: Infrared spectra of thermal decomposition during TGA of PHU foams prepared 1.0 TMPTC / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

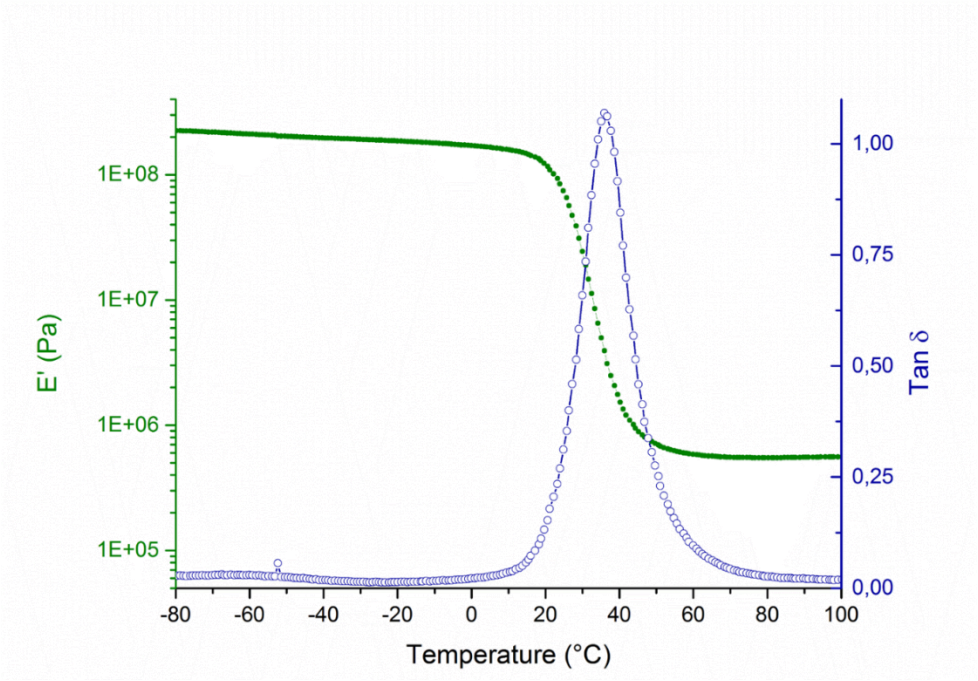


SI - Figure III-34: Infrared spectra of thermal decomposition during TGA of PHU foams prepared with 0.80 TMPTC / 0.20 PPOBC380 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

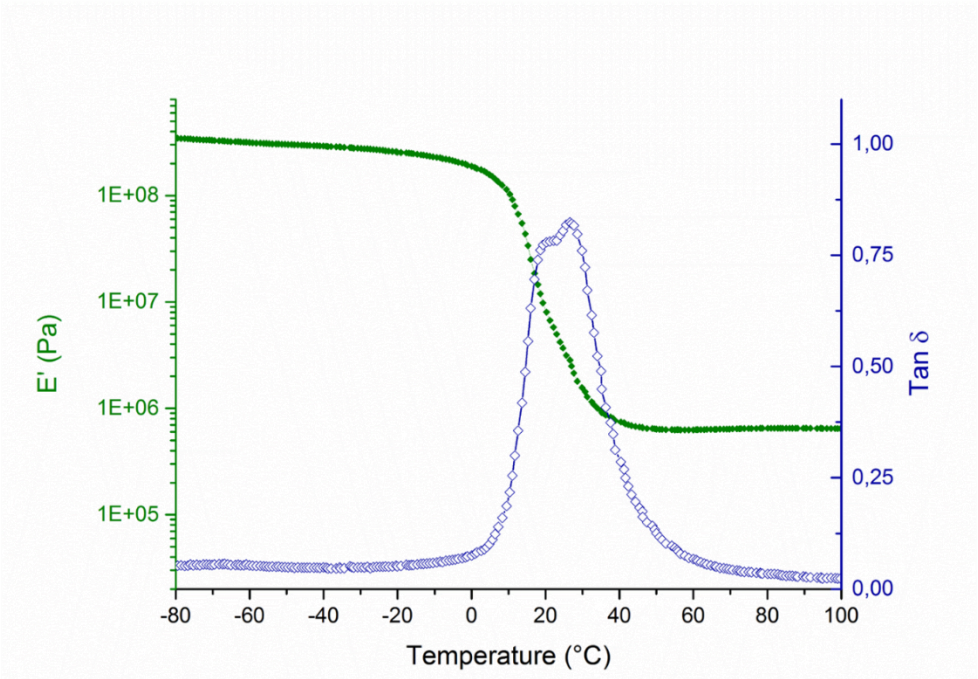
VIII.6 Dynamic mechanical analysis of foams



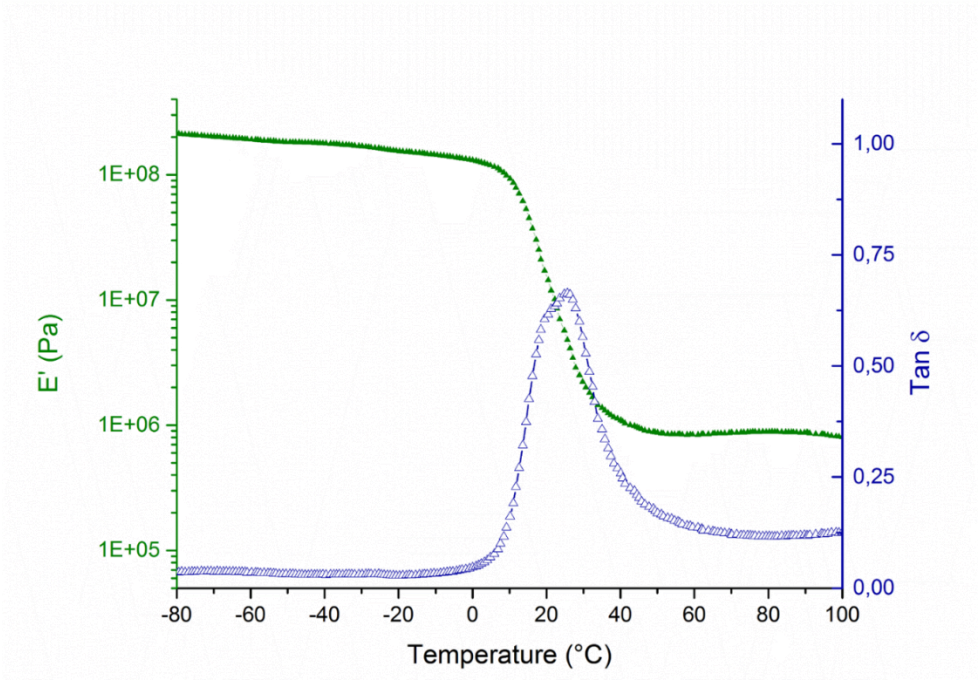
SI - Figure III-35 : DMA of PU foam reference



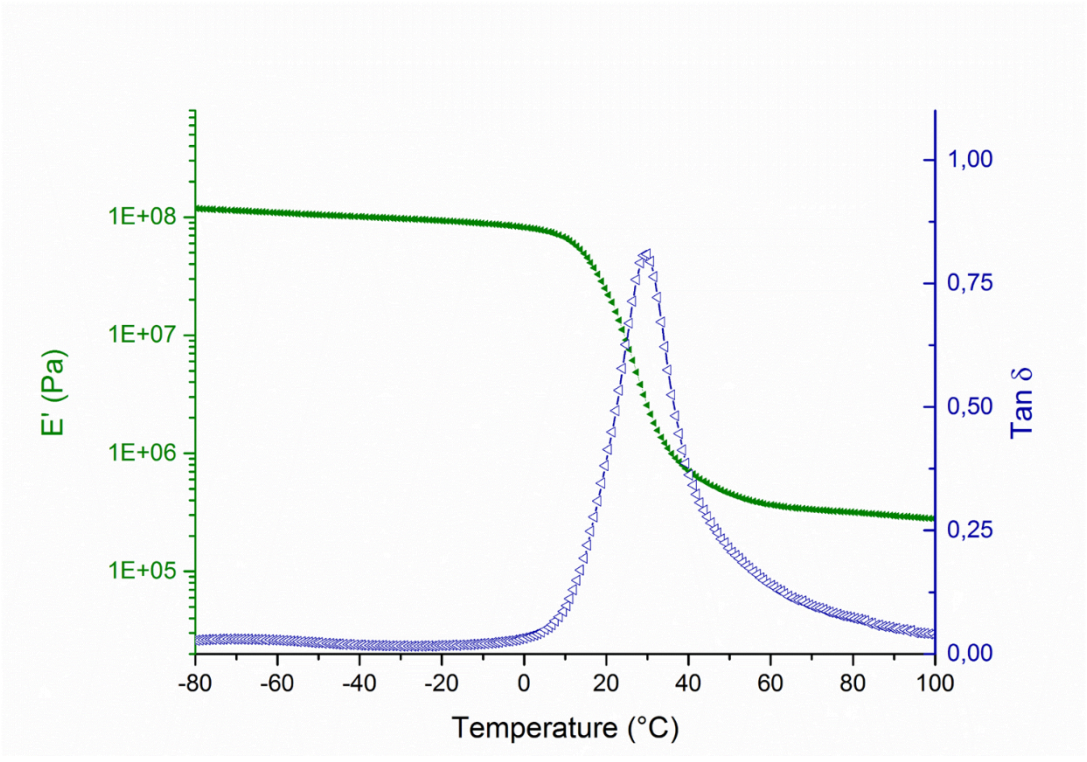
SI - Figure III-36 : DMA of PHU foam synthesized with 1.00 TMPTC / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



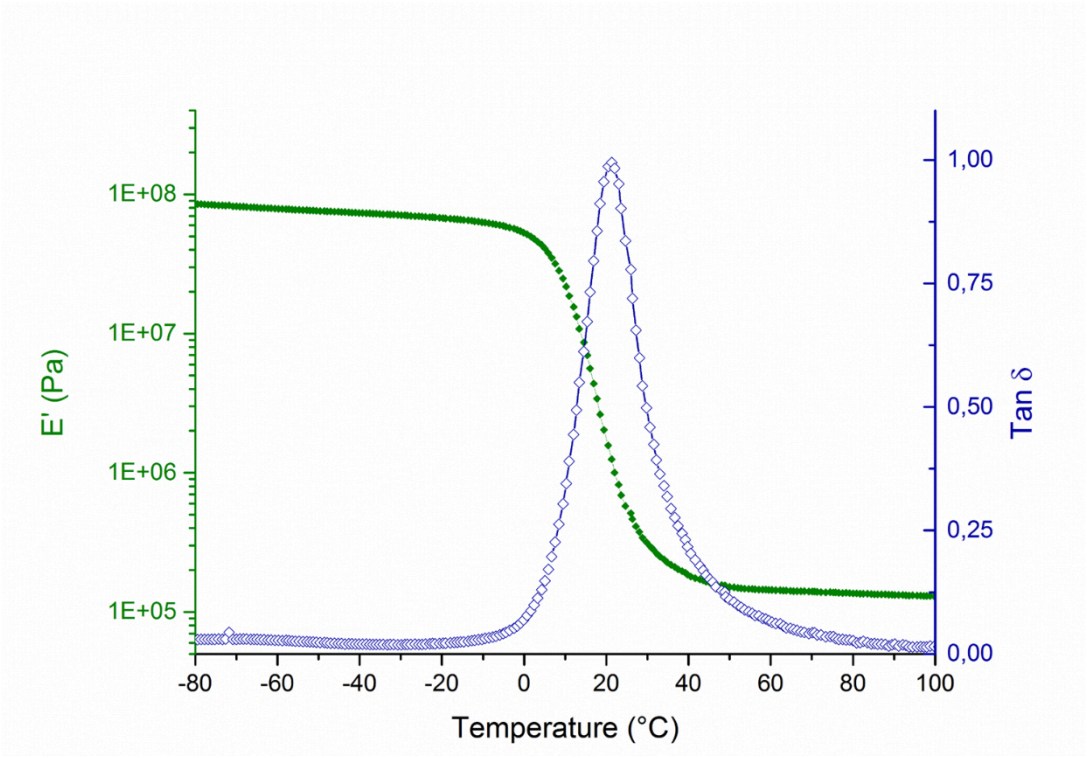
SI - Figure III-37 : DMA of PHU foam synthesized with 0.90 TMPTC / 0.10 PPOBC380 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



SI - Figure III-38: DMA of PHU foam synthesized with 0.80 TMPTC / 0.20 PPOBC380 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



SI - Figure III-39: DMA of PHU foam synthesized with 0.90 TMPTC / 0.20 PPOBC640 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15



SI - Figure III-40 : DMA of PHU foam synthesized with 0.80 TMPTC / 0.20 PPOBC640 / 1.02 EDR-148 / 0.01 Thiourea / 0.02 MH 15

Conclusion Partie 2

Ces articles scientifiques présentent la formulation de mousses flexibles polyuréthanes sans isocyanate en utilisant la voie carbonate cyclique / amine. Ces mousses PHUs sont synthétisées à partir d'un mélange de carbonates cycliques polyfonctionnels, de di-amines aliphatiques primaires, de catalyseur (TBD ou thiourée) et d'un agent moussant.

Ces études constituent une réelle innovation car il s'agit des premiers travaux qui rapportent dans la littérature la synthèse de tels matériaux. De plus, des matériaux PHUs sont pour la première fois synthétisés à température ambiante.

La possibilité de former des matériaux PHUs à température ambiante est dû à l'utilisation d'un agent moussant qui permet d'inhiber l'effet des liaisons hydrogène inter- et intra-chaînes lors de la polymérisation et d'apporter une micro-agitation aux précurseurs au cours de la polymérisation.

L'agent moussant utilisé pour expanser les matériaux PHUs est un polysiloxane. Ce dernier réagit avec l'amine en libérant un gaz. Néanmoins le gaz libéré est du dihydrogène, un gaz inflammable et peut représenter un danger pour les utilisateurs, même si les quantités libérées sont limitées. Des solutions sont envisagées et décrites dans la partie consacrée aux perspectives de ces travaux de thèse.

Conclusion Générale Chapitre III

Ce chapitre démontre l'importance des groupements hydroxyuréthane dans les propriétés mécaniques et d'adhésion des matériaux PHUs. Cependant, les procédés de formulation limitent leurs applications en comparaison aux matériaux PUs actuellement disponibles. En effet, bien qu'il existe des marchés où la réaction de réticulation s'effectue à température élevée, la plupart des applications des PUs se font à température ambiante. Or, il est démontré à travers les chapitres I, II et III de ce manuscrit l'impossibilité d'obtenir ces matériaux par la voie carbonate cyclique / amine dans de telles conditions, hormis pour les mousses. L'utilisation d'un agent moussant permet une micro-agitation des espèces réactives au cours de la polymérisation entraînant une conversion totale à température ambiante.

Par conséquent, dans le but de former des matériaux contenant le groupement hydroxyuréthane dans des conditions plus douces, une nouvelle chimie doit être utilisée. Cette dernière est décrite dans le chapitre IV de ce manuscrit de thèse.

Chapitre IV.Synthèses et Caractérisations de Matériaux H-NIPUs

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Introduction Chapitre IV

Dans ce quatrième et dernier chapitre de ce mémoire de thèse, une nouvelle approche de formulation de matériaux polyuréthanes sans isocyanate est décrite afin de pallier les limitations de la technologie des PHUs exposées dans les précédentes parties.

Cette nouvelle approche consiste à formuler des matériaux nommés H-NIPUs (Hybrid Non-Isocyanate PolyUrethane) en modifiant des matrices polymères par des groupements hydroxyuréthanes issus de la chimie carbonate cyclique / amine. Comme nous l'avons montré dans le chapitre précédent, le groupement hydroxyuréthane apporte des propriétés mécaniques intéressantes aux matériaux par l'effet des liaisons hydrogène supplémentaires dues aux groupements hydroxy formés lors de l'ouverture des carbonate cycliques.

En 2014, année du commencement de ces travaux de thèse, il existait deux procédés pour produire des matériaux H-NIPUs, tous deux initiés par le chimiste Israélien Oleg Figovsky. Le premier est fondé sur des composés époxydés partiellement carbonatés puis réticulés par des polyamines (Figure IV-1)[1-3]. La structure finale du polymère obtenu peut être classée comme un IPN (Interpenetrating Polymer Network) dans lequel les motifs hydroxyuréthanes sont enchevêtrés dans le réseau polyépoxide. Cette technologie est actuellement utilisée dans des matériaux composites pour le renforcement de fibres[4].

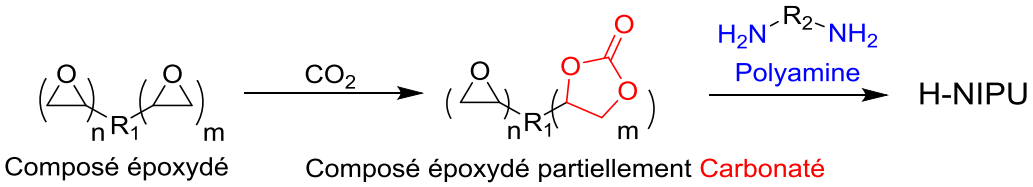

Figure IV-1: Formulation de matériaux H-NIPUs à partir de composés époxydés partiellement carbonatés

La seconde méthode est fondée sur la réticulation de HUM (HydroxyUrethane Modifiers) (Figure IV-2)[5]. Ces HUMs sont obtenus par réaction d'une di-amine avec un mono-carbonate cyclique. Ce dernier contient un groupement amino-réactif qui peut être réutilisé dans une seconde réaction avec des composés époxydés. En 2014, l'entreprise Polymate Ltd, a développé des polymères H-NIPUs à partir de cette technologie. L'entreprise décrit dans un de ses brevets [6] une réticulation à basse température de matériaux H-NIPUs contenant de longues chaines issues de la réaction époxy-amine et des unités hydroxyuréthanes pendantes (Figure IV-2). Ces matériaux hybrides sont actuellement disponibles dans le commerce sous

le nom de Green Polyurethane™ et représentent les seules applications des matériaux contenant des groupements uréthanes obtenus sans précurseurs phosgènes ou isocyanates.

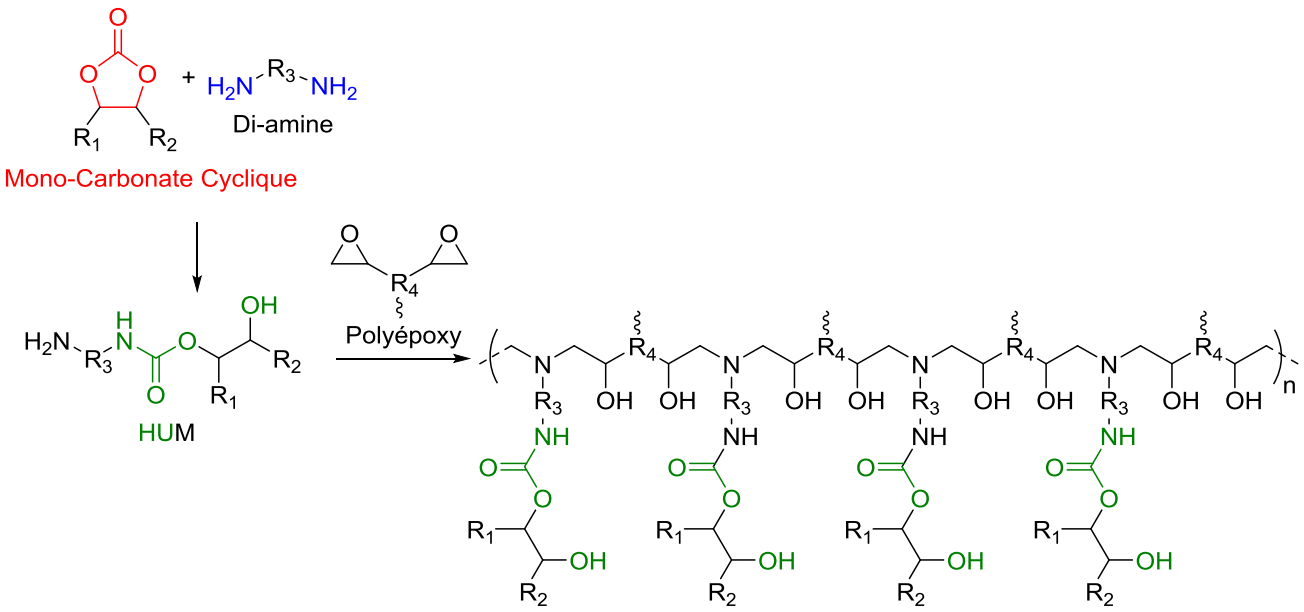

Figure IV-2: Synthèse de HUMs et formulation de matériaux H-NIPUs possédant des groupements hydroxyurethanes pendants

Au regard de ces résultats très intéressants, nous avons envisagé la synthèse de matériaux H-NIPUs sous une autre approche. Cette nouvelle voie est basée sur la réticulation de pré-polymères amino-téléchéliques contenant des groupements hydroxyuréthanes issus d'une réaction entre un bis-carbonate cyclique et un excès de di-amine. Ces prépolymères sont ensuite incorporés dans une matrice réactive, une matrice époxydée dans notre cas (Figure IV-3).

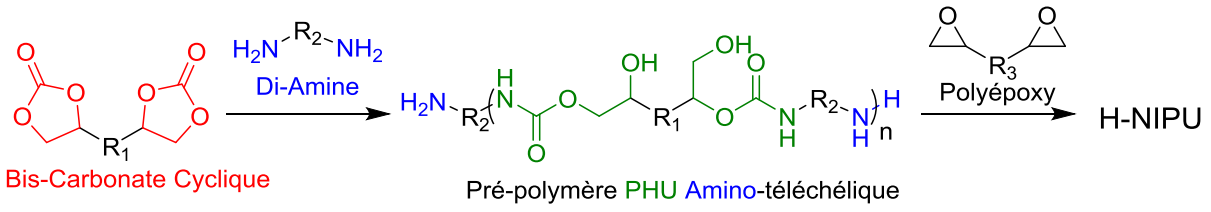

Figure IV-3: Formulation de matériaux N-NIPUs à partir de prépolymère PHU amino-téléchélique

Ces travaux novateurs sont décrits dans la suite de ce chapitre dans une publication parue dans *European Polymer Journal* en début d'année 2016.

Syntheses of epoxyurethane polymers from isocyanate free oligo-polyhydroxyurethane

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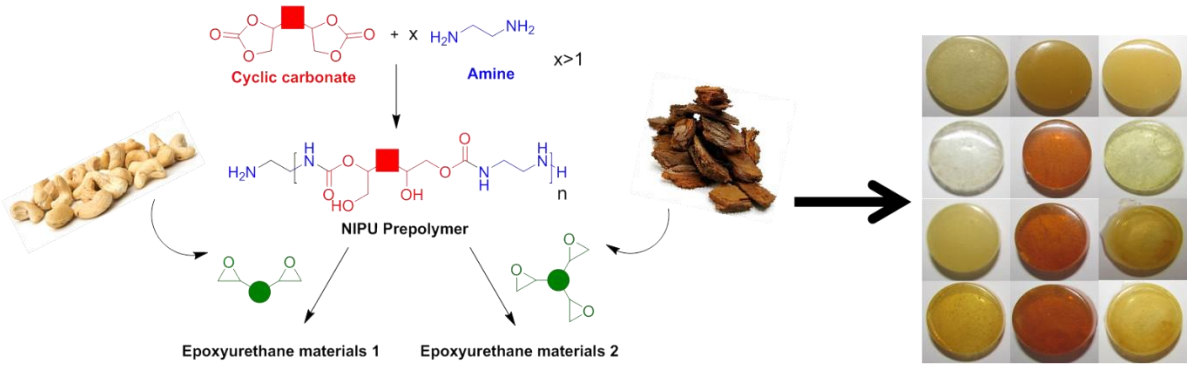
I. Abstract

H-NIPU polymers were synthesized from PolyHydroxyUrethane (PHU) prepolymers terminated amine and epoxy multifunctional. In order to ensure this, PHU prepolymers was synthesized from the reaction between α, ω-bis-cyclic-carbonates (poly(propylene)oxide bis-carbonates) and different excess of diamines (ethylenediamine) to terminate these prepolymers by amine with differents chain length. Then, these aminotelechelic PHU oligomers were re-used in formulation with multifunctional epoxy compound (Bisphenol A Diglycidyl Ether, Di-epoxydized Cardanol or Phloroglucinol Tris Epoxy) to synthesize H-NIPU polymers called also hybrid polymers. Firstly, the raw materials were analyzed in order to determine proportion stoichiometry for carbonate/amine and of hybrid materials formulations. Secondly, for the purpose to demonstrate that the reaction carbonate/amine form hydroxyurethane compound, a model study was realized. Then, syntheses and analyzes of prepolymers terminated amine by ^{1}H, ^{13}C NMR, TGA and DSC was conducted. Once these oligomers analyzed, the hybrid polymers were formulated from epoxy compounds at different temperatures to determine the best cross-linking proceed. H-NIPU polymers were characterized by ATG, DSC and measurement of their swelling index and gel content. These materials exhibited glass transition temperature between -5°C and 42°C and a thermal stability above 320°C at 30% of weight loss.



II. Introduction

Since the discovery by Otto Bayer and coworkers in 1947 of the reaction between diisocyanates and polyols, the demand of polyurethane has continued to increase and it will attain in 2016 a production of 18 million tons [7, 8]. These materials are used in a wide range of applications in everyday life: thermosets, thermoplastics, foams, elastomers, coatings, adhesives, sealants, fibers … However, nowadays, a large quantity of materials and syntheses are suspected to be responsible of negative effects on environment and human health [9-11]. It is in this context that the European regulation REACH is seriously considering the effects of the synthesis of polyurethanes[12]. Indeed, the diisocyanates necessary for the preparation of polyurethanes are harmful reactants for human health, particularly for people exposed during polyurethanes synthesis and could entail adverse health effects such as asthma, dermatitis, conjunctives and acute poisoning[9]. Actually, the two isocyanates most widely used in PU industry, ethylene diphenyl 4,4'-diisocyanate (MDI) and toluene diisocyanate (TDI), are classified as CMR (Carcinogen, Mutagen and Reprotoxic)[13].

In order to design a PU materials without isocyanate (NIPU: Non Isocyanate PolyUrethane), an interesting alternative consists mainly to use the polymerization between dicyclic carbonates and diamines. The resulting materials are called polyhydroxyurethanes (PHUs), since they contain also hydroxyl groups throughout the macromolecular chain. These hydroxyl groups create thus inter and intramolecular hydrogen bonds with urethane group which confers higher chemical and physical strength to these PHUs[14, 15]. Moreover, these PHUs exhibit also excellent thermal stability due to the absence of biurets and allophanates in the polymer chain. Additionally, studies have shown that PHUs were less sensitive to moisture than conventional polyurethanes[14, 16]. In the 1960s, Whelan *et al.*[17] and Ried *et*

al.[18] were the first researchers to pay attention to the reaction between five membered cyclic carbonates and amines. Since this date, this reaction has been tremendously studied and several methods of synthesis were described later [19-27], particularly by Endo *et al.*[28-32]. In 2015, Rokicki *et al.*[33] and Maisonneuve *et al.*[34] were published two reviews on NIPUs on their of synthesis, properties and applications. Moreover, recently Carré *et al.*[35] describes the syntheses of novel and fully biobased NIPU via a green chemistry process, without solvent and catalysts from vegetable oils.

However, this reaction has two major drawbacks: the low reactivity of carbonate / amine reaction at room temperature[32] when compared to iscocyanate/alcool and the low molar masses of PHUs obtained ($\overline{M}n$ between 1.800 and 28.000 $g.mol^{-1}$)[21, 28, 36-39]. To solve these problems, many studies in the literature have been conducted to design PHUs from more reactive cyclic-carbonates, bearing electro-withdrawing substituent [21, 23, 28, 30, 36, 37, 40-45] or by using six-membered, seven-membered or thio-cyclic carbonate[29, 32, 37, 46, 47]. But, the preparation of these compounds involves phosgene or its derivatives for six-membered carbonates or carbon disulfides for thiocarbonates, which remain harmful reactants[29, 32, 37, 39, 46, 47].

Since the thermoplastic PHUs do not exhibit high molar masses from five membered carbonate and amine, cross-linking of PHUs by curing polyfunctional carbonate with di- and polyamines can be envisaged to afford PHU thermoset rubbers. In addition to PHU networks, Figovsky *et al.* have worked on PHU/epoxy hybrid materials. Indeed, this team partially carbonated polyepoxy compounds and reacted them with amines to obtain hybrid epoxy/PHU materials[1, 2, 48-50]. These hybrid coatings are actually commercialized under the trade name *Green Polyurethane*™ and represent the first successful application of PHUs in everyday life. These hybrid polyurethanes offer several advantages with respect to conventional polyurethanes: zero volatile organic compounds, solvent-less, 30 to 50% more resistant to chemical degradation, 10 to 30% more adhesive (depending on substrate), 20% more wear resistant.

However, these hybrid materials do not solve the main issue of PHUs which is the low reactivity of reaction between cyclic carbonate and amine. This low reactivity entails uncomplete conversion which hurdles the development of PHUs.

In order to improve the kinetics of the carbonate / amine reaction, many researches have been devoted to the development of novel catalysts. Some of us and Lambeth *et al.* have shown

that the 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) and cyclohexylphenyl thiourea are the best catalysts for promoting the carbonate / amine reaction[51, 52].

We have developed another strategy to afford new hybrid PHUs with high conversion. This very innovative two-step approach consists in the first step in the synthesis of PHU prepolymers functionalized with primary amine functions that could easily react as co-monomers with various epoxy groups in a second step to yield a range of new PHUs.

These PHU prepolymers are synthesized by the reaction between bis-cyclic carbonate and diamines in excess. These amine functionalized telechelic PHU oligomers are then reacted with epoxide reactants used as chain extender to yield hybrid PHU networks. This approach provides a wide range oligomer of different molar masses in function of the amine excess in the reaction carbonate / amine. Then, owing to the epoxy reactants, we could yield hybrid PHUs with various properties. This articles present, for the first time, the synthesis of primary amine functionalized PHU prepolymers. These prepolymers are synthesized from di-carbonate derive by carbonation of poly(propylene oxide) diglycidyl ether prior to the reaction with ethylenediamine. The chain extenders used in this work were bisphenol A diglycidyl ether (BADGE) and two biobased epoxide reactants: the di-epoxy cardanol (NC-514) from Cardolite Company and the tri-epoxy phloroglucinol (PGTE) from Specific Polymers Company. Thus, one of the objectives of our study is to demonstrate the interest of PHU oligomers for the formulation of new hybrid non-isocyanate polyurethane networks.

III. Experimental Section

Materials

Poly(propylene oxide) bis-carbonate (PPOBC640) and phloroglucinol tris-epoxy (PGTE, SP-9S-5-003) were purchased from Specific Polymers (Castrie, France). Propylene carbonate, poly(propylene glyclol) diglycidyl ether ($\overline{M}n\approx380$ g.mol^{-1}, PPODGE380), lithium bromide (LiBr), ethylenediamine, bisphenol A diglycidyl ether (BADGE), dimethylformamide (DMF), ethyl acetate and toluene were purchased from Sigma Aldrich. Di-epoxydized cardanol (NC-514) was obtained from Cardolite. Deuterated solvents ($CDCl_3$ and DMSO-d_6) were purchased from Eurisotop (Saint-Aubin, France).

Nuclear Magnetic Resonance

Chemical structures of the molecules were determined by ^{1}H NMR spectroscopy using a Bruker Avance 400 MHz spectrometer equipped with a QNP z-gradient probe at room

temperature. External reference was tetramethylsilane (TMS). Shifts were given in ppm. NMR samples were prepared as follows: 10 mg of product for ^1H experiment in 0.5 mL of deuterated solvent ($CDCl_3$, DMSO-d_6).

Size Exclusion Chromatography

Sec was performed on a Varian Prostar Madol 210 equipped with a refractive index detector. Two Polar Gel-L 300 x 7.5 mm were used at 70°C with a flow rate of 0.8 $mL.MIN^{-1}$ of DMF, calibrated using PEO standards.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) were performed using a TGA Q50 (TA instrument) at a heating rate of 10 °C/min. Approximately 10 mg of sample was placed in an aluminum pan and heated from room temperature to 500°C under air atmosphere (60 $mL.min^{-1}$).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) analyses were carried out using a NETZSCH DSC200F3 calorimeter. Constant calibration was performed using indium, n-octadecane and n-octane standards. Nitrogen was used as the purge gas. 10-15 mg samples were sealed in aluminum pans. The thermal properties were analyzed at 20 °C/min in the range between -100 and 80°C to observe the glass transition temperature at the second ramp at the inflexion point and given at ±2°C.

Synthesis of hydroxyurethane model

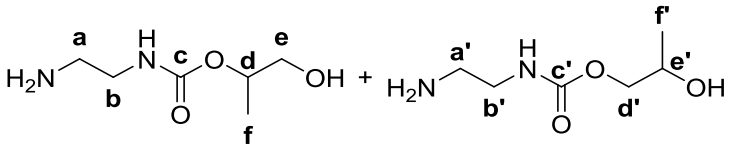


Figure IV-4: Hydroxyurethane model

In a round-bottom flask (10 mL), propylene carbonate (2g, 19.6 mmol, 1 eq) and ethylenediamine (2.35g, 39.2 mmol, 2 eq) were introduced dropwise via a syringe at 0°C. After 20 min, the reaction was allowed to proceed at room temperature for 2 h. At the end of reaction, ethylenediamine was removed by vacuum distillation to obtain the pure product as yellowish viscous liquid with 97% of yield.

^1H NMR (400.1 MHz, $CDCl_3$, ppm): δ: 1.12 (m, 6H, $H_{f\text{-}f'}$); 2.72 (t, 3.96H, $H_{a\text{-}a'}$); 2.85-3.05 (m and s; 4.44H, $H_{b\text{-}b'}$ and NH_2); 3.40-3.50 (m, 1.23H, H_e); 3.50-3.57 (dd, 1.02, $H_{d'}$); 3.76-3.85

(m, 0.78H, H_d); 3.86-3.94 (m, 0.95H, $H_{e'}$); 3.94-4.02 (dd, 0.96H, $H_{d'}$), 4.72-7.83 (dd, 1.21H, H_d); 5.88-6.31 (4m, NH and OH).

^{13}C NMR (400.1 MHz, $CDCl_3$, ppm): δ: 16.55 (s, C_f); 19.21 (s, $C_{f'}$); 40.73-44.33 (2dd, $H_{a\text{-}a'}$, $H_{b\text{-}b'}$); 65.01-65.43 (2s, $H_{e\text{-}e'}$); 70.03 (s, H_d); 72.19 (s, $H_{d'}$); 157.14-157.35 (2s, $H_{c\text{-}c'}$)

Synthesis of PPOBC380

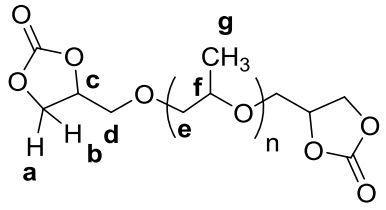


Figure IV-5: PPOBC380 idealized structure

In a round-bottom flask (500 mL), poly(propylene oxide) diglycidyl ether (PPODGE380) (20 g, 52.6 mmol) and LiBr (2.6 mmol, 5 mol %) were dissolved in DMF (100 mL). The solution was introduced onto a reactor and the atmosphere was replaced with CO_2 (P=15 bar). The solution was then allowed to stand at 80°C with continuous stirring for 36 h. DMF was removed by distillation under vacuum (70°C, P= 10 mbar). The pure product PPOBC380 was obtained quantitatively as brown oil with 76% of yield.

^1H NMR (400.1 MHz, CDC_3, ppm): δ: 1.06 (m, 22H, Hg); 3.24-3.90 (m, 32H, H_d, H_e, H_f); 4.28 (m, 2H, H_c); 4.52 (m, 2H, H_a); 4.91 (m, 2H, H_b).

Titration of the cyclic-carbonates PPOBC380 and -640 by ^1H NMR

A specified amount of PPOBC (around 50 mg) and a standard solution of DMSO with toluene (52.8 mg of toluene dissolved in 10 mL of DMSO-d_6) were weighed into an NMR tube. Once the ^1H NMR acquisition was completed, characteristics peaks of carbonate a, b and c (4.51, 4.27 and 4.88 ppm respectively) and CH3 (2.29 ppm) of toluene were integrated (Figure IV-6). The integration of CH_3 of toluene was fixed to 300. Carbonate equivalent weights (CEW) of PPOBC380 and -640 were calculated according to Equation IV-1, where m_{PPOBC} – mass of PPOBC introduced into the NMR tube, $n_{function\ of\ carbonate}$ – amount of function carbonate in PPOBC, I_a, I_b, I_c –integrations of characteristics peaks a, b and c of carbonate, $n_{toluene}$ – molar amount of toluene introduced in standard solution, I_{CH3} – integration of peak CH_3 of toluene. The CEW values for each carbonate were obtained in quadruplicate determinations. Moreover, the numbers of repetition (n) of each carbonate compound were calculated according to Equation IV-2.

Equation IV-1 $$CEW = \frac{m_{PPOBC640}}{n_{function\ of\ carbonate}} = \frac{m_{PPOBC640} \times I_{CH3}}{(I_a + I_b + I_c) \times n_{toluene}}$$

Equation IV-2 $$n = \frac{1}{3} \frac{I_d}{\frac{I_a + I_b + I_c}{6}}$$

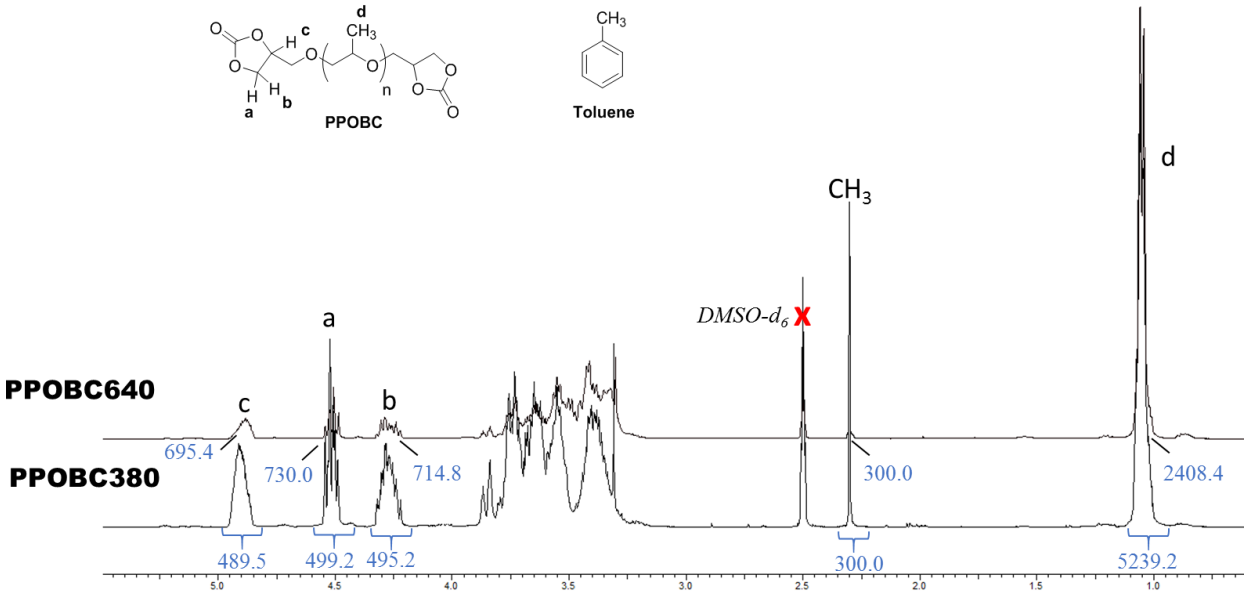


Figure IV-6: ^{1}H NMR spectra of PPOBC with standard solution for titration of cyclic-carbonate in DMSO-d_6

Titration epoxy compounds (BADGE, NC-514 and PGTE) by ^{1}H NMR

In order to calculated Epoxy Equivalent Weight (EEW) of epoxy compounds (BADGE, NC-514 and PGTE), the same method that the determination of CEW of PPOBC380 and -640 was used. However, a, b and c, the characteristics peaks of epoxy, were situated at 2.81, 3.30, and 2.69 ppm respectively for BADGE, NC-514 and PGTE.

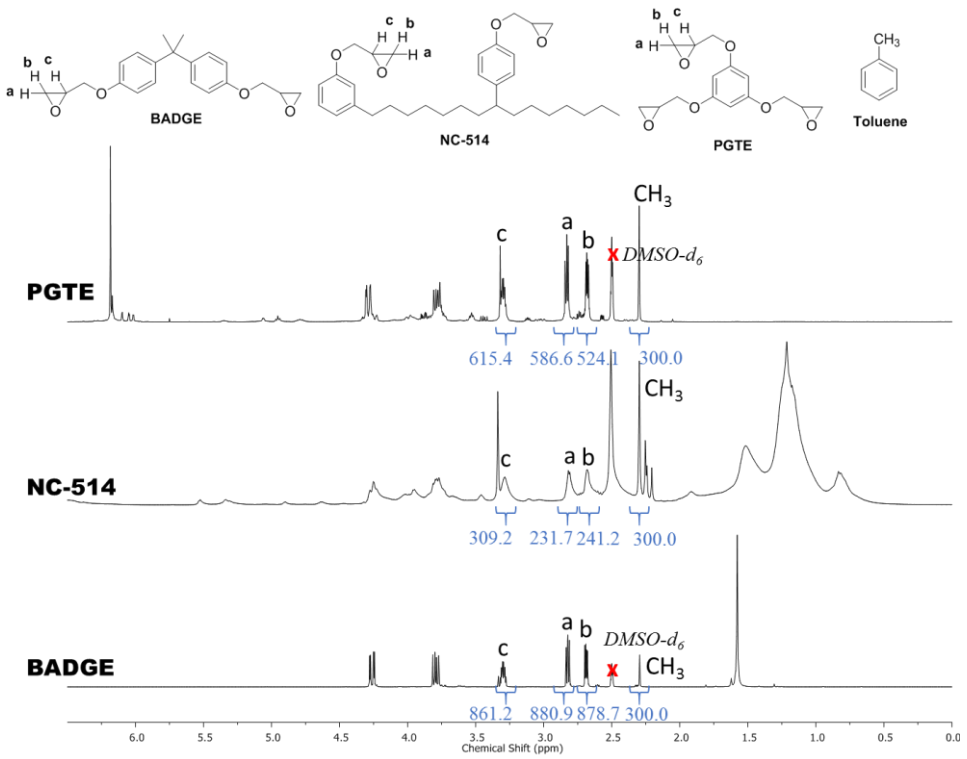


Figure IV-7: ^{1}H NMR spectra of BADGE, NC-514 and PGTE with standard solution for titration of epoxy in DMSO-d_6

Syntheses of PHU prepolymers

The formulations of PHU prepolymers were calculated with Equation IV-3 and Equation IV-4 from 10 g of PPOBC380 or -640 and different molar ratio of ethylenediamine (r=2, 3.3 or 6.5). The number of active hydrogen of ethylenediamine was fixed at 2 for carbonate/amine reaction. The reactions carbonate/amine were carried out without solvent. Once the additions carbonate/amine were performed, the mixtures were stirred during 4 hours at 60°C. At the end of the reaction, ethylenediamine was removed by distillation under vacuum. The pure PHU prepolymers were obtained quantitatively as yellowish viscous liquid with 97% of yield.

Syntheses of hybrid materials

The formulations of hybrid materials were realized from 1 g of epoxy (BADGE, NC-514 and PGTE). The quantities of PHU prepolymers were calculated from Equation IV-3 and Equation IV-4 with 4 actives hydrogens in the case of epoxy/amine reaction.

The reactions PHU prepolymers/BADGE were carried out without solvent. Once the additions PHU prepolymers/BADGE were performed, the mixture were stirred during 3 minutes then poured into an aluminum mold and cross-linked at room temperature, 50°C or 100°C.

Equation IV-3 $$m_{ethylenediamine\ or\ PHU\ prepolymer} = r\ \frac{AHEW}{CEW\ or\ EEW} \times m_{Carbonate\ or\ Epoxy}$$

Equation IV-4 $$AHEW = \frac{M_{ethylediamine\ or\ PHU\ prepolymer}}{Number\ of\ Active\ Hydrogen}$$

Swelling Index and gel content

Swelling index: three samples (30mg each) were separately put into 30 mL THF for 24 h. The swelling index, SI, is given by Equation IV-5, where m_0 is initial mass of tab and m_1 is mass of tab after swelling in solvent.

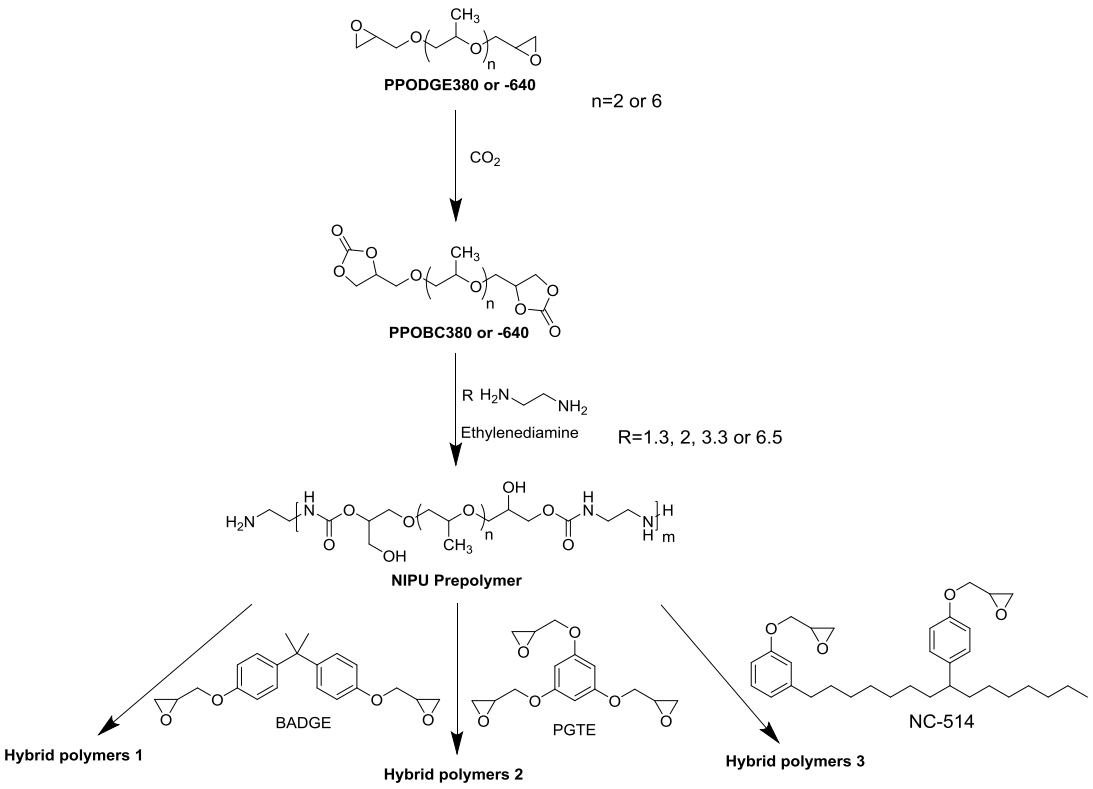
Equation IV-5 $$SI = \frac{m_1 - m_0}{m_0} \times 100$$

Gel content: After SI measurement, the three tabs are dried in a ventilated oven at 50°C during 24 h. The gel content GC is given by following Equation IV-6, where m_0 is initial mass of tab and m_2 is mass of tab after drying.

Equation IV-6 $$GC = \frac{m_2}{m_0} \times 100$$

III. Results and Discussion

The syntheses of various hybrid polymers from PHU prepolymers and epoxy extenders are summarized in Scheme IV-1. Firstly, cyclic carbonate oligomers (PPOBC380 and -640) are obtained by direct carbonation of corresponding epoxy oligomers (PPODGE380 and -640) in an autoclave. Then, PHU oligomers are synthetized by reaction of cyclic carbonate oligomers with different excess of ethylenediamine to functionalize the PHU prepolymers with primary amines. In order to purify PHU prepolymers, ethylenediamine was removed by distillation under vacuum. Eventually, hybrid polymers were obtained by polyaddition between PHU prepolymers and epoxy reactants such as bisphenol A diglycidyl ether (BADGE), di-epoxidized cardanol (NC-514) and phloroglucinol tris-epoxy (PGTE). The main advantage of this new route is the ability to synthesize a structured polymer with soft segments, from PHU oligomers, and hard segments, from epoxy (aromatic rings of BADGE and PGTE), as for classical PUs. However, before the synthesis of PHU oligomers, a model study was performed from propylene carbonate and ethylenediamine in order to determine the reaction conditions for the functionalization of PHUs with primary amines. Actually, the functionality of the prepolymers is crucial for the second reaction of cross-linking with epoxy reactants.



Scheme IV-1: General scheme of synthesis of hybrid materials

III.1 Model study

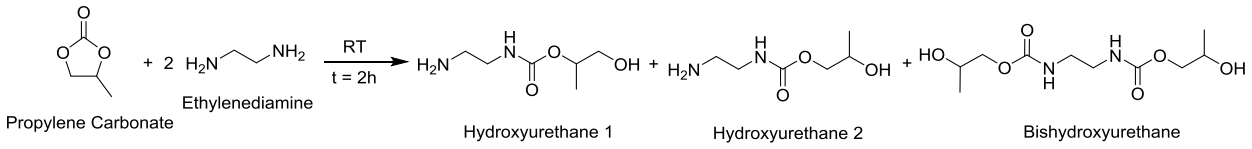
In order to determine the reaction conditions and enable the characterization of PHU oligomers, a model study was performed. Model study was performed on the synthesis of model hydroxurethane from propylene carbonate and ethylenediamine (Scheme IV-2).

The reaction was realized at room temperature without solvent and catalyst during two hours. This reaction was monitored by ^{1}H and ^{13}C NMR (Figure IV-8 and Figure IV-9). At the end of reaction, ^{1}H NMR spectrum of synthesized product showed the total disappearance of the characteristic peaks of carbonate protons at 4.73, 4.43 and 3.90 ppm (SI - Figure IV-1 and Figure IV-8). Moreover, peaks of protons b and b' at 2.5 ppm which integrate for 3.79 protons, characteristics of protons CH_2 at α of carbamate group were observed in the ^{1}H NMR spectrum. According to the opening direction of the carbonate group with the amine, two hydroxyurethane compounds were created. These two compounds correspond both to hydroxyurethanes of primary (Hydroxyurethane 1) and secondary alcohol (Hydroxyurethane 2). Indeed, on the ^{1}H spectrum of purified hydroxyurethane (Figure IV-8-B), we observe both signals of protons e and e' integrating for 1.21 and 1.98 protons respectively, characteristic of CH or CH_2 in α position of hydroxyl group. This formation of two hydroxyurethane compounds was confirmed by ^{13}C NMR spectrum (Figure IV-9). Indeed, characteristic signal

of carbonyl group of urethane at 157 ppm is split into two peaks, corresponding to carbons c and c', thus proving the formation of the two hydroxyurethane compounds, corresponding respectively to primary or secondary alcohol. Moreover, ^{13}C NMR spectrum (Figure IV-9) shows clearly the duplication of d', e, e', f and f' peaks. This confirms the formation of a bishydroxyurethane, resulting from di-addition of ethylenediamine on propylene carbonate (Scheme IV-2).

In order to remove residual ethyleneamine at the end of reaction, a volatile amine should be preferred. Therefore we used ethylenediamine in this study since this amine has a high vapor pressure (12.4 mbar at 20°C, 66.3 mbar at 50°C). This characteristic allowed easily to remove the amine excess by vacuum distillation at the end of the hydroxyurethane synthesis. Moreover, extracted ethylenediamine can be recycled for further functionalization reactions. Figure IV-8 describes the formation of hydroxyurethane with overlaying ^{1}H spectra of crude product (Figure IV-8-A) and purified product (Figure IV-8-B). After distillation under vacuum at 80°C, ethylenediamine was completely removed and the hydroxyurethane product was purified.

This model study proved that the carbonate/amine reaction was quantitative and the product is functionalized with two primary amines and traces of bishydroxyurethane. This reaction will then be transposed to cyclic carbonate oligomers to yield PHU oligomers with the same purification method.



Scheme IV-2: Synthesis of urethane model from propylene carbonate and ethylenediamine

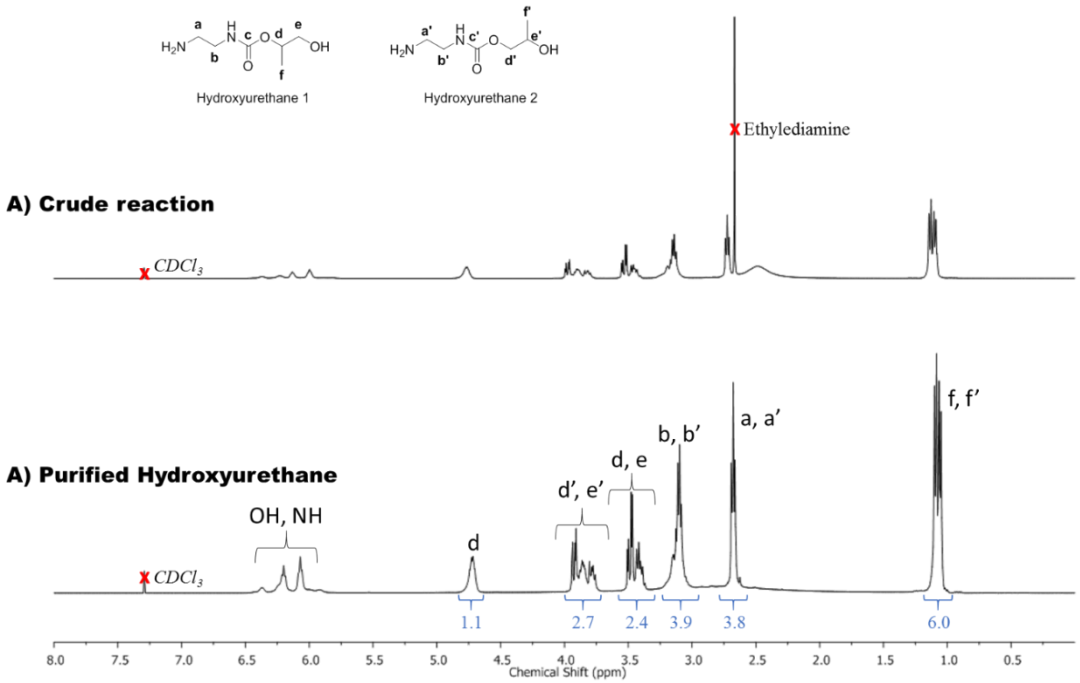


Figure IV-8: ^{1}H NMR spectra evolution for the synthesis of hydroxyurethane model in $CDCl_3$

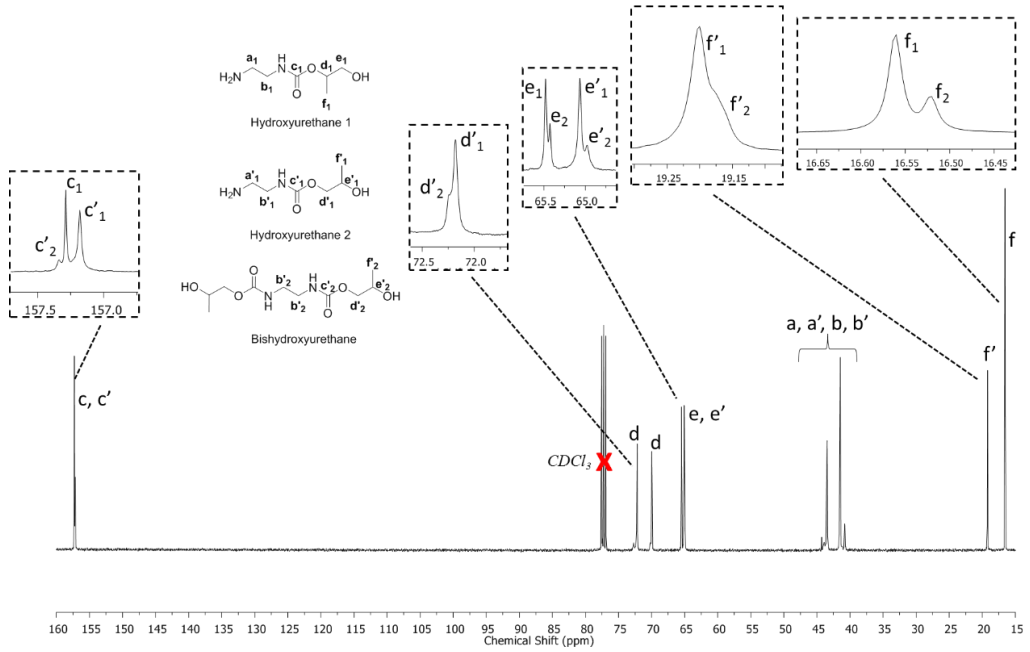


Figure IV-9: 13C NMR spectrum of hydroxyurethane model in $CDCl_3$

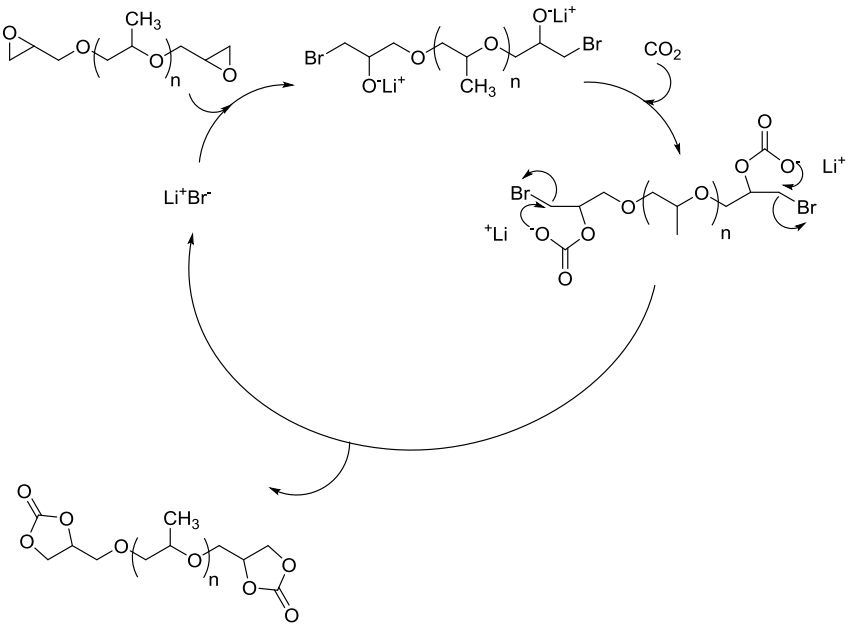
III.2 Characterizations of reactants

Before the synthesis of the PHU prepolymers, a complete characterization of raw materials has been carried out to determine the functionality in carbonate (CEW) of poly(propylene

oxide) bis carbonates: PPOBC380 and PPOBC640; in epoxy (EEW) of bisphenol a diglycidyl ether (BADGE), di-epoxydized cardanol (NC-514) and phloglucinol tris-epoxy (PGTE).

III.2.1 Cyclic Carbonates: PPOBC380 and -640

Specific Polymers Company synthesized one five-membered cyclic carbonate by carbonation of poly(propylene oxide) diglycidyl ether (PPODGE640, $\overline{Mn}$=640 g.mol^{-1}) in presence of lithium bromide to obtain poly(propylene oxide) bis-carbonate (PPOBC640) (Scheme IV-3). On the same model, we have synthesized PPOBC380 was synthesized from PPODGE380 ($\overline{Mn}$ =380 g.mol^{-1}). The carbonate equivalent weights (CEW) of these products were determined by ^{1}H NMR titration with standard solution (DMSO-d_6 with few milligram of toluene). Moreover, the unity of repetition (n) of carbonate compounds was calculated according to ^{1}H NMR and Equation IV-2 and the real molar masses were deducted. CEW and molar mass of the PPOBC380 and-640 were summarized in Table IV-1.



Scheme IV-3: Mechanism of the carbonation of PPODGE380 and -640

III.2.2 Characterizations of NC-514

NC-514 is an epoxidized cardanol supplied by Cardolite Company, synthesized by phenolation of aliphatic chain of cardanol, followed by epoxidation of phenol with epichlorohydrin. The structure of NC-514 was fully characterized in a previous paper by our team[48]. The ^{1}H NMR spectra of NC-514 (SI - Figure IV-4) shows that it contains only saturated and mono-olefinic chains with respective composition of 95% saturated chains and

5% of mono-olefinic chains. This composition is calculated from the integration of aromatic protons of cardanol and protons n of internal bond. We do not observe protons of unsaturated double bonds corresponding to internal and terminal double bonds. Moreover, we do not observe the peaks of proton of phenol group of the initial cardanol around 4.8 ppm and we observe the peaks of protons of glycidyl group (a, b, c, d, e). In addition, we observe the presence of peak of proton k of CH resulting of phenolation of aliphatic chain at 2.5 ppm with the peak of g proton CH_2 of aliphatic chain. The phenol is totally functionalized by epichlorohydrin but we also observe the presence of characteristic peaks of opened epoxy rings (30%) at 3.7 and 4.1 ppm. Furthermore, we observe the presence of the three aromatic peaks of cardol between 6.1 and 6.4 ppm. The integrations of these peaks and aromatic protons of cardanol allow to determine the presence of 1% cardol in the sample. Finally, the final epoxy functionality of NC-514 was found to be 1.3 epoxy functions per aromatic rings.

III.2.3 Characterizations of PGTE

PGTE is an epoxidized phloroglucinol supplied by Specific Polymers Company, synthesized in two steps. The fist step consists in solubilizing the biophenol in a large excess of epichlorohydrin by preparing its phenolate ammonium salt in presence of an ammonium phase transfer catalyst. The phenolate is then able to react with epichlorohydrin, by forming chlorinated intermediates. The crude mixture is traited with NaOH solution to form oxirane rings from chlorinated intermediates. The ^{1}H-NMR spectrum of PGTE (SI - Figure IV-5) allows determining its epoxy functionality by using the method developed by Ménard *et al.*[53] which consists in comparing the integration of the signal of the aromatic protons at 6.20 ppm with the integration of the signal of the proton of the tertiary carbon of the glycidyl group at 3.30 ppm. The final epoxy functionality of PGTE is 2.5 epoxy functions per aromatic rings. The product is a mixture of diepoxided and triepoxided phloroglucinol.

As for carbonates, the Epoxy Equivalent Weight (EEW) of epoxy compounds is titrated by ^{1}H NMR with the same protocol than titration of PPOBC. The values of EEW and molar mass of the BADGE, NC-514 and PGTE are summarized in Table IV-1.

Table IV-1: Characterizations of substrates

Reactants	CEW[1] (g.eq^{-1})	EEW[1] (g.eq^{-1})	Functionality carbonate, epoxy or amine	M (g.mol-1)	Tg (°C)
PPOBC380	210	-	2	392[2]	-39
PPOBC640	343	-	2	625[2]	-46
BADGE	-	181	2	340[3]	-
NC-514	-	356	1.32[54]	1108[3]	-
PGTE	-	160	2.8	316[3]	-

1: CEW and EEW determined by 1H NMR titration with standard solution: DMSO-d6 with toluene
2: Molar mass of PPOBC380 and -640 from 1H NMR
3: Molar mass of BADGE and ethylenedamine from data provided by Sigma Aldrich and ethylenediamine, NC-514 by Cardolite and PGTE by Specific Polymers

III.3 Syntheses and characterizations of PHU prepolymers

III.3.1 Syntheses of PHU prepolymers

In this study, five PHU prepolymers functionalized with primary amine were synthesized from two cyclic carbonate prepolymers of different chain length: PPOBC380 and -640. Different excess of ethylenediamine were used, without catalyst and solvent. The excess of ethylenediamine allowed the functionalization of the oligomers by -NH_2 groups and, from Flory's theory and Carothers' equation, permitted the determination of the degree of polymerization of the oligomers and, therefore, their molar masses. Indeed, the degree of polymerization of a polyaddition decreases dramatically as soon as a reagent is in excess. In this case, according to Carothers' equation, when the conversion (p) tends toward 1, the degree of polymerization is equal r ratio of reactants (Equation IV-7). r is the molar ratio of reactants. For this reason the degree of polymerization and molar masses decrease with amine excess.

Equation IV-7 $$\lim_{p\to 1} \overline{DPn} = \frac{1+r}{1-r}$$

The PHU prepolymers were prepared by using formulations based on molar equivalent of reactants (Table IV-2) with excess of amine to end cap the PHU pre-polymer by NH_2. Firstly, formulations (1) and (2), PPOBC380 or -640 were used with the same excess of ethylenediamine (carbonates/amine: 1/2). These two formulations allowed to study the influence of chain length of the poly(propylene oxide), firstly, on the structural and thermal properties of PHU prepolymers and, secondly, on the properties of hybrid materials. In the second time, a different excess of ethylenediamine was used in combination with the PPOBC640 (2, 3, 4, 5). These four syntheses allowed to study the influence of the amine excess on the structural properties of PHU oligomers and hybrid materials.

The syntheses of these PHU prepolymers were realized in bulk without catalyst at 60°C during 12 hours. The residual excess of ethylenediamine is removed at the end of the reaction by distillation under vacuum in order to obtain pure PHU oligomers.

The differences between the structures of PHU oligomers were characterized by NMR, size exclusion chromatography (SEC), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

III.3.2 Characterizations of PHU prepolymers

Synthesized PHU oligomers were characterized by ^{1}H NMR and SEC. The ^{1}H NMR spectra of PPOBC640 and PHU prepolymer 2 are reported respectively Figure IV-10-A and Figure IV-10-B. The ^{1}H NMR spectrum of PHU prepolymer 2 shows the disappearance of peaks at 4.45 ppm, corresponding to carbonates protons e of PPOBC640, which confirms a quantitative opening of cyclic carbonates of PPOBC by ethylenediamine. Moreover, according to model study, the appearance of peaks at 2.75 ppm and 3.2 ppm on the ^{1}H NMR of purified PHU prepolymer (Figure IV-10-B) corresponds respectively to CH_2 in α and β position of NH_2, which confirms the functionalization of oligomers by primary amine groups. In order to purify the PHU oligomers, the excess of ethylenediamine was removed by vacuum distillation. The ^{1}H spectrum of ethylenediamine (SI - Figure IV-2) proved the total removing of amine excess in the PHU prepolymers.

Once purified, the average $\overline{DP}n$ and molar masses of oligomers were determined experimentally by ^{1}H NMR analysis, comparing CH_2 in α position of NH_2 integrations (g', 2.75ppm) with CH_3 integrations (a', 1.1ppm).

From these data, the functionality in amine and therefore AHEW were calculated from Equation IV-4. The molar mass was determined by ^{1}H with 4 active hydrogens. These values were necessary to determine the amount of polyepoxy reactant (BADGE, NC-514 and PGTE) to add in order to yield hybrid polymers. The values of AHEW of these PHU oligomers are summarized in Table IV-2.

$\overline{M}n$ and dispersity of these oligomers were also determined by size exclusion chromatography (SEC) with PEO standards. Values of $\overline{DP}n$ and $\overline{M}n$ are summarized in Table IV-2. The $\overline{DP}n$ and $\overline{M}n$ of oligomer 1 were not determined by ^{1}H NMR analysis since ethylenediamine excess had not been completely removed due to a too high viscosity of this oligomer (see the

Tg_0 of this oligomer). The molar masses of oligomers 1 and 3 are respectively 1,900 $g.mol^{-1}$ and 1,300 $g.mol^{-1}$ with the same excess of ethylediamine. Only the chain lengths of PPOBC were different.

Moreover, $\overline{DP}n$ and molar mass of the PHU prepolymers obtained from PPOBC640 and different excess of ethylenediamine (1.3, 2, 3.3 and 6.5 molar equivalent) verify Carothers' equation (Table IV-2).

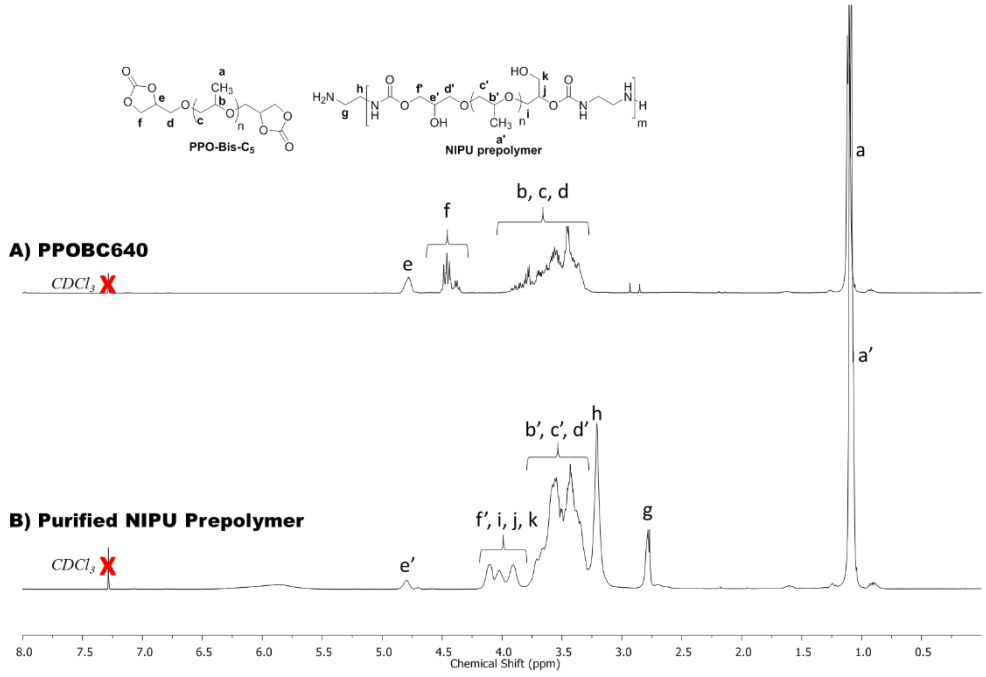


Figure IV-10: ^1H NMR spectra evolution for the synthesis of PHU prepolymer 2 in $CDCl_3$

III.3.3 Thermal characterization of PHU prepolymers

Table IV-2 summarizes the thermal properties of the PHU oligomers. First, the Tg_0 were measured by DSC. Two dynamic temperature ramps were performed between -100 and 100°C at 20°C.min^{-1}. The glass transition values obtained for oligomers 1, 2, 3, 4, 5, noted Tg_0, are respectively equal to 20, -14, -16, -18 and -19°C. The Tg values of the precursors are -39°C for PPOBC380 and -46°C for PPOBC640. The increase of Tg_0 can be explained by a structuration the PHU prepolymer with the increase of hydrogen bonds between the hydroxy groups created and the carbamate group. Moreover, the glass transition of PHU oligomer 1 is higher than 3 for the same amine excess since the chain length of PPOBC380 is smaller than those of the PPOBC640. Finally, Tg_0 of 2, 3, 4, 5 are similar and can be included in the error of DSC: ±2°C.

The TGA traces under an air atmosphere of all of the prepared polymers showed a three-step degradation. TGA thermograms and DTG curves are reported in Figure IV-12 and Figure IV-13. They show that the PHU prepolymers remained stable up to 200°C. The fist of degradation occurred after 200°C. Based on a previous TGA study performed on polyhydroxyurethanes analogues[55], the first degradation corresponds mainly to the urethane linkage degradation, leading to evaporation of small molecules, such as CO_2, ammonia, water; and/or small organic fragments. The second and the third steps correspond to the soft segment degradation characterized by hydrocarbon chain of PPO. The temperatures at 50% of weight loss are summarized in Table IV-2. For all oligomers, $Td_{30\%}$ were around 290°C and conform with the thermal stability of classic polyurethanes[56-58].

Table IV-2: NIPU prepolymers syntheses in molar equivalent and structural and thermal characterization

PHU	PPOBC-380	PPOB-C640	Ethylene-diamine	$\overline{DP}n^{1/2}$	$\overline{M}n^{3/4}$ (g.mol^{-1})	Đ	Tg (°C)[5,6→7]	$Td_{50\%}$ (°C)	AHEW [8](g.eq^{-1})
1	1	-	2	3/-	1900/-	3.6	-39[5]→20	-	-
2	-	1	1.3	8/4	3000/2800	2.0	-46[6]→-14	304	725
3	-	1	2	3/2	1300/1430	1.6	-46[6]→-16	310	358
4	-	1	3.3	1.9/1.7	1200/1310	1.8	-46[6]→-18	311	328
5	-	1	6.5	1.4/1.4	1000/1240	1.6	-46[6]→-19	311	310

[1]: $\overline{DP}n$ limiting determined by Carothers' equation (Equation IV-7)
[2]: $\overline{DP}n$ determined by ^{1}H NMR analysis
[3]: $\overline{M}n$ determined by size exclusion chromatography (SEC)
[4]: $\overline{M}n$ determined by ^{1}H NMR analysis
[5;6]: Tg_0 of PPOBC380 and PPOBC640
[7]: Tg of NIPU prepolymer
[8]: AHEW determined from $\overline{M}n$ calculated by ^{1}H NMR analysis and Equation IV-4

III.4 Syntheses and characterization of hybrids polymers

For the formulation of H-NIPU polymers, only PHU oligomers 2, 3, 4 and 5 were used. PHU oligomer 1 was not usable for a formulation at room temperature (Tg_0=20°C). PHU oligomer 2 was used to determine the best cross-linking conditions that will be applied to the other PHU oligomers in a second time.

III.4.1 Determination of the best cross-linking process for the hybrid materials

PHU oligomer **2** was used in reaction with BADGE, NC-514 and PGTE to synthesize H-NIPU networks at different temperatures. The epoxy/amine mixtures were carried out without solvent. Mixtures were stirred during three minutes then poured into an aluminum pan and cured at room temperature, 50°C or 100°C during 12 hours. Firstly, reaction at room

temperature did not yield a cross-linked network. However, at 50 and 100°C, H-NIPU networks were obtained. Polymers were characterized by DSC and ATG. For all these materials, the degradation temperatures at 50% under air are similar (328-348°C) and conform to classic polyurethane[56-59] or epoxy[53, 54] material. Glass transitions are between -5 and 0°C. Therefore, concerning the thermal stability, there is not great difference between reaction at 50 and 100°C whatever the epoxy reactants used. Therefore, for the rest of this study, all the polymers were cross-linked at 50°C during 12 hours.

Table IV-3: Thermal characterization of hybrid materials cross-linked at different temperature during 12 hours

PHU Prepolymers	Epoxy	Temperature of crosslinking (°C)	$Td_{50\%}$ (°C)	Tg (°C)
2	BADGE	RT	NC	NC
2	BADGE	50	328	0
2	BADGE	100	329	1
2	NC-514	RT	NC	NC
2	NC-514	50	348	-5
2	NC-514	100	346	-6
2	PGTE	RT	NC	NC
2	PGTE	50	330	-4
2	PGTE	100	333	-5

III.4.2 Synthesis of H-NIPU networks at 50°C

Twelve H-NIPU networks were synthetized: four with bisphenol A diglycidyl ether (BADGE), four with diepoxy cardanol (NC-514) and, four with tris epoxydized phloroglucinol (PGTE). The formulations were established from Equation IV-3 with EEW of epoxy and AHEW of oligomers calculated with Equation IV-1 (Table IV-2 and Table IV-3). The epoxy/amine mixtures were carried out without solvent. Mixtures were stirred during three minutes then poured into an aluminum pan and cured at 50°C during 12 hours. Figure IV-11 shows the pictures of the different hybrid polymers. All the materials present a color. The networks made with PHU prepolymers 2, 3 and 4 exhibit a high flexibility, giving first information about a lower glass transition temperature.

The H-NIPU networks were characterized by measurement of swelling index and gel content. Finally, thermal properties were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

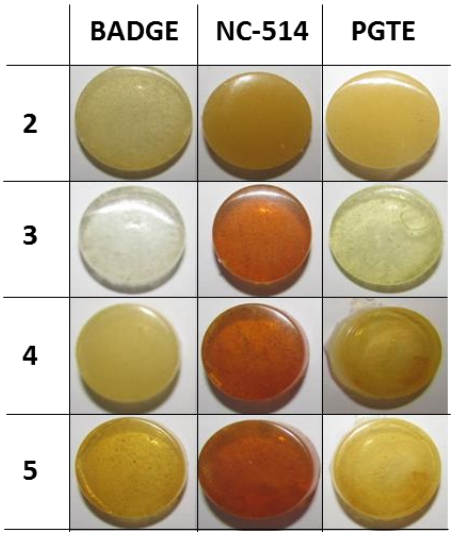


Figure IV-11: Pictures of the hybrid polymers

III.4.3 Characterization of H-NIPU materials

In order to compare the cross-linking of the different polymers, the swelling index and gel content were measured. Four samples of known mass (m_0) of H-NIPU polymers were immersed in 15 mL of THF during 24h, and then reweighed to get the wet mass (m_1). The swelling index was calculated from Equation IV-5. The results are summarized in Table IV-2. The lowest swelling index and the highest gel content correspond to the optimum cross-linking of polymer. PHU prepolymer 2 gives a higher swelling index than other PHU prepolymers. Indeed PHU prepolymer 2 has the longer aliphatic chain thereby separating the cross-link nodes. The swelling index decreases with the length of the oligomer chain.

Moreover, for all PHU oligomers, the swelling index depends on the epoxy reactants. Indeed, values are different with BADGE, NC-514 or PGTE. The di-epoxy cardanol gives the highest swelling index. This result is due to the same reasons than PHU oligomer: NC-514 has a long carbon chain in its structure which facilitates swelling by solvent. However the hybrid polymers formulated from PGTE give the lowest swelling index. Indeed, PTGE is trifunctional which increases the degree of cross-linking compared to a di-functional epoxy such as BADGE.

For the determination of the gel content, the samples of hybrid materials swelled by THF were placed in an oven under vacuum during 12 h and afterwards the samples were weighed and as a result the dry mass (m_2) were determined. The gel content was calculated from Equation IV-6. Table IV-2 summarizes all the results obtained for the 12 formulations.

All the values of gel content of hybrids polymers formulated from BADGE and PGTE are ranged between 92 and 99% which proves the high degree of cross-linking of networks that contain less than 8% of soluble chains. However, polymers formulated from NC-514 give lower gel content (77-86%). In fact, the di-epoxydized cardanol present monofunctional chains and opened epoxy rings which decreases the functionality and then the gel content of polymers. Jaillet *et al.*[54] reported precisely the structure of NC-514 in their study.

III.4.4 Thermal characterization of hybrids materials

The thermal properties of these H-NIPU polymers were firstly measured by DSC (SI - Figure IV-6-9). Two dynamic temperature ramps were performed between -80 and 100°C at 20°C/min under nitrogen flow. The results were summarized in theTable IV-2. Depending on their functionality and their chemical structure, both the PHU oligomers and the epoxy monomers have a strong influence on the thermosetting material properties. They allow polymers to exhibit properties ranging from flexible materials, with low glass transition temperature, to strong and hard materials with higher Tg values[60, 61]. Firstly, the glass transition temperature values for hybrid materials were influenced by the length of the PHU prepolymers. Indeed, for the same extender chain, BADGE for example, the Tg of the synthesized H-NIPUs increased with the length of PHU oligomers. Tg values are 0, 18, 23 and 28°C for hybrid materials formulated respectively with PHU prepolymers 2, 3, 4 and 5. Moreover, the structure of epoxy monomer influences the glass transition of materials. Indeed, for the PHU 3, Tg are respectively 18, 4 and 14°C with BADGE, NC-514 and PGTE. The low Tg of 3/NC-514 material is due to the long aliphatic chain of the cardanol. On the contrary, the 3/BADGE and 3/PGTE materials have a higher Tg (18 and 14°C for BADGE and PGTE respectively) which comes from the aromatic ring of epoxy monomers. For PHU oligomer 2, the tri-functionality of PGTE does not influence the glass transition. Whereas, for lower length chains of prepolymers 3 to 5, the functionality of PGTE increases the Tg of hybrid materials compared to polymers obtained from BADGE. Indeed, the Tg of 5/BADGE polymer (42°C) is higher than Tg of 5/PGTE (28°C). All these results allowed proposing several types of materials from PHU prepolymers and epoxy monomers.

TGA were performed in order to determine thermal stability of synthetized networks under air (Figure IV-12 and Figure IV-13). The principal steps of the mass loss as function of temperature (until 580°C) are given in Table IV-2. The thermal stability of all the H-NIPU materials from all PHU oligomers and epoxy monomers are similar with $Td_{50\%}$ ranging

between 328 and 408°C. Materials exhibited good thermal stability until 210°C. After that temperature, polymer degradation occurred in one or two steps owing to the epoxy monomers. The fist step corresponds to the degradation of the main hydrocarbon chain (PPO). In the case of materials formulated with NC-514, the second step corresponds to the degradation of the aliphatic chain of NC-514. A slight shoulder is observed on DTG curves of H-NIPU around 260°C, which corresponds to urethane degradation. The char at 500°C is between 3% and 13%. However, 3,4 or 5/PGTE networks with higher cross-linking degree and aromatic content present the highest char contents, around 10%.

Table IV-4: Swelling index, Gel content and thermal characterization of hybrid materials

PHU	Epoxy	Swelling Index (%)	Gel Content (%)	$Td_{50\%}$[1] (%)	Char at 500°C (%)	Tg (°C)[2→3→4]
2	BADGE	272	98	328	3	-46→-14→0
2	NC-514	382	84	348	4	-46→-14→-5
2	PGTE	156	98	328	2	-46→-14→-4
3	BADGE	144	93	330	4	-46→-16→18
3	NC-514	246	77	391	4	-46→-16→4
3	PGTE	103	92	324	6	-46→-16→14
4	BADGE	135	94	333	10	-46→-18→23
4	NC-514	218	84	408	11	-46→-18→4
4	PGTE	81	93	333	13	-46→-18→24
5	BADGE	97	97	341	8	-46→-19→28
5	NC-514	165	86	401	7	-46→-19→11
5	PGTE	75	99	352	11	-46→-19→42

1: TGA were realized under air
2: Tg_0 of PPOBC640
3: Tg of PHU prepolymers
4: Tg of hybrid polymers

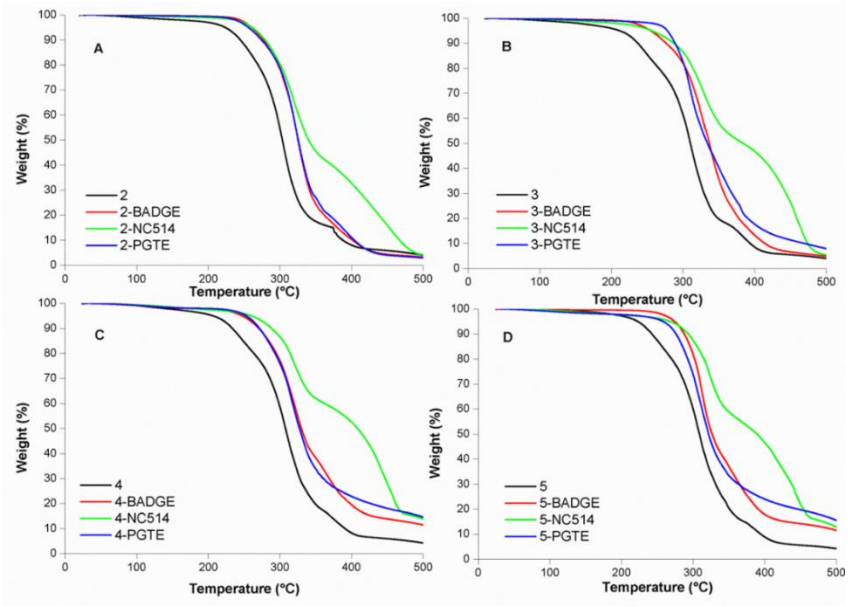


Figure IV-12: TGA thermograms of the hybrid polymers from 2 (A); 3 (B); 4 (C) and 5 (D) and various epoxy compounds under air flow at 10°C.min^{-1}

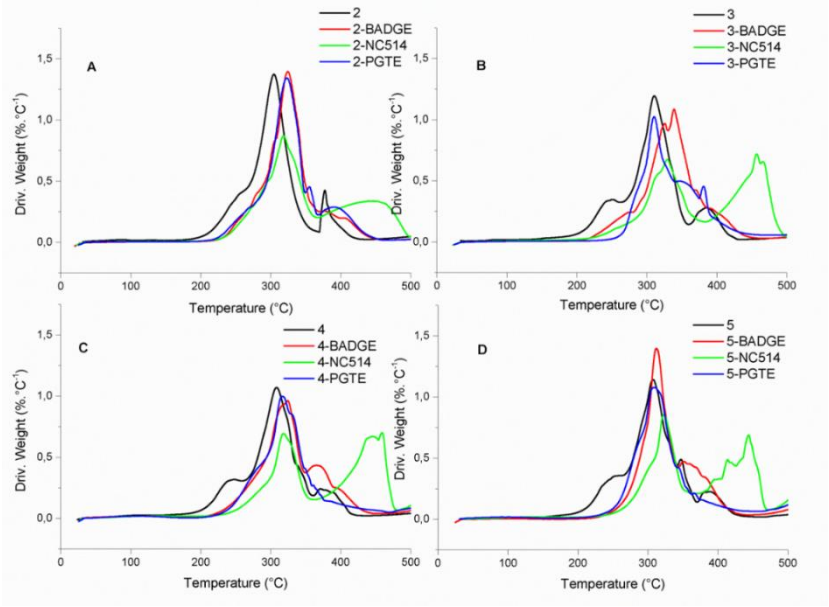


Figure IV-13: DTG curves of hybrid polymers from 2 (A); 3 (B); 4(C) and 5(D) and various epoxy comppunds under air flow at 10°C.min^{-1}

IV. Conclusion

Nowadays, the alternative PHU (PolyHydroxyUrethane) constitutes a significant opportunity to replace isocyanate in the formulation of PU materials. However, a lower kinetics of reaction carbonate/amine and lower molar masses of materials issue of these reactions are technical locks of this technology limiting its development. This is why, this study report, for the first time, the syntheses of H-NIPU polymers from oligo-polyhydroxyurethane terminated amine and multifunctional epoxy. PHU prepolymers were prepared from poly(propylene oxide) bis-carbonate and different excess of ethylenediamine. Excess of ethylenediamine were allowed to terminate the prepolymers by amine and control the degree of polymerization of this oligomers. These properties were demonstrated by model study and analyzed the structure of oligomers by ^{1}H NMR and SEC. Moreover, the Amine Hydrogen Equivalent Weight (AHEW) of obtained prepolymers terminated amine was calculated for each of them. Then, PHU oligomers were re-used with epoxy compounds (BADGE, NC-514 and PGTE) to formulate at 50°C H-NIPU polymers. These materials were then studied by characterizing the degree of crosslinking (swelling index, gel content) and thermal properties (TGA and DSC). The thermal characterizations of the materials depend of the chain length of oligomers and the nature of epoxy compounds. These H-NIPU materials formulated in this study have good thermal properties compared to polyurethane and nonisocyanate polyurethane materials. The main advantage of this technology is the ability to obtain PHU materials with a sequence of soft and hard segments as for classic polyurethanes.

V. Acknowledgement

This study was supported by ANR project CYRRENAS. The authors also thank Specific Polymers for the synthesis of poly(propylene oxide) bis carbonate (PPOBC640), Cardolite for NC-514 and Marine Blain, PhD student in our group, for fruitful discussion.

IV. References

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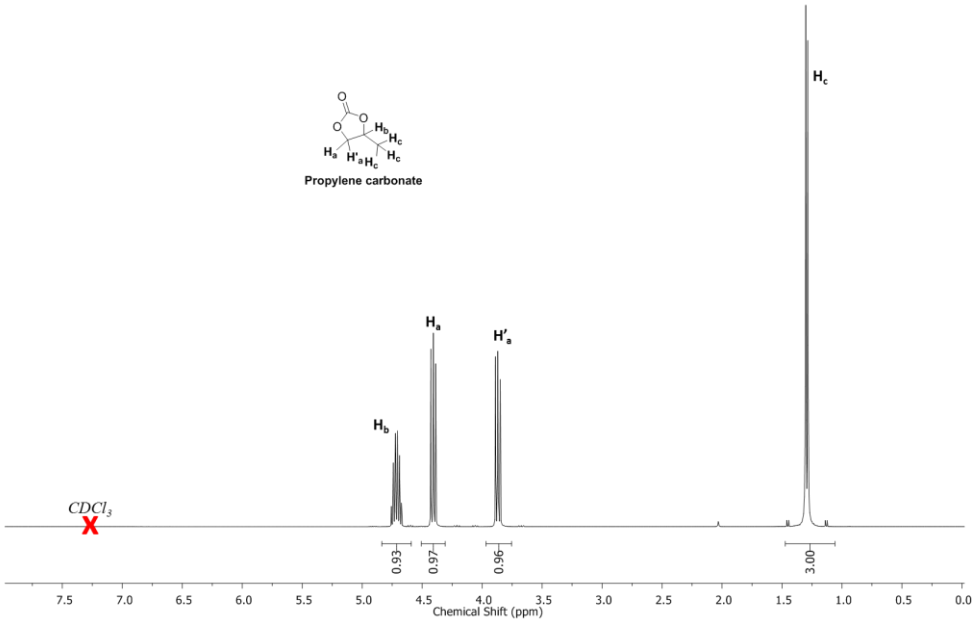
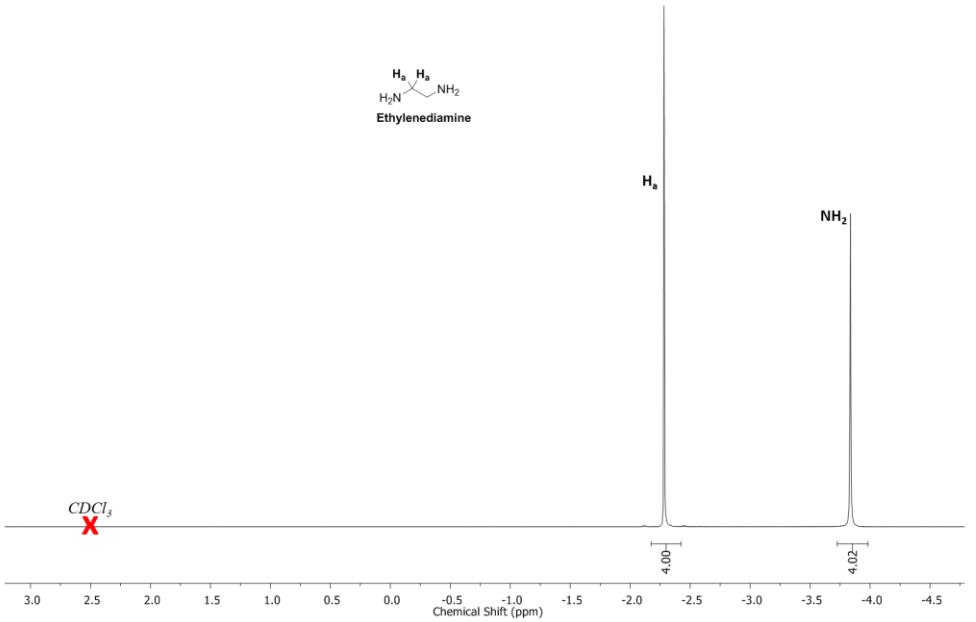
V. Supporting Informations

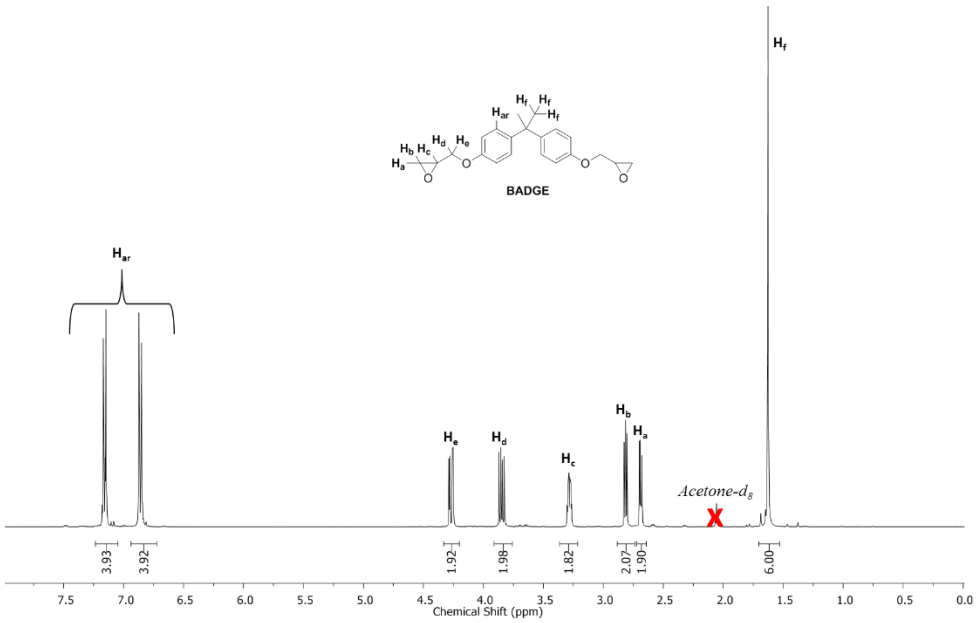
V.1 ^{1}H NMR spectra of raw materials



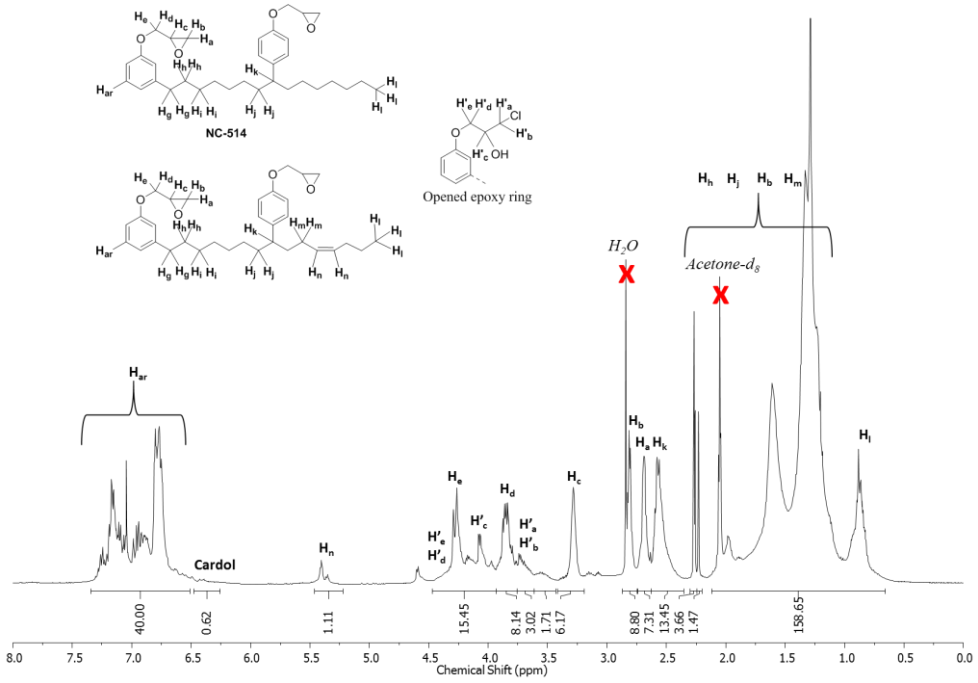
SI - Figure IV-1: ^{1}H NMR spectrum of propylene carbonate in $CDCl_3$



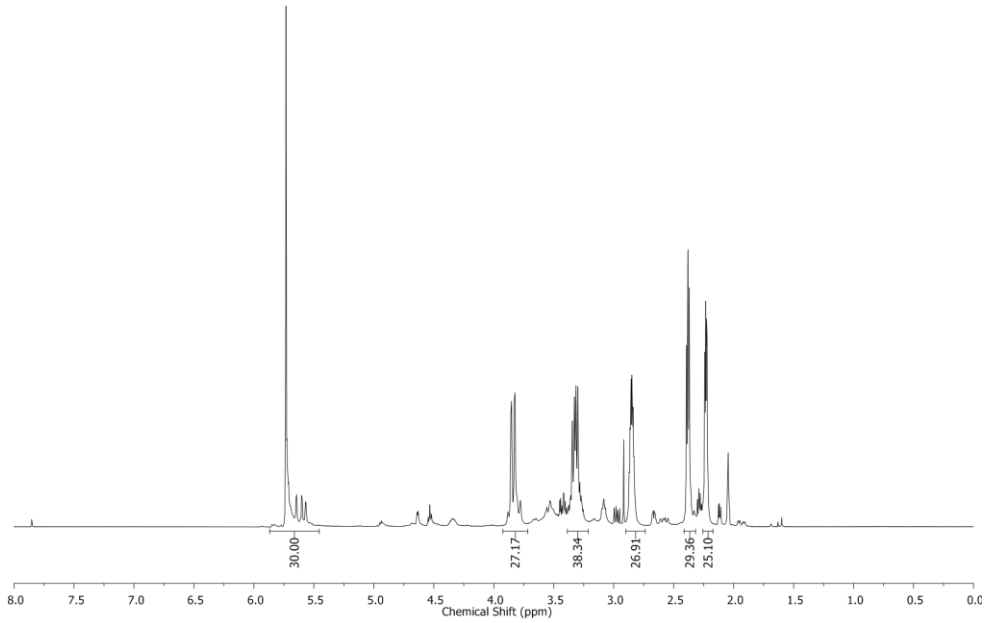
SI - Figure IV-2: ^{1}H NMR spectrum of ethylenediamine in $CDCl_3$



SI - Figure IV-3: ^{1}H NMR spectrum of BADGE in acetone-d_8

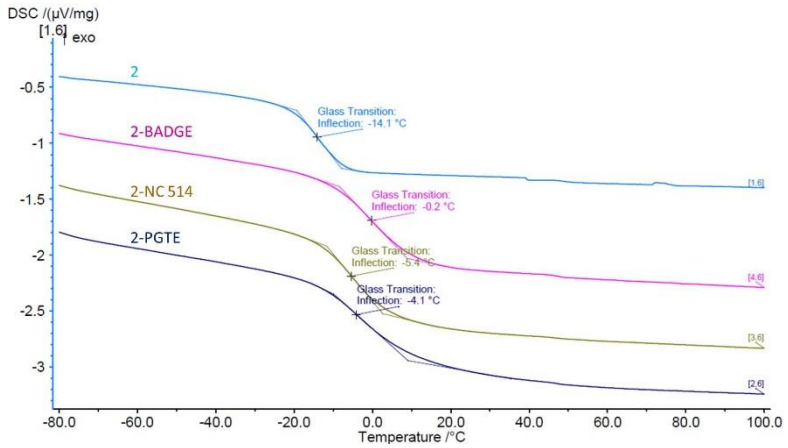


SI - Figure IV-4: ^{1}H NMR spectrum of NC-514 in acetone-d_8

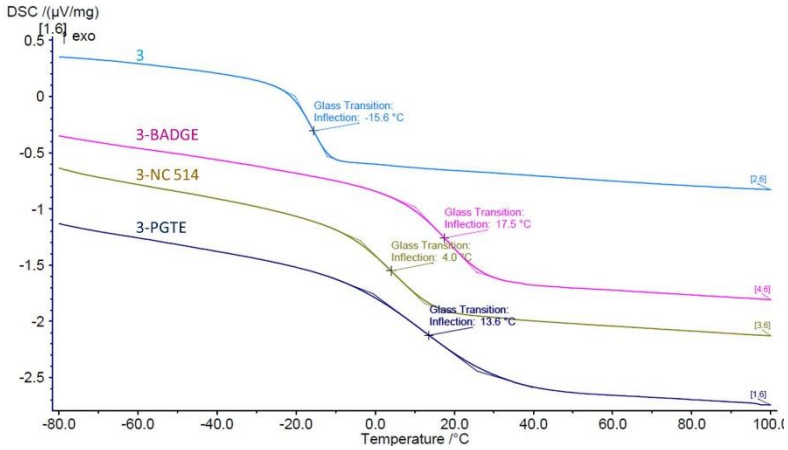


SI - Figure IV-5: ^{1}H NMR spectrum of PGTE in DMSO-d_6

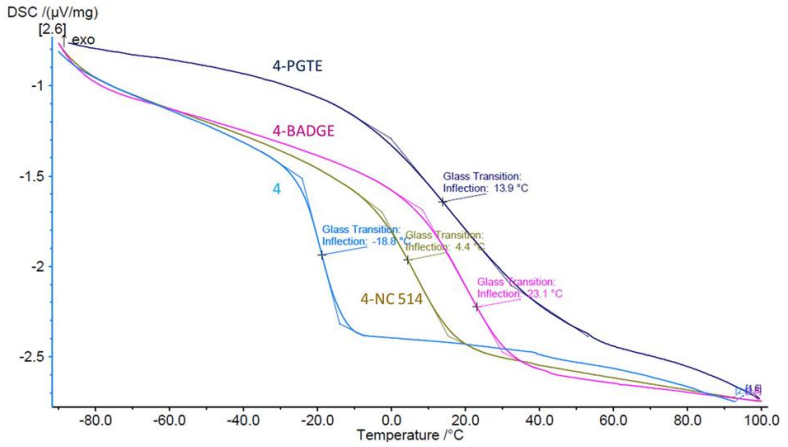
V.2Tg measured by DSC on the second heating ramp for NIPU oligomers and H-NIPU materials



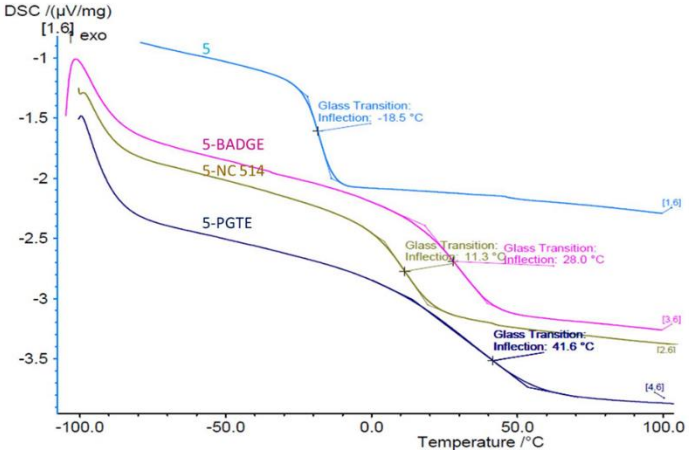
SI - Figure IV-6: DSC curves of NIPU oligomer 2 and H-NIPU materials obtained from NIPU oligomer 2



SI - Figure IV-7: DSC curves of NIPU oligomer 3 and H-NIPU materials obtained from NIPU oligomer 3



SI - Figure IV-8: DSC curves of NIPU oligomer 4 and H-NIPU materials obtained from NIPU oligomer 4



SI - Figure IV-9: DSC curves of NIPU oligomer 5 and H-NIPU materials obtained from NIPU oligomer 5

Conclusion Générale Chapitre IV

Dans ce chapitre, une nouvelle approche a été développée afin de concevoir des matériaux polyuréthanes sans isocyanate. Cette nouvelle voie est analogue à celle de la synthèse de la plupart des PUs. En effet, des matériaux appelés H-NIPUs sont obtenus à partir d'un procédé en deux étapes consistant à former, dans une première étape, un prépolymère PHU amino-téléchélique qui sont réticulé dans une seconde étape. Afin de réticuler ces oligomères, des monomères époxydés issus de ressources renouvelables (cardanol et phlorotannin) ont été utilisés.

Cette voie d'accès à ces nouveaux matériaux permet de réduire l'effet négatif des liaisons hydrogène qui limitent l'avancement de la réaction carbonate cyclique / amine. En effet, les prépolymères sont formulés au préalable à chaud avec un excès d'amine. Par conséquent, la conversion totale des carbonates cycliques est atteinte.

Cette nouvelle voie permet d'intégrer des groupements hydroxyuréthanes à des réseaux époxydes et d'accéder à des matériaux structurés possédant un enchainement de segments souples et rigides dans leurs chaînes macromoléculaires. Ce type de structure est caractéristique aux matériaux PUs.

De plus, cette approche peut être très intéressante industriellement pour formuler des mastics ou adhésifs par un procédé bi-composant. Le premier contiendrait le prépolymère PHU amino-téléchélique formulé préalablement par l'industriel et le second, le réticulant. L'industriel n'aurait qu'à jouer sur les structures des précurseurs pour moduler les propriétés des matériaux.

Néanmoins, les prépolymères obtenus dans cette étude ont une viscosité très élevée obligeant à formuler les matériaux H-NIPUs à une température supérieure à l'ambiante. Bien que cette nouvelle approche est très intéressante, de nombreuses perspectives découlent de ces travaux préliminaires afin d'accéder à des matériaux polyuréthanes sans isocyanate à température ambiante. Ces perspectives sont décrites dans la partie correspondante à la fin de ce manuscrit.

Conclusion Générale et Perspectives

Conclusion Générale

A l'heure actuelle, le contexte social, économique et réglementaire engage l'industrie chimique à concentrer ses efforts dans l'optique d'un développement durable. De nouveaux objectifs s'imposent aux chimistes, comme la substitution de substances dangereuses, l'utilisation de ressources renouvelables ou le choix de procédés plus respectueux de l'environnement. Le projet collaboratif CYRRENAS s'inscrit directement dans cette optique. Ce projet financé par l'Agence Nationale de la Recherche vise à substituer les précurseurs isocyanate et phosgène dans les formulations de matériaux polyuréthanes. Cette thématique de recherche a fait l'objet de nombreux travaux antérieurs au projet.

Le premier chapitre de cette thèse est consacré à l'étude de la bibliographie existante, sous la forme d'un article de perspective, et expose les quatre procédés actuels de synthèse de matériaux H-NIPUs. Ces voies de synthèses sont :

- La polycondensation de polycarbamates avec des polyaldéhydes ou des polyols ou encore des polyamines avec des polychlorures de carbonyle ou des polycarbamates ;
- Les réarrangements de Curtius, de Lossen ou d'Hoffman d'azotures ou de carboxamides ;
- La polymérisation par ouverture de cycles de carbamates cycliques ou d'aziridines ;
- La polyaddition de polycarbonates cycliques et de polyamines.

Les trois premières voies nécessitent l'utilisation de monomères dangereux et/ou conduisent à la formation de sous-produits. Cela explique que seule la polyaddition de polycarbonate cyclique et de polyamine a connu un essor particulier ces dernières années dans le but de formuler des matériaux NIPUs. Cependant, la littérature rapporte deux verrous scientifiques à cette technologie : la faible cinétique de réaction comparée à celle du système alcool / isocyanate ainsi que les faibles masses molaires des matériaux résultant de cette réaction. Afin de répondre à l'objectif de cette thèse, la stratégie envisagée a tout d'abord été d'identifier les verrous scientifiques limitant la réactivité des précurseurs et les masses molaires des PHUs, d'en proposer des alternatives et enfin de tester ces dernières sur la polymérisation de composés polyfonctionnels. C'est dans ce contexte qu'ont débuté ces travaux de thèse au début de l'année 2014.

L'état de l'art du système carbonate cyclique / amine dressé dans le premier chapitre a mis en évidence que les paramètres tels que la nature et les substituants des précurseurs, le solvant de synthèse ou la catalyse de la réaction influencent la cinétique de réaction. Malgré ces nombreux travaux, des conversions partielles des monomères sont observées lors de la polyaddition à température ambiante. Ces conversions partielles sont à l'origine des faibles masses molaires des matériaux PHUs.

Afin d'envisager des alternatives à ces conversions partielles, le second chapitre s'est intéressé à la compréhension de la réactivité des précurseurs à travers deux études.

La première étude du chapitre II s'est focalisée sur la réactivité et les conversions des carbonates cycliques lors de la réaction d'aminolyse. Ces paramètres ont été évalués à l'aide de composés carbonatés modèles monofonctionnels, de structures et de natures de substituants différentes. D'après ces études, les di-thio-carbonates cycliques et les carbonates cycliques à 6 membres sont les précurseurs les plus réactifs. Néanmoins, leur synthèse nécessite l'utilisation de composés dangereux et nocifs pour l'utilisateur. De plus les carbonates cycliques à 6 membres sont souvent issus d'une synthèse lourde mettant en jeu plusieurs intermédiaires. Par conséquent, bien qu'ils soient moins réactifs, les carbonates cycliques à 5 membres sont préférés pour des raisons économiques et sanitaires. L'activation de ces derniers peut être réalisée en jouant sur la nature de leur substituant. En effet, trois paramètres corrélés influencent la réactivité des carbonates cycliques en fonction de leurs substituants :

- l'approche de l'amine par la création de liaisons hydrogène entre le groupement NH_2 et un hétéroatome du substituant ;
- leurs effets électroniques ;
- leur encombrement stérique.

Par conséquent, parmi les carbonates cycliques modèles synthétisés dans ces travaux, les précurseurs porteurs de groupements esters de faible encombrement stérique activent de manière conséquente ces précurseurs. Cependant, lors de l'aminolyse, une réaction secondaire d'amidification entre l'ester et l'amine peut avoir lieu, perturbant ainsi la stœchiométrie de la réaction. Par conséquent, les carbonates cycliques à 5 membres porteurs de fragments éthers sont préférés pour le reste de notre étude. Leur aminolyse à température ambiante ne conduit pas à la formation de sous-produits. De plus, leur synthèse est réalisée carbonatation en autoclave de composés époxydés, selon un procédé économiquement viable. Ces composés

époxydés sont disponibles commercialement sous une grande variété de structures chimiques pouvant moduler les propriétés des matériaux suivant les applications visée.

Ce second chapitre s'est également intéressé au faible degré d'avancement de la polymérisation à température ambiante pouvant expliquer les faibles masses molaires des matériaux. Ce faible degré d'avancement semble lié aux nombreuses liaisons hydrogène présentes dans le matériau qui limitent la diffusion des espèces et figent le système. Néanmoins, quatre solutions sont envisageables afin d'augmenter l'avancement de la réaction.

- La première consiste à augmenter la température de réaction. Cet apport d'énergie redonne de la mobilité aux chaînes polymères, en cassant ces liaisons hydrogène, permettant ainsi aux extrémités de réagir à nouveau. Néanmoins, il est important de rester à des températures inférieures à 100°C pour éviter la formation de produits secondaires tels que les urées ou les amides. Ces dernières sont formées par la réaction entre l'amine et le groupement uréthane.
- La seconde solution est d'effectuer la réaction dans un solvant protique tel que le méthanol, l'éthanol… Ces alcools permettent de limiter les liaisons hydrogène inter- et intra-chaînes. La mobilité du système ainsi améliorée permet d'augmenter l'avancement de la réaction.
- La troisième solution est d'ajouter aux formulations du diglycerol ou du triglycérol comme plastifiants. Ces plastifiants joueront le même rôle qu'un solvant protique.
- Enfin, la quatrième solution est d'utiliser un additif, tel qu'un agent moussant, permettant une agitation continue tout le long de la polymérisation.

Ces quatre alternatives que sont la température, le solvant, l'ajout de plastifiant ou d'agent moussant limitent, en terme de procédé, le champ d'application de ces matériaux qui ne pourront dès lors pas remplacer toutes les applications des polyuréthanes classiques sans le développement d'une nouvelle approche.

Ce travail a permis de réaliser de nombreuses avancées sur la réactivité carbonate cyclique / amine ainsi que sur la synthèse de PHUs linéaires qui a été l'objet de la seconde étude du chapitre II.

Néanmoins les matériaux polyuréthanes se présentent le plus souvent sous la forme de matériaux thermodurcissables obtenus à partir de polyol et d'isocyanate de fonctionnalités

supérieures à deux. Par conséquent, pour mimer le système polyuréthane, des monomères de fonctionnalités supérieures à 2 peuvent être utilisés pour obtenir des réseaux PHUs.

Ainsi, dans le troisième chapitre, deux des quatre solutions proposées précédemment (la température et l'ajout d'agent moussant) ont été testées afin de formuler des matériaux PHUs. Les matériaux ont été obtenus à partir de composés polyfonctionnels tels que le triméthylolpropane tri-carbonate pour réticuler les matériaux. Leurs propriétés ont été modulées en incorporant différentes proportions d'oligomères de polyoxyde de propylene dicyclic carbonate de masses molaires différentes (POBC380 et PPOBC640). Les propriétés des matériaux PHUs ont été comparées à des matériaux polyuréthanes de référence.

L'augmentation de la température de formulation a conduit à une gamme de PHUs de température de transition vitreuse variable et de propriétés mécaniques extrêmement intéressantes. De plus les propriétés d'adhésion de cas PHUs sont supérieures à celles des PUs classiques. Cela est dû principalement à l'apport de liaisons hydrogène supplémentaires créées avec le support par l'intermédiaire des groupements hydroxy primaires et secondaires.

Dans un second temps, l'ajout d'un agent moussant dans les formulations a permis d'obtenir les premières mousses polyuréthanes sans isocyanate jamais décrites dans la littérature. Ces mousses ont été obtenues dans une première étude à température élevée puis dans une seconde à température ambiante et représentent actuellement les seuls matériaux PHUs obtenus dans de telles conditions. L'agent moussant permet une homogénéisation du système tout au long de la polymérisation. La synthèse de mousse nécessite une réaction de polymérisation et une libération de gaz simultanée. Pour cela, les réactions de polymérisation ont été catalysées par les deux meilleurs catalyseurs (TBD et thiourée) décrits par Marine Blain au cours de ses travaux de thèse menés dans le laboratoire IAM. Un important travail de formulation a donc été réalisé afin d'obtenir des mousses homogènes. Cette application représente deux tiers du marché des PUs.

Ce troisième chapitre a montré qu'il était possible d'obtenir des matériaux PHUs possédant des propriétés mécaniques et d'adhésion très intéressantes comparées à celles des PUs. Les nombreuses liaisons hydrogène créées par l'intermédiaire des groupements uréthane et hydroxy permettent une augmentation accrue de ces propriétés. De plus, il a été montré que l'ajout d'un agent moussant conduit à la formulation de mousses à température ambiante. Cette application représente deux tiers du marché des PUs.

Les conclusions du chapitre II et III démontrent que les liaisons hydrogène apportent un effet antagoniste à la chimie des PHUs. En effet, ces interactions limitent l'avancement de la réaction de polymérisation en figeant les espèces mais apportent des propriétés mécaniques et d'adhésion très intéressantes aux matériaux résultants. Ce dernier point démontre un grand intérêt du groupement hydroxyuréthane pour les propriétés des matériaux. Par conséquent, une nouvelle approche consistant à incorporer ce groupement dans des matrices réactives à température ambiante sans ajout d'additif a été envisagée. Ceci a fait l'objet du quatrième et dernier chapitre de ce manuscrit. Des matériaux H-NIPUs ont été obtenus par l'intermédiaire de prépolymères amino-téléchéliques contenant des groupements hydroxyuréthanes. Ces derniers sont synthétisés par une réaction entre un bis-carbonate cyclique et un excès de diamine. Cet excès de diamine présente un double avantage : convertir totalement les carbonates cycliques en hydroxyuréthanes et synthétiser des prepolymères terminés par des groupements NH_2. Ces prépolymères sont ensuite réticulés par des composés époxydés réagissant avec les groupements terminaux du prépolymère PHU. Dans le cadre de cette étude, des composés époxydés issus de ressources renouvelables ont été utilisés (cardanol diépoxydé issu de la noix de cajou et phloroglucinol tris-epoxy issu de phlorotannins). Ces matériaux sont donc formulés sur le même principe que les matériaux PUs obtenus par réaction entre un prépolymère isocyanate et un allongeur de chaînes. Cette nouvelle approche permet de moduler les propriétés des matériaux en les structurant par un enchainement de segments souples et durs. De plus, l'effet négatif des liaisons hydrogène limitant l'avancement de la réaction carbonate cyclique / amine est éliminé puisque les prepolymères sont formulés au préalable. Néanmoins, ces liaisons hydrogène apportées par les groupements hydroxyuréthanes et hydroxy confèrent une certaine viscosité au prépolymère obligeant de formuler les matériaux à une température supérieure à l'ambiante (50°C dans l'étude). Un certain nombre de perspectives découlant de ces travaux sont abordées dans la partie suivante.

Pour finir, ce travail a permis de réaliser de nombreuses avancées sur la synthèse de matériaux polyuréthanes sans isocyanate et plus particulièrement sur la formulation de polyhydroxyuréthanes. Malgré les limites de la réaction carbonate cyclique / amine, des solutions sont envisageables pour accéder à des matériaux ayant des propriétés intéressantes et comparables aux PUs. Cependant, ces alternatives ne permettront pas aux matériaux PHUs de remplacer toutes les applications des matériaux PUs industrialisés actuellement. Pour pallier cela, une nouvelle chimie utilisant et incorporant le groupement hydroxyuréthane dans des matrices réactives doit être envisagée. Le professeur Oleg Figovsky a compris cela depuis

déjà de nombreuses années en décrivant dans de multiples brevets la formulation de matériaux H-NIPUs à partir de HUM.

Perspectives

Les perspectives qui découlent de ces travaux sont nombreuses. Tout d'abord les monomères choisis pour synthétiser les matériaux PHUs (TMPTC, PPOBC380 et PPOBC640) sont obtenus à partir de la réaction de carbonatation de composés de type éthers glycidylés. Ces derniers sont synthétisés le plus souvent par un procédé mettant en jeu l'alcool correspondant et l'épichlorhydrine. L'épichlorhydrine peut être synthétisée à partir de ressources renouvelables - par le procédé Epicerol® de l'entreprise Solvay - mais elle reste néanmoins toxique pour l'homme (classé CMR 1B) et peut constituer un danger pour l'utilisateur si des traces sont présentes dans le produit final. Par conséquent, pour des raisons sanitaires, des études doivent être menées sur l'époxydation d'alcool en utilisant des composés moins dangereux pour l'homme. De plus, des études de toxicité des monomères TMPTC, PPOBC380 et PPOBC640 doivent être envisagées pour confirmer leur non nocivité pour l'homme.

Dans ces travaux de thèse, il a été montré que la synthèse de PHUs est limitée par l'effet des liaisons hydrogène limitant la diffusion des espèces au cours de la polymérisation. Quatre solutions ont été proposées afin de remédier à ces inconvénients et deux d'entre elles ont été testées sur des matériaux. Par conséquent, deux voies restent à être expérimentées sur la formulation de PHUs. En effet, il a été montré que l'incorporation de diglycérol ou triglycérol en tant que plastifiant permet de modifier l'enthalpie de réaction du système carbonate cyclique / amine. L'impact de l'ajout de tels plastifiants dans un matériau réticulé sera donc à étudier. De plus, les solvants protiques améliorent la conversion des carbonates cycliques lors de leur aminolyse. La synthèse de revêtements PHUs à partir de tels solvants est à envisager.

Ce manuscrit décrit également la formulation de mousses PHUs à température ambiante et constitue une grande avancée dans la formulation de matériaux polyuréthanes sans isocyanate. Néanmoins, l'expansion de ces matériaux est réalisée à partir de libération de dihydrogène obtenu par réaction entre le groupement Si-H de l'agent moussant et NH_2 de l'amine. Ce gaz est inflammable et constitue un danger pour le formulateur, même si les quantités libérées sont limitées. Des travaux sur des nouveaux agents moussants à température ambiante doivent donc être menés pour obtenir ces mousses par un procédé moins dangereux. Des travaux réalisés par Ren *et al.* [1] ont montrés la possibilité d'obtenir des mousses époxy à partir d'amines préalablement carbonatées. Ces dernières sont des sels qui, lorsqu'ils sont chauffés à une température au-delà de 90°C, reforment l'amine correspondante tout en libérant du CO_2

[2] et permettent d'expanser la résine epoxy-amine et obtenir une mousse. Par analogie, cette technologie peut être expérimentée afin d'obtenir des mousses PHUs dans un premier temps en température, puis dans un second temps, à température ambiante en recherchant des catalyseurs capables de décarbonater l'amine à des températures plus basses. Une autre solution peut être envisagée et consiste à utiliser une technique d'imprégnation de gaz dans les matériaux PHUs afin de les expanser. Cette technique a été expérimentée et décrite par Detrembleur *et al.* [3] dernièrement. Cependant, seules des mousses rigides ont été obtenues par ce procédé. Un travail de formulation peut être envisagé pour obtenir des mousses flexibles à partir de ce procédé.

Enfin, les travaux préliminaires sur la formulation de matériaux H-NIPUs à partir de prépolymères amino-téléchéliques contenant des motifs hydroxyuréthanes sont encourageant et nous semblent les plus prometteurs afin de couvrir un plus large éventail d'applications. Néanmoins, l'étude des propriétés mécaniques des matériaux obtenus par cette voie n'a pas été menée en comparaison à des matériaux PUs de référence. De plus, les prépolymères PHUs utilisés ont été synthétisés à partir d'éthylène diamine, une amine volatile facilement extractible par évaporation sous vide mais également très nocive. Enfin, ces prépolymères présentaient une viscosité élevée, les rendant difficilement utilisables à température ambiante pour formuler les matériaux H-NIPUs. Afin de remédier à ces inconvénients, des alternatives sont envisageables. Ces dernières consistent à ne pas extraire l'excès d'amine dans le prépolymère PHUs. Par conséquent, l'excès d'amine restant pourra jouer le rôle de diluant réactif capable de réagir avec des composés époxydés. Dans ce cas, des amines biosourcées tels que celles issues de la dimérisation d'acide gras, connues sous le nom de Priamine et commercialisées par l'entreprise Croda, peuvent être utilisées. Enfin, ces prépolymères peuvent être réticulés par des composés époxydés mais il peut être envisagé d'obtenir des matériaux H-NIPUs à partir de la réaction de Michael entre les groupements NH_2 des prépolymères et des composés acrylates ou maléimides.

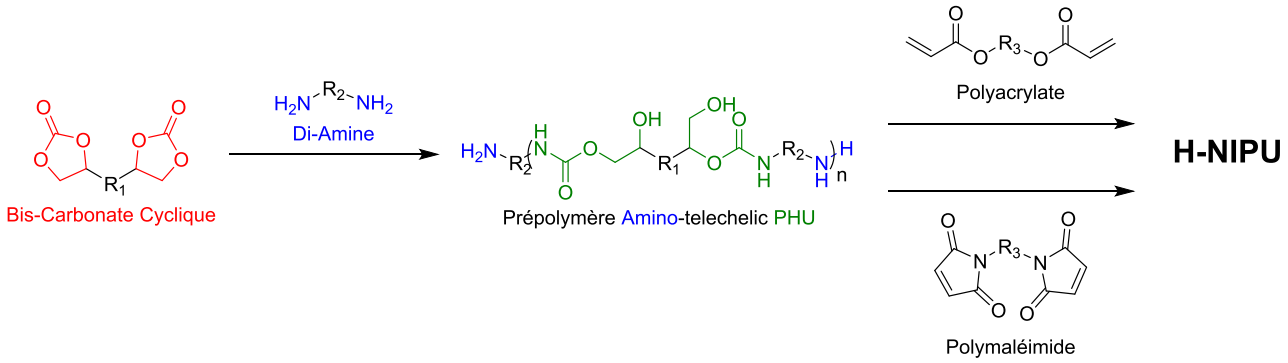


Figure 0-1: Formulation de H-NIPU à partir de prépolèmere PHU et d'acrylate ou maléimide

Enfin, Figovsky *et al.* décrivent la synthèse de matériaux H-NIPUs à partir de HUMs réticulés par des composés époxydés. Les matériaux ainsi obtenus sont des réseaux époxydes contenant des groupements hydroxyuréthane latéraux qui confèrent aux matériaux des propriétés d'adhésion et de résistance à la dégradation chimique accrues. Cette approche peut être utilisée dans de nouveaux travaux en réticulant les HUMs par des composés acrylates ou maléimides. Ces travaux sont actuellement en cours dans l'équipe IAM.

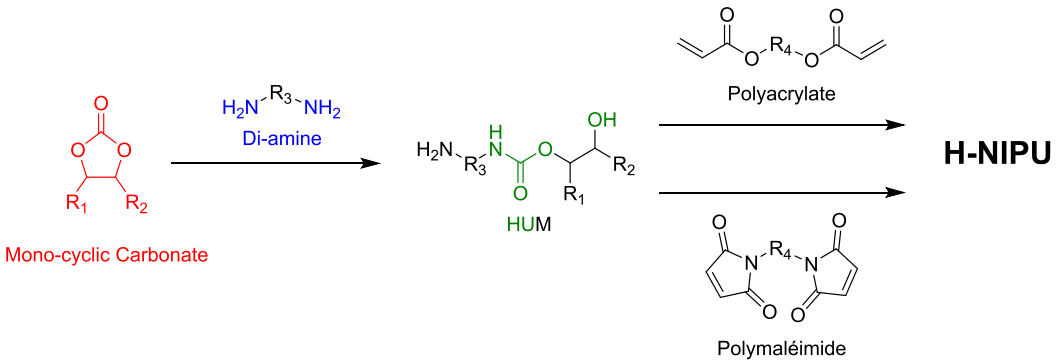


Figure 0-2: Formulation de H-NIPU à partir de HUM et d'acrylate et de maléimide

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    Claire Negrell, Adrien Cornille, Sylvain Caillol

Substitution des isocyanates dans les polyuréthanes pour l'élaboration de matériaux adhésifs et expansés

Résumé

A l'heure actuelle, de nombreuses entreprises commercialisent des matériaux polyuréthanes pour diverses applications. Le polyuréthane se place au sixième rang des polymères les plus produits au monde. Néanmoins, ces matériaux sont préparés à partir de monomères dangereux : les isocyanates. Ces derniers sont toxiques ou même parfois CMR (Cancérigène, Mutagène, Reprotoxique) et représentent un danger pour l'environnement, le formulateur et l'utilisateur. Pour protéger leurs employés et consommateurs et dans le cadre de la législation REACH, Bostik et Arkema, les deux entreprises du consortium CYRRENAS financé par l'Agence Nationale de la Recherche, visent à substituer les isocyanates dans les polyuréthanes et ainsi former des matériaux Non-Isocyanate PolyUrethane (NIPU). Parmi les différentes voies d'accès aux NIPUs, la voie novatrice carbonate cyclique/amine a été envisagée afin de synthétiser des matériaux polyhydroxyuréthanes (PHU). Une étude approfondie par des analyses spectrométriques (RMN) et thermiques (DSC) sur des réactions modèles entre des mono-carbonates cycliques et des mono-amines ont permis de mettre en évidence les paramètres influençant la réactivité ainsi que les limitations de cette technologie. Ce manuscrit s'intéresse également à l'élaboration de matériaux PHU, à leurs propriétés mécaniques, thermomécaniques et d'adhésion sur différents supports. Le polyuréthane est également très largement employé sous forme de mousses flexibles et rigides qui représentent 2/3 du marché mondial des matériaux polyuréthane. Dans cette optique, les premières mousses PHUs ont été élaborées et caractérisées. Enfin, dans le but de pallier la limitation de la synthèse des PHUs, une nouvelle approche de formulation de matériaux a été mise au point à partir de pré-polymères amino-téléchéliques contenant des groupements hydroxyuréthanes et des extendeurs de chaîne bio-sourcés. Les matériaux résultant de cette formulation sont appelés H-NIPUs.

Mots-clés : Polyuréthane, NIPU, H-NIPU, PHU, Carbonate Cyclique, Amine, Adhésif, Mousse

Substitution of isocyanates in polyurethanes for the elaboration of adhesive and porous materials

Abstract

Nowadays, several companies commercialize polyurethane materials for various applications. Polyurethane ranks as the sixth most produced polymer in the world. Nevertheless, these materials are obtained from harmful monomers: isocyanates. Isocyanates are toxic and sometimes CMR (Carcinogenic, Mutagenic, Reprotoxic) and represent a danger for the environment, the formulator and the final user. To protect their employees and consumers and in the context of the REACH regulation , Bostik and Arkema, the two companies of the consortium CYRRENAS funded by the Agence Nationale de la Recherche, target the substitution of isocyanates in polyurethanes and thus the production of Non-Isocyanates Polyurethane (NIPU) materials. Among the different access routes to NIPUs, the innovative cyclic carbonate/amine way was considered in order to synthesize polyhydroxyurethane (PHU) materials. A detailed study by spectrometric (NMR) and thermic (DSC) analyses on model reactions between mono-cyclic carbonates and mono-amines allowed to bring to light the parameters influencing the reactivity as well as the limitations of this technology. This manuscript also focuses on the elaboration of flexible and rigid PHU materials, on their thermal, mechanical, thermomechanical and adhesive properties on different substrates. The polyurethane is also very largely employed in flexible and rigid foams which represent 2/3 of the worldwide market. In this context, the first PHU foams were synthesized and thermally and mechanically characterized. Finally, with the objective to circumvent the limitations of the PHU synthesis, a new approach for the formulation of polyurethanes without isocyanates was developed from aminotelechelic prepolymers containing hydroxyurethane moieties and biobased epoxidized compounds used as chain extenders. The materials resulting from this formulation are called H-NIPUs.

Key words: Polyurethane, NIPU, H-NIPU, PHU, Cyclic Carbonate, Amine, Adhesive, Foam