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Synthèse et caractérisation de nouveaux matériaux polyuréthanes respectueux de l'environnement et de la santé

Soutenue le 12 mars 2015 à huis clos

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« Chaque difficulté rencontrée doit être l’occasion d’un nouveau progrès. »

Pierre de Coubertin

Cette thèse de doctorat a été rédigée en utilisant pour chaque chapitre le format habituellement adopté pour la rédaction d'articles scientifiques paraissant dans des revues à comité de lecture. L'indulgence du lecteur est ainsi sollicitée pour les répétitions et redites nécessairement inhérentes à la forme de rédaction choisie.

Le présent mémoire de thèse a ainsi été partiellement rédigé en langue anglaise, conformément à l'autorisation délivrée par le Professeur Jean-Pierre Bucher, professeur des universités à l'Institut de Physique et Chimie des Matériaux de Strasbourg et directeur de l'Ecole Doctorale de Physique et Chimie-Physique.

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Communications liées à l'étude

Publications

Les résultats présentés dans cette thèse font l'objet de quatre articles et d'une revue bibliographique.

- ***Article publié***

1. C. Carré, L. Bonnet and L. Avérous – Original biobased nonisocyanate polyurethanes: solvent- and catalyst-free synthesis, thermal properties and rheological behavior, *RSC Advances*, 2014, 4, 54018-54025.

- ***Articles en cours de publication***

2. C. Carré and L. Avérous – Cyclic carbonate from 2,5-furandicarboxylic acid, a promising rigid building block for biobased nonisocyanate polyurethane synthesis, *soumis dans Green Chemistry (janvier 2015)*.

3. C. Carré and L. Avérous – Solvent- and catalyst-free synthesis of fully biobased nonisocyanate polyurethanes, from two dimer fatty acids. Effect of the macromolecular architecture, *soumis dans Green Chemistry (janvier 2015)*.

4. C. Carré, H. Zoccheddu, S. Delalande, P. Pichon and L. Avérous – Synthesis and characterization of advanced thermoplastic nonisocyanate polyurethanes, based on controlled aromatic-aliphatic architectures, *soumis dans Polymer (janvier 2015)*.

5. C. Carré and L. Avérous – Biobased nonisocyanate polyurethanes, *soumis dans Progress in Polymer Science (janvier 2015)*.

Conférences

1. C. Carré, L. Avérous – *Automobile et matériaux verts : polymères biosourcés*, Atelier ConectInnov, 23 mai 2013, Mulhouse (France) – *Communication orale*.

2. C. Carré, L. Avérous – *Development of new healthy and environmentally friendly polyurethanes*, 4th International Conference on Biodegradable and Biobased Polymers (Biopol-2013), 1 au 3 octobre 2013, Rome (Italie) – *Poster*.

3. C. Carré, L. Avérous – *Novel biobased NonIsocyanate PolyUrethanes from dimer diamines obtained from solvent- and catalyst-free synthesis: Study of the structure-properties relationships*, 7th Workshop on Fats & Oils as Renewable Feedstock for the Chemical Industry, 23 au 25 mars 2014, Karlsruhe (Allemagne) *– Communication orale (en anglais)*.

4. C. Carré – *Quelle percée des matériaux biosourcés dans l'industrie automobile?*, Matinées Plant Based Summit dans le cadre du salon FIP Solution Plastique, 18 juin 2014, Lyon (France) *– Table ronde*.

Liste des abréviations

%deg	Pourcentage de dégradation
5CC	Carbonate cyclique à 5 membres (Five-membered cyclic carbonate)
6CC	Carbonate cyclique à 6 membres (Six-membered cyclic carbonate)
ACV	Analyse du Cycle de Vie
AIBN	Azobisisobutyronitrile
ATG	Analyse thermogravimétrique
ATR	Réflexion totale atténuée (Attenuated Total Reflectance)
AV (%)	Indice d'amine (Amine Value)
BDA	1,4-diaminobutane
BDO	1,4-butanediol
BisCC	Biscyclocarbonate
$CDCl_3$	Chloroforme deutéré
CIRC	Centre International de Recherche sur le Cancer
CLP	Règlement relatif à la classification, à l'étiquetage et à l'emballage des substances chimiques et des mélanges (Classification, Labelling, Packaging)
CLSO	Huile de lin carbonatée (Carbonated Linseed Oil)
CNSL	Liquide issu des coques de noix de cajou (Cashew Nut Shell Liquid)
CO_2	Dioxide de carbone
CSBO	Huile de soja carbonatée (Carbonated Soybean Oil)
D ($m^2.s^{-1}$)	Coefficient d'autodiffusion
DA8	1,8-diaminoctane
DBisCC	Biscyclocarbonate issu d'un dimère d'acide gras
DBTDL	Dilaurate de dibutylétain
DCC	N,N'-dicyclohexylcarbodiimide
DCI	N, N'-diisopropylcarbodiimide
DCl	Chlorure issu d'un dimère d'acide gras
DCM	Dichlorométhane

DDA	Dimère diamine
DDI	2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane (diisocyanate issu d'un dimère d'acide gras)
DFA	Dimère d'acide gras (Dimer Fatty Acid)
DHU	N,N'-dicyclohexylurée
Dia	Diamine
DMAP	4-(dimethylamino)pyridine
DMF	Diméthylformamide
DMSO-d_6	Diméthylsulfoxide deutéré
DMTA	Analyse thermo-mécaniquedynamique (Dynamic Mechanical Thermal Analysis)
DNIPU	Poyuréthane sans isocyanate issu d'un dimère d'acide gras
DoE	Département de l'énergie (Department of Energy)
DOH	Diol issu d'un dimère d'acide gras
DOSY	Technique de RMN à deux dimensions basée sur la séparation des molécules en fonction de leur coefficientd'autodiffusion (Diffusion ordered spectroscopy)
d_P	Densité du polymère
DPU	Polyuréthane issu d'un dimère d'acide gras
DRA	Analyse rhéologique dynamique (Dynamic Rheological Analysis)
d_S	Densité du solvant
DSC	Calorimétrie différentielle à balayage (Differential Scanning Calorimetry)
DTG	Dérivée de la perte de masse
Đ	Dispersité
E (MPa)	Module d'Young
E' (Pa)	Module de conservation (DMTA)
E'' (Pa)	Module de perte (DMTA)
EDA	1,2-diaminoéthane (Ethylene diamine)

ELSO	Huile de lin époxydée (Epoxydized Linseed Oil)
ESBO	Huile de soja époxydée (Epoxydized Soybean Oil)
ESI	Renseignements électroniques supplémentaires (Electronic supporting information)
EVO	Huile végétale époxydée (Epoxidized Vegetable Oil)
FDCA	Acide 2,5-furane dicarboxylique (2,5-furandicarboxylic acid)
fn	Fonctionnalité moyenne de l'amine
FTIR	Spectroscopie infrarouge à transformée de Fourier (Fourier Transform InfraRed spectroscopy)
G (%)	Taux de gel
G' (Pa)	Module de conservation (ARES)
G'' (Pa)	Module de perte (ARES)
GC	Carbonate de glycérol (Glycérol Carbonate)
HCl	Chlorure d'hydrogène
HDI	Diisocyanate d'hexaméthylène (Hexamethylene diisocyanate)
HMDA	Hexaméthylène diamine
HMF	5-hydroxyméthylfurfural
HNIPU	Polyuréthane sans isocyanate hybride
HS	Segment rigide (Hard Segment)
I_{OH} (mg KOH/g)	Indice d'hydroxyle (Hydroxyl index)
IPDA	Isophorone diamine
IPDI	Diisocyanate d'isophorone (Isophorone diisocyanate)
IR	Infrared
KI	Iodure de potassium
KOH	Hydroxyde de potassium
LBisCC	Biscyclocarbonate linéaire
LCA	Analyse du cycle de vie (Life Cycle Analysis)
LNIPU	Polyuréthane sans isocyanate linéaire

LPU	Polyuréthane linéaire
MDI	Diisocyanate de diphénylméthane (Methylene diphenyl diisocyanate)
M_n (g.mol^{-1})	Masse molaire moyenne en nombre
M_w (g.mol^{-1})	Masse molaire moyenne en poids
*m*XDA	m-xylylène diamine
NaOH	Hydroxyde de sodium
NCO	Isocyanate
NCO%	Teneur en isocyanate
NIPF	Mousse polyuréthane sans isocyanate (Nonisocyanate polyurethane foam)
NIPU	Polyuréthane sans isocyanate (Nonisocyanate polyurethane)
NMR	Résonnance magnétique nucléaire (Nuclear Magnetic Resonance)
ODO	Groupe 2-oxo-1,3-dioxolane
OH	Groupe hydroxyle
OH8	Diaminooctane
PA	Polyamide
P_{CO2} (bar)	Pression de dioxyde de carbone
P_{DDA}	Prépolymère synthétisé avec un dimère diamine
PEF	Polyéthylène furanoate
PET	Polyéthylène téréphtalate
PHU	Polyhydroxyuréthane
P_{Jeff}	Prépolymère synthétisé avec la Jeffamine®
PU	Polyuréthane
PUU	Polyuréthane-urée
*p*XDA	p-xylylène diamine
Q	Taux de gonflement
R (J.mol^{-1}.K^{-1})	Constante des gaz parfaits

REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Enregistrement, évaluation, autorisation et restriction des substances chimiques)
RI	Indice de réfraction (Refractive Index)
RMN	Résonnance Magnétique Nucléaire
SBBisCC	Biscyclocarbonate issu de l'acide sébacique (Sebacic biscyclocarbonate)
SBCl	Chlorure d'acide sébacique (Sebacoyl chloride)
$scCO_2$	Dioxyde de carbone supercritique
SEC	Chromatographie d'exclusion stérique (Size Exclusion Chromatography)
SGH	Système Général Harmonisé
$SOCl_2$	Chlorure de thionyle
SR	Segment rigide
SS	Segment souple
T (°C ou K)	Température
T_α (°C)	Température de transition (DMTA)
T_g (°C)	Température de transition vitreuse (DSC)
T_m (°C)	Température de fusion
T_{max} (°C)	Température maximale (ATG)
$T_{x\%}$ (°C)	Température à laquelle la masse est égale à x% de la masse initiale (ATG)
tan δ	Facteur de perte
TBAB	Bromure de tétra-n-butylammonium
TBD	Triazabicyclodecène
TDI	Diisocyanate de toluène (Toluene diisocyanate)
TEA	Triéthylamine
TerAc	Acide téréphtalique (Terephthalic Acid)
TerBisCC	Biscyclocarbonate issu de l'acide téréphtalique (Biscyclocarbonate from terephthalic Acid)
TerCl	Chlorure d'acide téréphtalique (Terephthaloyl Chloride)

TGA	Analyse thermogravimétrique (Thermogravimetric analysis)
THF	Tétrahydrofurane
TNIPU	Polyuréthane sans isocyanate thermoplastique (Thermoplastic nonisocyanate polyurethane)
TPE	Elastomère thermoplastique (Thermoplastique elastomer)
TPU	Polyuréthane thermoplastique (Thermoplastic polyurethane)
UV	UltraViolet
V (mL)	Volume
W_D (g)	Weight of dry polymer after swelling
W_P (g)	Masse du polymère sec (Weight of dry polymer)
W_{P0} (g)	Masse initiale de l’échantillon (Initial sample weight)
W_S (g)	Masse de solvent à l’équilibre (Weight of solvent at equilibrium)
wt%	Pourcentage massique
ε_{max} (%)	Allongement à la rupture
δ (ppm)	Déplacement chimique (RMN)
ν_e ($mol.m^{-3}$)	Densité de réticulation
σ_{max} (MPa)	Contrainte maximale
φ_R	Phase rigide
φ_S	Phase souple

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Introduction générale

Les polymères issus de la biomasse sont utilisés depuis très longtemps. En effet, ce n'est qu'à partir de 1907, avec la découverte de la bakélite, que sont apparus les premiers polymères entièrement synthétiques. De plus en plus innovants et techniques, les matériaux polymères synthétiques ont progressivement envahi le monde de l'industrie et notre vie quotidienne. Conçus à partir de dérivés fossiles avec une forte empreinte carbone, les matériaux polymères doivent depuis la fin du XX$^{\text{ème}}$ siècle faire face à de nouvelles contraintes qui sont (i) la fluctuation et l'augmentation du prix du pétrole ainsi que la disponibilité de certaines fractions et (ii) les pressions à la fois réglementaires et sociétales (REACH, Grenelle de l'environnement…). De plus, certains de leurs composants chimiques de base (bisphénol A, isocyanate…) sont actuellement suspectés comme étant nocifs pour la santé et l'environnement. Des solutions alternatives doivent aujourd'hui être proposées et apparaître afin de (i) réduire la dépendance aux ressources fossiles, (ii) synthétiser des (macro)molécules moins toxiques, avec des empreintes environnementales réduites (au travers de l'analyse du cycle de vie - ACV), et en accord avec les grands principes de la chimie verte.[1]

Les polyuréthanes (PU) constituent une famille importante de matériaux polymères avec une production mondiale de 17,5 Mt en 2011 (6$^{\text{ème}}$ matériau polymère, au niveau mondial). Extrêmement adaptables, ils sont principalement utilisés dans des secteurs tels que l'ameublement et la literie, le transport, la construction et l'électroménager. Les PU sont essentiellement synthétisés par la réaction de polyaddition entre un polyisocyanate et un polyol. Ces derniers sont de plus en plus souvent biosourcés et notamment issus d'huiles végétales, ce qui permet de produire des matériaux renouvelables avec de nouvelles architectures macromoléculaires. En revanche, peu d'isocyanates commercialisés sont issus de ressources renouvelables, et ils restent néanmoins dangereux pour la santé. En effet, ils sont toxiques et une exposition répétée peut causer des problèmes respiratoires graves et incurables. Certains isocyanates sont même classés cancérigènes. Par ailleurs, la synthèse d'isocyanates nécessite l'utilisation de substances toxiques telles que des dérivés du phosgène. Des réglementations strictes limitent désormais la teneur en isocyanates libres tolérée. Cette réglementation va prochainement évoluer et devenir encore plus drastique. Ces différents éléments poussent aujourd'hui les fabricants en relation avec les utilisateurs de polyuréthanes à envisager de nouvelles perspectives, avec notamment de nouvelles voies de synthèse. Parmi celles-ci on trouve les polyuréthanes sans isocyanate, en anglais : « Non-Isocyanate Polyurethanes », ou NIPU.

C’est dans ce contexte qu’a vu le jour ce présent projet de thèse, mené en étroite collaboration entre l’équipe BioTeam dirigée par le Pr. Luc AVÉROUS au sein de l’Institut de Chimie et Procédés pour l’Energie, l’Environnement et la Santé (ICPEES – UMR 7515 – Université de Strasbourg), la société SOPRÉMA (SOciété des Produits et Revêtements d’Étanchéité « MAmmouth »), et l’entreprise automobile PSA Peugeot Citroën. Ce travail doctoral fait partie intégrante d’un projet collaboratif nommé PURES, relatif à de nouveaux polyuréthanes plus respectueux de l’environnement et de la santé. Il est financé par les entreprises partenaires mentionnées mais également par la région Alsace dans le cadre d’un financement FRI (Fonds Régional pour l’Innovation) et la Communauté Urbaine de Strasbourg (CUS).

Les objectifs de la société SOPRÉMA s’inscrivent dans sa démarche globale d’écoconception et sont de proposer de nouvelles générations de matériaux à plus faibles impacts environnementaux afin de présenter à ses clients une gamme de produits plus « verts » et moins toxiques. SOPRÉMA utilise à ce jour les polyuréthanes pour trois types de produits bien distincts : (i) l’étanchéité liquide avec réaction in-situ, (ii) les membranes bitumineuses contenant des élastomères thermoplastiques PU (TPU) pour améliorer les propriétés originales du bitume dans une application d’étanchéité, et (iii) les panneaux d’isolation thermique à base de mousses PU rigides.

Dans le cadre de sa politique environnementale, PSA Peugeot Citroën souhaite accroître la part déjà significative de matériaux verts dans ses véhicules (30% prévu en 2014). L’entreprise désire développer de nouvelles voies de synthèse PU qui (i) incluront une quantité importante de ressources renouvelables et (ii) supprimeront l’intermédiaire isocyanate des mélanges. Les PU représentent plusieurs dizaines de kilogrammes par automobile. Leurs principales applications sont les mousses de sièges et autres mousses insonorisantes, les PU pour les peaux de planches de bord, les vernis et peintures, et les polyuréthanes thermoplastiques (TPU) pour la fabrication de certains joints.

L’enjeu global de ce travail de thèse est donc d’explorer de nouvelles voies de synthèse de PU plus respectueuses de l’environnement et de la santé. Lorsque cela a été possible, des voies de synthèse sans solvant et/ou sans catalyseur, et utilisant un minimum de réactifs chimiques ont été privilégiées. En outre, des procédés optimisés, c’est-à-dire limitant le nombre d’étapes de purification, ont été choisis en accord avec les douze principes de la chimie verte[1] mais également afin de faciliter l’industrialisation potentielle de ces techniques.

Notre stratégie est, après identification de molécules issues de la biomasse, de synthétiser et caractériser des matériaux NIPU biosourcés et innovants selon le schéma en 4 parties présenté dans la Figure I-1.

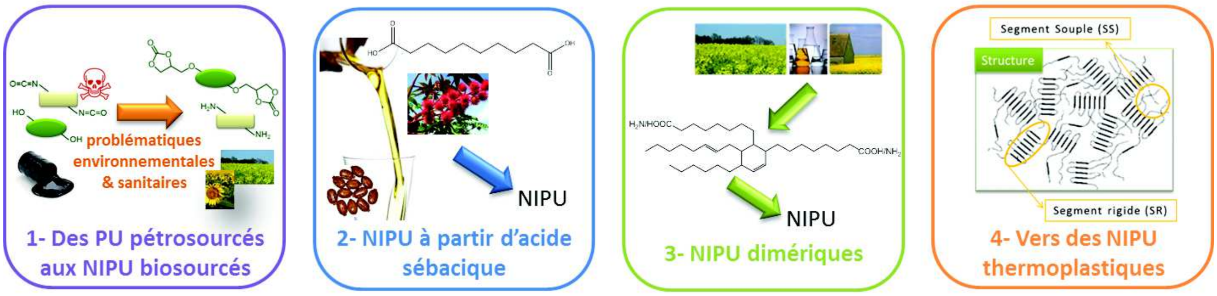


Figure I-1. Structure de l'étude et du manuscrit

Un état de l'art (**Chapitre 1**) présente tout d'abord l'état actuel de la synthèse des PU et des NIPU biosourcés ainsi que leurs propriétés respectives. Cette partie est essentiellement présentée sous forme d'un article de synthèse bibliographique (Review) intitulé « Biobased nonisocyanate polyurethanes ». Les différentes voies de synthèse de NIPU existantes ainsi que les synthons potentiels issus de ressources renouvelables compatibles pour une synthèse de NIPU biosourcés sont passés en revue. De manière générale, il ressort de cette étude que de nombreux NIPU ont été synthétisés depuis quelques dizaines d'années cependant peu sont issus de molécules biosourcées. Il apparait que la synthèse de NIPU est envisageable selon différentes voies. Parmi ces différentes approches, et afin de présenter des solutions viables et pertinentes dans le contexte de cette étude, nous nous sommes concentrés sur la formation de liaisons uréthanes *via* la réaction d'aminolyse, entre un carbonate cyclique (ou cyclocarbonate) et une amine. Cette réaction d'aminolyse permet d'utiliser différentes matières premières biosourcées ou « biosourçables ». Aussi cette voie a été privilégiée dans le contexte de cette étude. Au préalable, nous nous sommes intéressés à la synthèse de PU conventionnels afin de bien cerner les problèmes inhérents à cette chimie et élaborer clairement notre stratégie de recherche. En outre, l'analyse des relations « structure-propriétés » des PU nous a permis de mieux appréhender les stratégies de synthèse abordées dans la suite de ce manuscrit, en particulier en ce qui concerne les NIPU thermoplastiques et élastomères. Ces connaissances permettent également de comparer les systèmes conventionnels à base d'isocyanates, avec les NIPU.

Pour ce qui concerne le volet expérimental de ce projet, nous nous sommes attardés dans un premier temps à la synthèse originale de NIPU obtenus à partir de l'acide sébacique et de dimères d'amine (**Chapitre 2**). Le biscyclocarbonate est synthétisé à partir de l'acide sébacique (pouvant être issu de l'huile de ricin) et du carbonate de glycérol. Cette voie de synthèse, en plus d'utiliser des synthons biosourcés, permet une valorisation du glycérol, l'un des plus importants coproduits biosourcés (par exemple de l'industrie du biodiesel). De leur côté, les dimères d'amine avec de longues chaînes grasses hydrophobes, issus de l'oléochimie, sont largement disponibles pour des applications de masse dans l'automobile et le bâtiment. Comme de nombreuses substances biosourcées, les dimères diamines ont une fonctionnalité moyenne, variable en fonction des variabilités de la ressource botanique. Cette étude a donc été aussi l'occasion d'étudier l'influence de la fonctionnalité des diamines sur les propriétés des matériaux NIPU. Après une caractérisation chimique et thermique détaillée, le comportement rhéologique de ces matériaux a été plus particulièrement étudié. Pour les fonctionnalités plus élevées, un NIPU très prometteur par rapport aux applications visées a été obtenu. Des analyses mécaniques dynamiques supplémentaires ont été réalisées afin d'évaluer pleinement le potentiel de ce matériau.

Afin d'obtenir des matériaux entièrement biosourcés par aminolyse, ce qui présente un aspect très novateur et jamais précédemment rapporté, des NIPU dimériques ont été synthétisés et étudiés (**Chapitre 3**). En outre, les NIPU synthétisés par la voie aminolyse, également nommés polyhydroxyurethanes (PHU), ont la particularité d'avoir des fonctions hydroxyles. Ces dernières, formant des liaisons hydrogène intermoléculaires particulières, peuvent améliorer certaines propriétés des NIPU (résistance chimique, stabilité thermique, …). Cependant ces fonctions peuvent être néfastes lorsque l'hydrophobie du matériau est recherchée. Cette hydrophilie inhérente aux groupes hydroxyles semble pouvoir être compensée par les chaînes pendantes hydrophobes des dimères d'acide et d'amine. En plus des caractérisations classiques, des essais de prise en eau ont été réalisés afin de tester cette dernière hypothèse. Ce chapitre a également été l'occasion d'étudier l'effet de la structure dimérique sur les propriétés finales des NIPU correspondants. De plus, cette étude a permis de comparer les matériaux NIPU obtenus avec des PU conventionnels élaborés avec des synthons de même type.

La dernière partie du manuscrit est consacrée à l'élaboration de NIPU thermoplastiques, à caractère élastomère (**Chapitre 4**). La stratégie a été ici de s'appuyer sur les voies classiquement utilisées pour l'obtention de produits équivalents avec isocyanates, à savoir une synthèse en 2 étapes avec obtention de prépolymères lors d'une première phase. Dans un premier temps, le biscyclocarbonate réagit avec une diamine longue et souple. Une seconde diamine jouant le rôle d'allongeur de chaîne est ajoutée dans un second temps. Cette approche permet ainsi de mieux contrôler l'architecture macromoléculaire des NIPU obtenus, contrairement à ce qui aurait été obtenu lors d'une synthèse mono étape. Afin d'obtenir la structuration souhaitée, il a fallu choisir avec attention les synthons de base. Ainsi, un « nouveau » biscyclocarbonate, plus rigide, a dû être synthétisé. Parmi les intermédiaires de synthèse très rigides et biosourcés ou biosourçables disponibles, on trouve notamment l'isosorbide et l'acide téréphtalique. Ce dernier a été sélectionné car il possède déjà les fonctions acides nécessaires à la synthèse du carbonate cyclique. L'influence du pourcentage de segments rigides et de la structure de la diamine sur la structuration de ces matériaux a été étudiée en particulier. La suite de l'étude a été menée sur son équivalent biosourcé, l'acide 2,5-furane dicarboxylique (FDCA) qui est, de plus, fortement développé actuellement, notamment dans l'optique du développement d'un équivalent de PET 100% biosourcé (*i.e.*, PEF). Ce second synthon a montré qu'il était un candidat très prometteur pour l'élaboration de NIPU thermoplastiques, à caractère élastomère.

L'objectif de cette thèse était double. Il s'agissait de développer des nouveaux matériaux PU adaptés dans un contexte industriel pour le domaine de l'automobile ainsi que pour l'étanchéité et le bâtiment, tout en préservant une approche scientifique de qualité avec une bonne compréhension des mécanismes d'élaboration des systèmes synthétisés, d'analyse des structures et des propriétés correspondantes.

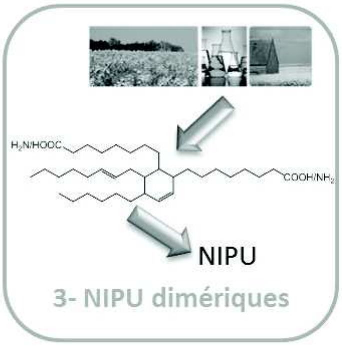
Le développement de nouvelles architectures macromoléculaires PU sans isocyanate et issues de ressources renouvelables a permis non seulement d'apporter une expertise supplémentaire à l'institut (ICPEES) et à l'équipe BioTeam mais aussi de proposer des solutions innovantes et viables pour la synthèse de nouveaux polyuréthanes fonctionnels, dans un contexte de collaborations mixtes, industrielles et académiques.

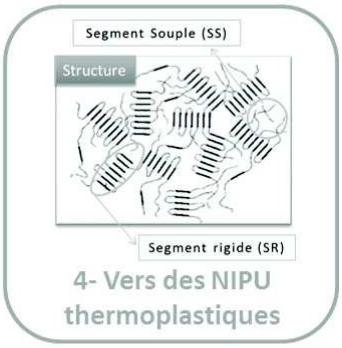
Références bibliographiques

1. P. Anastas and J. Warner, *Green Chemistry: Theory and Practice*, Oxford Univ Press, 1998.

Chapitre 1

Des polyuréthanes conventionnels aux NIPU biosourcés – Etat de l'art





Introduction

La synthèse bibliographique présentée dans ce chapitre est composé de trois parties distinctes. La première partie est consacrée à la présentation des polyuréthanes (PU) conventionnels. La compréhension de la synthèse des PU, liée à la morphologie et aux propriétés correspondantes du matériau final, doit nous permettre de mieux appréhender les stratégies de synthèse développées dans la suite du manuscrit. La seconde partie de ce chapitre est dédiée au réactif isocyanate et en particulier à ses effets sur la santé. Le contexte règlementaire est également abordé afin de mieux comprendre les problématiques actuelles et envisager des solutions pérennes plus respectueuses de l'environnement et de la santé pour l'élaboration d'une future génération de matériaux PU. La stratégie retenue dans le cadre de ce travail doctoral étant la suppression totale des isocyanates en tant que réactifs, et ceci grâce à de nouvelles méthodes de synthèse. La troisième et dernière partie de ce chapitre bibliographique porte sur l'état de l'art de cette nouvelle chimie de synthèse de PU sans isocyanate, appelés NIPU. Elle se présente sous la forme d'un article de synthèse bibliographique (review) intitulé « Biobased Nonisocyanate Polyurethanes », soumis dans le journal *Progress in Polymer Science*. Dans un premier temps, une synthèse de l'ensemble de la bibliographie sur les NIPU est présentée. L'accent a été plus particulièrement mis sur la réaction d'aminolyse qui semble être la voie la plus prometteuse. L'objectif second de nos travaux étant aussi de substituer les synthons pétrosourcés par des molécules issues de ressources renouvelables, une étude concentrée sur les « building blocks » potentiels et renouvelables pour la synthèse de NIPU biosourcés *via* la réaction d'aminolyse a été ensuite réalisée. Dans un dernier temps, les propriétés physiques et physico-chimiques ainsi que les performances de cette nouvelle classe de PU sont également discutées.

1. Présentation générale des polyuréthanes

Les polyuréthanes (PU) font partie des polymères les plus couramment utilisés dans l'industrie. Cela est dû à la multiplicité de leurs structures, de leurs propriétés, et donc de leurs applications. Comme l'illustre la Figure 1-1, on peut trouver les PU sous forme de mousses (flexibles ou rigides) mais également en tant que matières compactes (élastomères, thermoplastiques ou encore thermodurcissables).

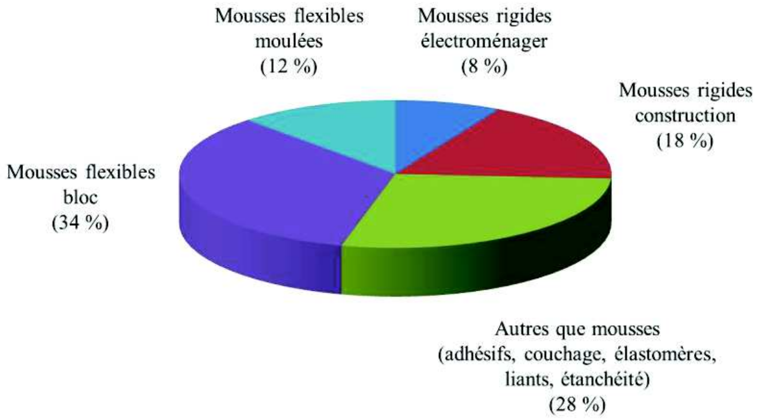


Figure 1-1. Répartition des PU dans le monde par type d'applications.[1]

1.1. La chimie des PU

Depuis les premiers développements et en particulier les travaux d'Otto Bayer au début des années 1900, les PU sont obtenus par la réaction de polyaddition entre des polyols et des polyisocyanates (Figure 1-2).[2, 3] Les deux réactifs sont généralement issus de ressources fossiles. Cependant, dans un contexte de développement durable et poussés par la limitation de l'accès aux ressources fossiles ainsi que par les contraintes réglementaires et sociétales, de plus en plus de chercheurs et d'industriels ont recours à des substituts biosourcés, notamment au niveau des polyols issus de l'oléochimie ou de la glycochimie. La chimie reste néanmoins identique à celle utilisée avec des constituants dérivés du pétrole.

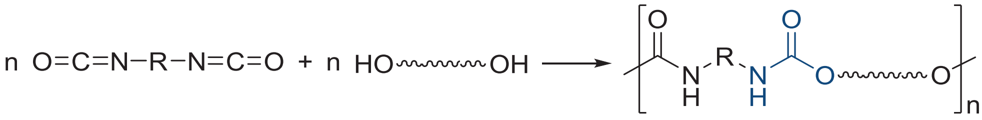


Figure 1-2. Schéma de la réaction de formation d'un PU.

1.1.1. Mécanisme réactionnel

La fonction uréthane est obtenue par la réaction entre un alcool et un isocyanate. Le mécanisme général de la réaction est représenté sur la Figure 1-3. Le centre nucléophile de l'alcool attaque le carbone électrophile du groupement isocyanate puis le proton de l'alcool est arraché et transféré à l'atome d'azote pour former la fonction uréthane. Il s'avère qu'un mécanisme auto-catalytique faisant intervenir une deuxième molécule d'alcool est également accepté.[4]

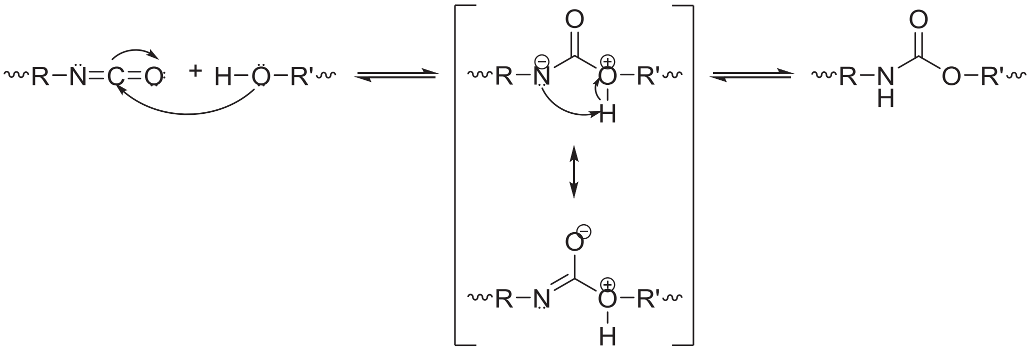


Figure 1-3. Mécanisme général de la réaction isocyanate/alcool.

La réactivité de la synthèse de PU est liée aux isocyanates. En effet, de par le fort caractère électrophile de l'atome de carbone lié à l'azote et à l'oxygène, les isocyanates sont très réactifs vis-à-vis de nucléophiles tels que les alcools. Ce caractère électrophile est d'autant plus marqué que la fonction isocyanate est associée à des radicaux aromatiques. En revanche, un encombrement stérique autour du groupement isocyanate peut affecter sa réactivité. Les principaux isocyanates utilisés dans la synthèse de PU sont bifonctionnels de structure aliphatique ou aromatique. Les structures chimiques des isocyanates les plus rencontrés dans l'industrie sont représentés sur la Figure 1-4.

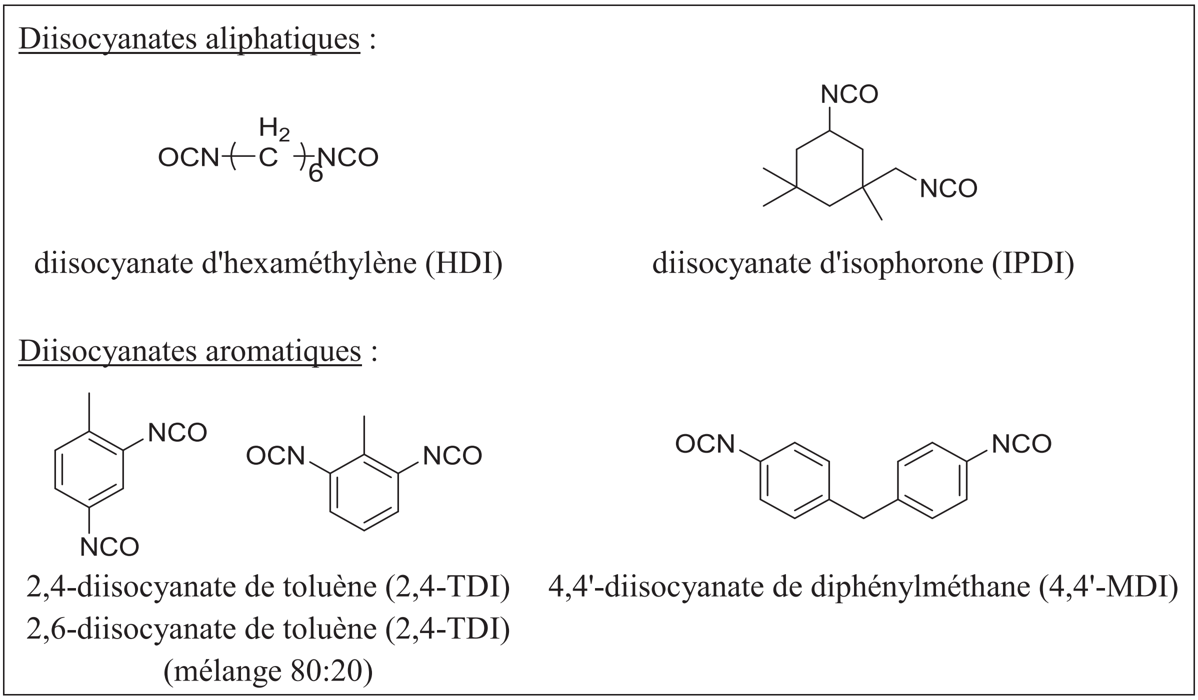


Figure 1-4. Structure des isocyanates les plus couramment rencontrés.

Malgré la forte réactivité des isocyanates, la réaction de synthèse des PU peut être catalysée. Cette catalyse est tout particulièrement importante pour la sélectivité. Les catalyseurs les plus utilisés sont des bases de Lewis de type amine tertiaire ou encore des complexes métalliques essentiellement à base d'étain comme le dilaurate de dibutylétain (DBTDL) ou l'octanoate stanneux, bien que ces derniers tendent à être remplacés par des composés moins toxiques.[5]

1.1.2. Réactions secondaires

L'importante réactivité des isocyanates est également responsable de nombreuses réactions secondaires pouvant influencer le procédé de polymérisation.[6, 7] La Figure 1-5 offre un aperçu des principales réactions mettant en jeu un ou plusieurs isocyanates. Toutes ces réactions sont exothermiques.

En présence d'eau, les isocyanates forment des amines. Cette réaction est accompagnée d'un dégagement de dioxyde de carbone, pouvant générer la structure cellulaire des mousses PU. L'eau est alors considérée comme agent d'expansion chimique. Les amines formées peuvent alors réagir spontanément avec d'autres fonctions isocyanates pour donner des urées. Ces groupements urées confèrent une excellente résistance chimique et thermique aux matériaux et sont recherchés dans certains systèmes PU. Les amines sont particulièrement utilisées comme allongeurs de chaînes pour la formation de polyuréthanes-urées (PUU).[8]

Des biurets ou des groupements allophanates peuvent également être obtenus à des températures élevées (supérieures à 110°C) suite à la réaction des isocyanates avec, respectivement, des groupements urées ou uréthanes. Ces réactions secondaires sont des sources supplémentaires de réticulation dans les systèmes PU.

Si les polyols contiennent des groupements carboxyles, il est possible de former un anhydride carbamique par réaction avec un isocyanate. Instable, ce composé se décompose pour créer des fonctions amides et libérer du CO_2. Cependant, la réactivité des isocyanates envers les acides carboxyliques est beaucoup plus faible qu'avec les alcools, l'eau ou les amines.

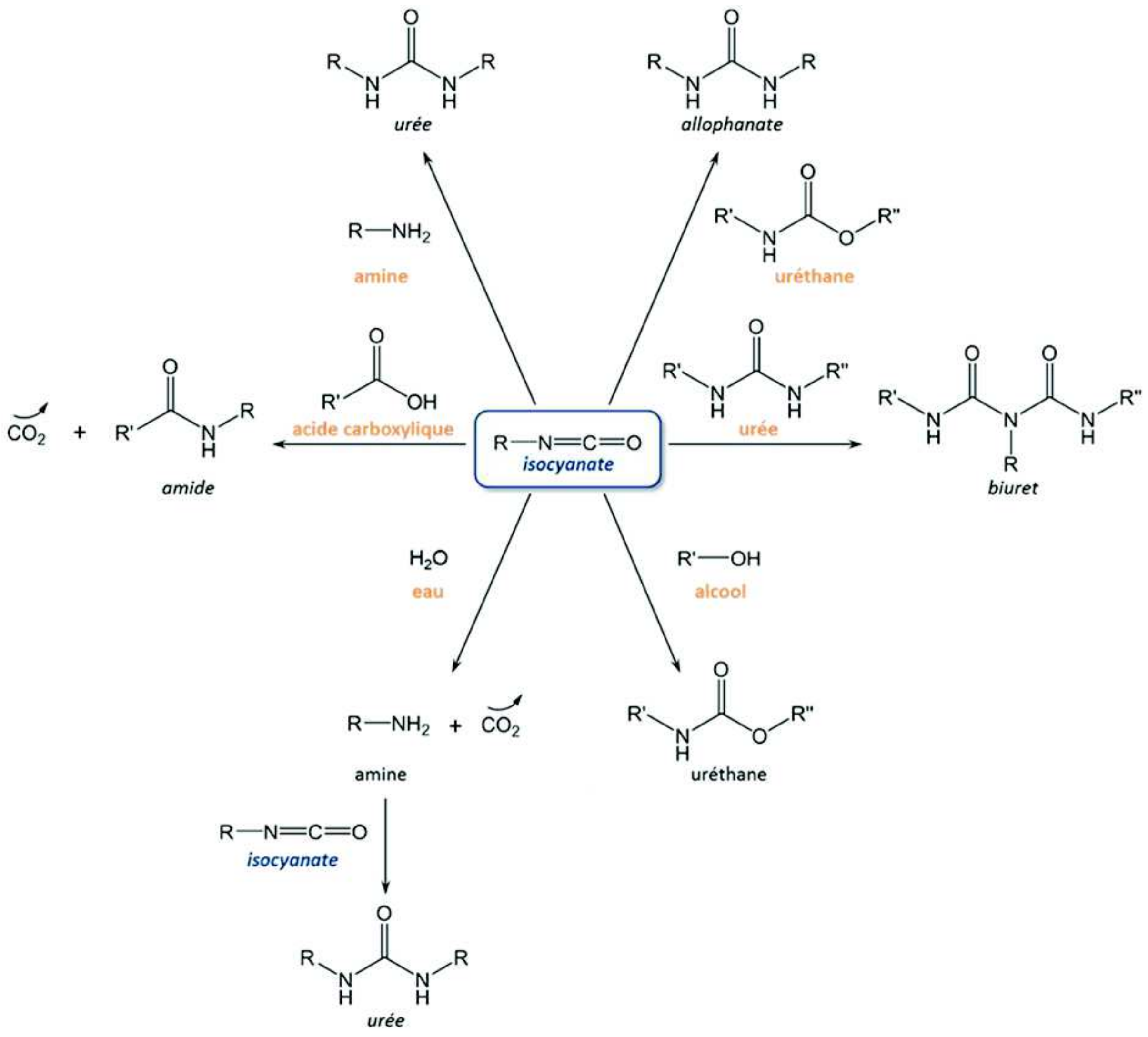


Figure 1-5. Principales réactions des isocyanates.

Les isocyanates peuvent également réagir entre eux et former des dimères (également appelés uretidinediones, Figure 1-6a), des trimères (ou isocyanurates, Figure 1-6b) ou encore des polymères d'isocyanates en présence de catalyseurs spécifiques (Figure 1-6c). La formation de carbodiimides à des températures supérieures à 180°C est un autre type de dimérisation des isocyanates (Figure 1-6d).

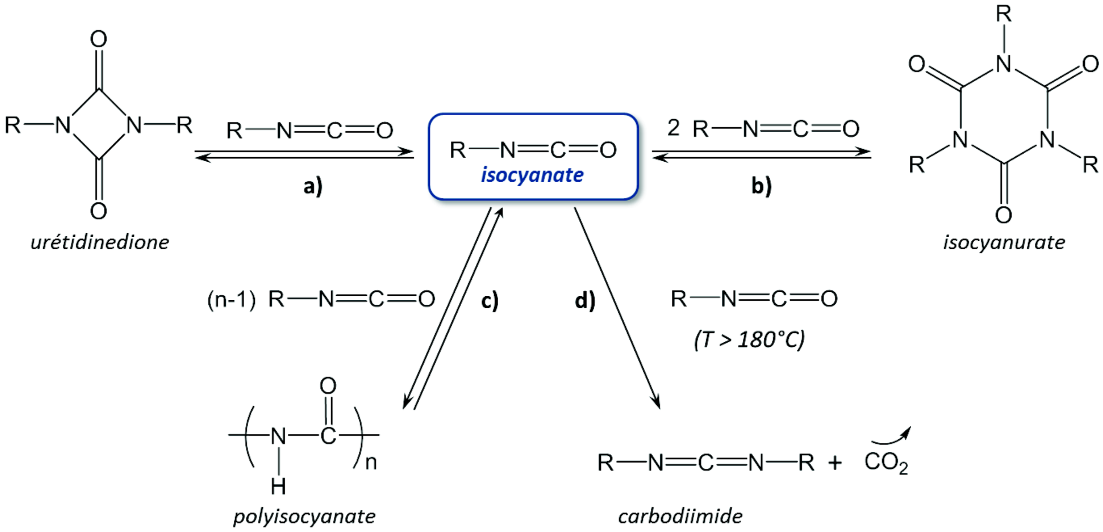


Figure 1-6. Réactions entre isocyanates.

Il est important de signaler qu'à des températures supérieures à 150°C, la liaison uréthane peut se dissocier pour reformer les réactifs initiaux (isocyanates et alcools).[9] D'autres voies de dégradation conduisant à la formation d'amines primaires et secondaires, de CO_2 et d'oléfines sont également possibles mais se produisent plus lentement et à des températures plus élevées. La réaction de formation des PU est donc réversible, tout comme la plupart des réactions secondaires.[4] La dégradation thermique des PU est donc un phénomène important, qui doit être pris en compte lors de l'étude de ces matériaux polymères.

1.2. Procédés de synthèse des PU

Deux techniques de synthèse des PU sont essentiellement rencontrées. Elles se distinguent principalement par l'ordre et la façon dont sont ajoutés les réactifs. On parlera ainsi de procédé en une ou deux étapes.

1.2.1. La technique « one shot »

Le procédé « one shot » consiste à mélanger directement et en un temps très court l'ensemble des réactifs et additifs nécessaires à la synthèse du PU. Cette technique est principalement utilisée pour l'obtention de mousses mais convient également à l'élaboration de PU thermodurcissables.

1.2.2. La technique multi-étapes

De nombreuses synthèses de PU font par exemple intervenir un procédé en 2 étapes avec passage par un prépolymère intermédiaire (Figure 1-7). Ce prépolymère est synthétisé lors de la première étape *via* la réaction entre un polyol et un diisocyanate en excès. Dans un second temps, ce prépolymère terminé par des fonctions isocyanates va réagir avec un allongeur de chaîne pour terminer la réaction et obtenir un PU linéaire de haute masse molaire. Cet allongeur de chaîne est généralement un diol de faible masse molaire, ou diol court, tel que le butanediol (BDO). Cependant, il peut également s’agir d’une diamine courte, en particulier dans les cas des PUU. Ce procédé en deux étapes permet de contrôler la structure du polymère et est ainsi particulièrement adapté pour l’obtention de PU thermoplastiques (TPU) élastomères.

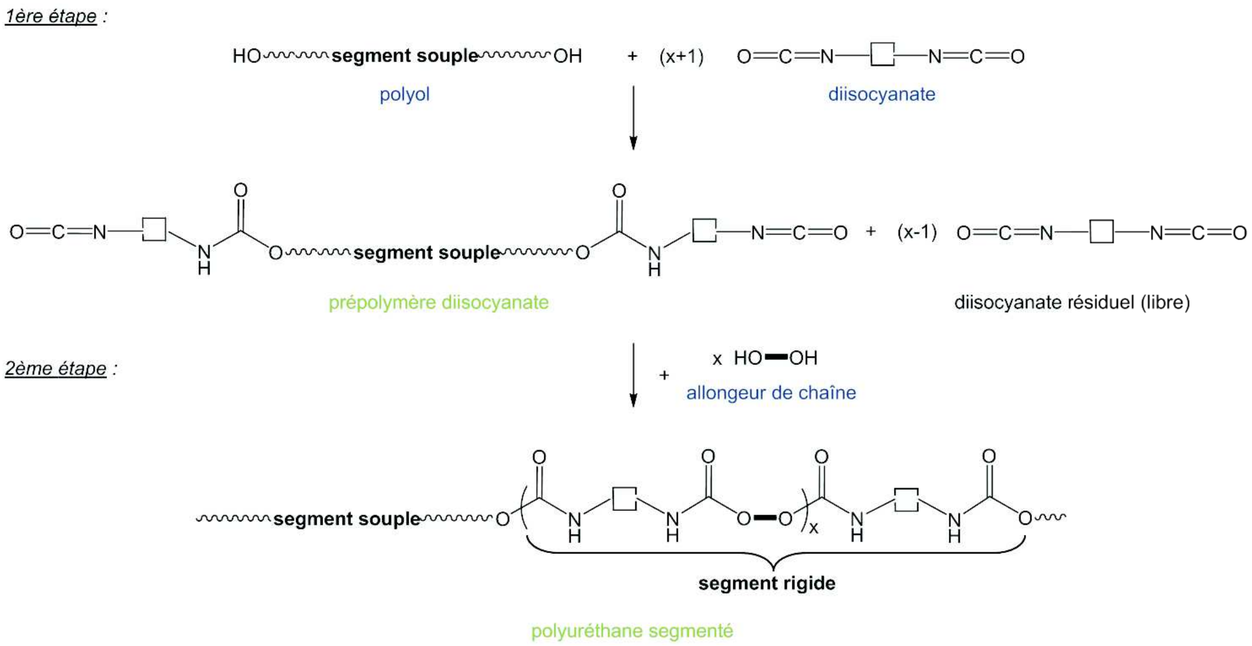


Figure 1-7. Schéma du procédé en 2 étapes pour la synthèse de TPU.

1.3. Morphologie des PU

1.3.1. Les grands types de PU

La polyvalence des PU est due à la fois à la diversité des structures chimiques des monomères mais également aux diverses architectures de chaînes qui permettent de moduler les propriétés physiques et chimiques des matériaux finaux. On peut retrouver dans les matrices PU trois grands types d’architectures macromoléculaires : linéaire, linéaire segmenté et réticulé.

Les PU linéaires sont obtenus à partir de monomères de fonctionnalité strictement égale à deux. L'utilisation de composés aliphatiques de masse molaire élevée entraîne la formation de PU ayant une température de transition vitreuse (T_g) relativement faible. En revanche, les diols de faible masse molaire ou les diisocyanates aromatiques permettent de former des chaînes linéaires plus rigides avec une T_g plus élevée. Lors d'un procédé en deux étapes, il est possible d'obtenir des PU linéaires segmentés, ou TPU. Ces TPU à morphologie spécifique seront détaillés dans la partie 1.3.2.

Lorsqu'au moins un des monomères est de fonctionnalité supérieure à deux, des PU thermodurcissables sont obtenus. En effet, en présence de monomères polyfonctionnels, un réseau tridimensionnel fortement réticulé est formé. La T_g de ces systèmes PU est élevée, pouvant atteindre 130°C.

1.3.2. Cas particulier des PU segmentés

Les PU segmentés, ou TPU, sont constitués d'une alternance de chaînes flexibles, ou segments souples (SS), formées principalement par le polyol et de blocs rigides issus de la réaction du diisocyanate avec l'allongeur de chaînes, appelés segments rigides (SR). Les différences de structures chimiques et l'incompatibilité thermodynamique entre les SS et les SR se manifestent par une séparation de phase. Comme l'illustre la Figure 1-8, cette microségrégation de phase entraîne la formation d'un système multiphasique où les SR se réorganisent et forment des microdomaines cristallins et/ou organisés (appelés phases rigides, φ_R) dispersés dans une matrice de SS (appelée phase souple, φ_S).

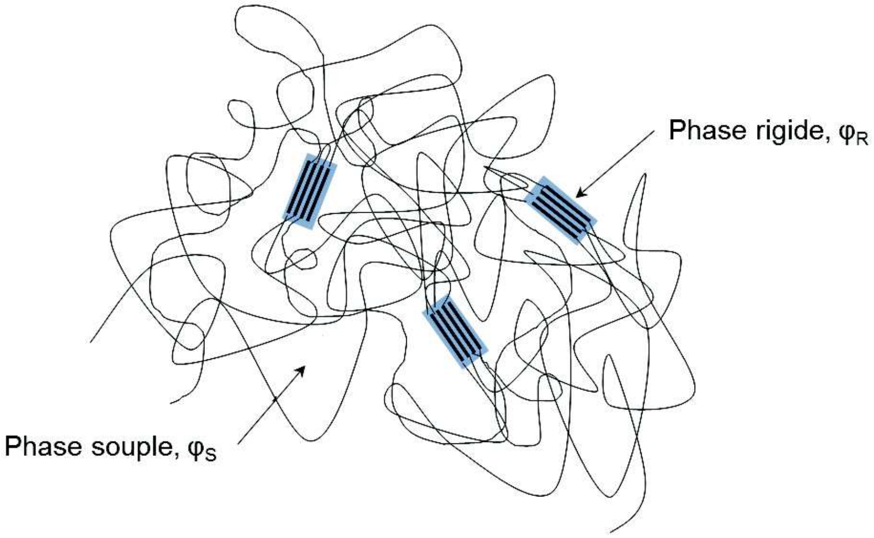


Figure 1-8. Structure multiphasique d'élastomères polyuréthanes.

Cette structuration particulière permet d'obtenir des propriétés mécaniques élastiques intéressantes. La φ_S confère au matériau une certaine flexibilité tandis que la φ_R assure sa rigidité et sa stabilité dimensionnelle. La qualité de la séparation de phase entre domaines souples et rigides va fortement influencer les propriétés finales de ces matériaux. Elle peut être reliée à différents facteurs.[10] Par exemple, le phénomène de ségrégation est accentué par la présence de liaisons hydrogène entre les divers groupements (uréthane, ester, éther, …) de chaînes voisines d'une même phase. En revanche, la formation de liaisons hydrogène entre des segments de domaines différents limite la séparation de phase. La masse molaire des segments souples est également un élément important dans la structuration des TPU. Pour une même quantité de segment rigide, l'augmentation de la masse molaire du segment souple améliorera la séparation de phase dans la matrice.[8]

2. Toxicité des isocyanates et PU : vers de nouvelles approches

2.1. Impacts des isocyanates sur la santé

L'explosion d'un réservoir contenant de l'isocyanate de méthyle survenu en 1984 à Bhopal en Inde sur un site de production de pesticide d'Union Carbide est l'accident le plus marquant illustrant le danger des isocyanates. L'émission d'isocyanates dans l'air a causé le décès de plus de 3000 personnes dans les heures suivant la catastrophe, plus de 25 000 sur le long terme, et des effets (pulmonaires, ophtalmiques, reprotoxiques, immunologiques, neurologiques et hématologiques) extrêmement néfastes pour la santé de plusieurs dizaines de milliers de survivants résidants aux environs de l'usine.[11]

Les isocyanates sont des irritants et des sensibilisants cutanés et pulmonaires puissants dont la manifestation la plus sévère, occasionnée par une exposition prolongée, est l'asthme professionnel.[12] Une surexposition aux isocyanates peut également causer différentes inflammations dont des irritations de la peau (dermatites), des yeux (conjonctivites) ou de diverses parties du système respiratoire. Certains isocyanates sont même classés comme agents cancérigènes, c'est-à-dire pouvant provoquer, aggraver ou sensibiliser l'apparition d'un cancer.

Les premiers problèmes médicaux liés aux isocyanates ont été détectés chez des ouvriers dès le début de la production industrielle de TDI en 1951.[13] Peu de temps après, des effets similaires sur la santé ont été observés pour les autres diisocyanates. À l'époque, l'exposition aux diisocyanates avait été associée uniquement à leur phase vapeur, inhalée ou absorbée par la peau. Pour cette raison, une des premières approches élaborées afin de minimiser l'exposition des travailleurs aux vapeurs d'isocyanates a été de remplacer dans les formulations les monomères isocyanates par des prépolymères, de plus hautes masses molaires donc moins volatiles. Il a été démontré plus tard que l'exposition aux prépolymères pouvait également conduire à des problèmes de santé.[14, 15]

2.2. Normes et classifications

Des normes d'exposition ont été mises en place afin de préserver la santé des travailleurs. La différence de volatilité entre les divers isocyanates a entraîné des règlementations et limitations généralement spécifiques à chacun d'eux. Le Tableau 1-1 regroupe les teneurs en isocyanates libres tolérées dans les prépolymères ainsi que leur étiquetage associé. Les valeurs des quatre principaux isocyanates employés dans l'industrie des PU ont été retenues. Les isocyanates aromatiques sont les plus nocifs. Le TDI, avec sa pression de vapeur saturante élevée, est l'isocyanate le plus néfaste pour la santé.

Tableau 1-1. Étiquetage et teneurs limites en isocyanates dans les prépolymères (d'après le règlement (CE) N°1272/2008).

	4,4'-MDI	**TDI**			**IPDI**		**HDI**	
Pression de vapeur saturante (Pa)	< 0,002 (à 20°C)	1,3 (à 20°C)			0,04 (à 20°C) 0,9 (à 50°C)		0,7 (à 20°C) 6,7 (à 25°C)	
Teneur tolérée*	C ≥ 1%	0,1% ≤ C < 1%	1% ≤ C < 7%	C ≥ 1%	0,5% ≤ C < 2%	C ≥ 2%	1% ≤ C < 7%	C ≥ 1%
Etiquetage	Xn, nocif	Xn, nocif	T, toxique	T+, très toxique	Xn, nocif	T, toxique	Xn, nocif	T, toxique
Effet cancérogène suspecté	**OUI**	NON	**OUI**		NON		NON	

La teneur tolérée C correspond à un pourcentage en poids du monomère libre, calculé par rapport au poids total du mélange.

En ce qui concerne la cancérogénicité, il existe plusieurs classifications. Les plus connues sont celles du Centre International de Recherche sur le Cancer (CIRC) et celle de l'Union Européenne qui est en train d'être supprimée progressivement au profit du Système Général Harmonisé (SGH ou GHS en anglais), à l'initiative des nations unies afin d'harmoniser les différents systèmes d'évaluation des risques chimiques existants à travers le monde. C'est le règlement (CE) N°1272/2008 actuellement en vigueur, également appelé CLP (de l'anglais Classification, Labelling, Packaging), qui permet de faire appliquer les règlementations du

SGH au sein de l’Union Européenne. Le règlement CLP s'intègre dans le dispositif REACH d’enregistrement des produits chimiques. Les agents cancérigènes y sont classés en deux catégories, dont la première peut être subdivisée en deux sous-catégories (Figure 1-9). Seuls les isocyanates aromatiques TDI et MDI sont classés, tous deux en catégorie 2 depuis 2006 pour le premier et 2009 pour le second. C’est d’ailleurs cette classification révisée du MDI, l’isocyanate le plus utilisé dans l’industrie, qui a fait réagir les fabricants de PU et les a poussé à envisager de nouvelles voies de synthèse.

Catégorie 1 : Cancérogènes avérés ou présumés pour l’être humain

- Catégorie 1A : L’effet cancérogène de ces substances pour l’être humain est AVÉRÉ : l’affectation des substances dans cette catégorie s’appuie largement sur des données humaines.
- Catégorie 1B : L’effet cancérogène de ces substances pour l’être humain est SUPPOSÉ : l’affectation des substances dans cette catégorie s’appuie largement sur des études animales.

Catégorie 2: Substances suspectées d’être cancérogènes pour l’être humain

L’affectation d’une substance dans cette catégorie repose sur des résultats provenant d’études humaines et/ou animales, mais qui ne sont pas suffisamment convaincants pour classer la substance dans la catégorie 1.

Figure 1-9. Catégories de danger pour les substances cancérogènes.[16]

2.3. Solutions envisagées

Afin de diminuer la toxicité des PU et ainsi répondre aux normes actuelles, trois méthodes peuvent être adoptées. La première voie vise à diminuer la concentration résiduelle en isocyanates libres dans le milieu (évaporation, recristallisation, …). Une seconde approche consiste à masquer les fonctions isocyanates libres restantes c’est-à-dire à les fonctionnaliser avec des composés à hydrogène labile, appelés agents de blocage, afin d’obtenir des monomères libres non volatiles et donc moins toxiques. Un exemple de cette technique est la synthèse des polyuréthanes silylés. Enfin, la troisième solution est la suppression totale d’isocyanate en tant que réactif. C’est cette dernière approche qui va être décrite dans la suite de ce manuscrit.

3. Les PU sans isocyanate – Etat de l'art

La troisième partie de ce chapitre bibliographique présente un état de l'art sur les polyuréthanes sans isocyanate (NIPU), et plus particulièrement les NIPU biosourcés obtenus *via* la réaction d'aminolyse. Les ressources renouvelables disponibles, les différentes voies de synthèse des monomères et des NIPU ainsi que les propriétés des matériaux finaux sont abordées.

Review :

Biobased nonisocyanate polyurethanes

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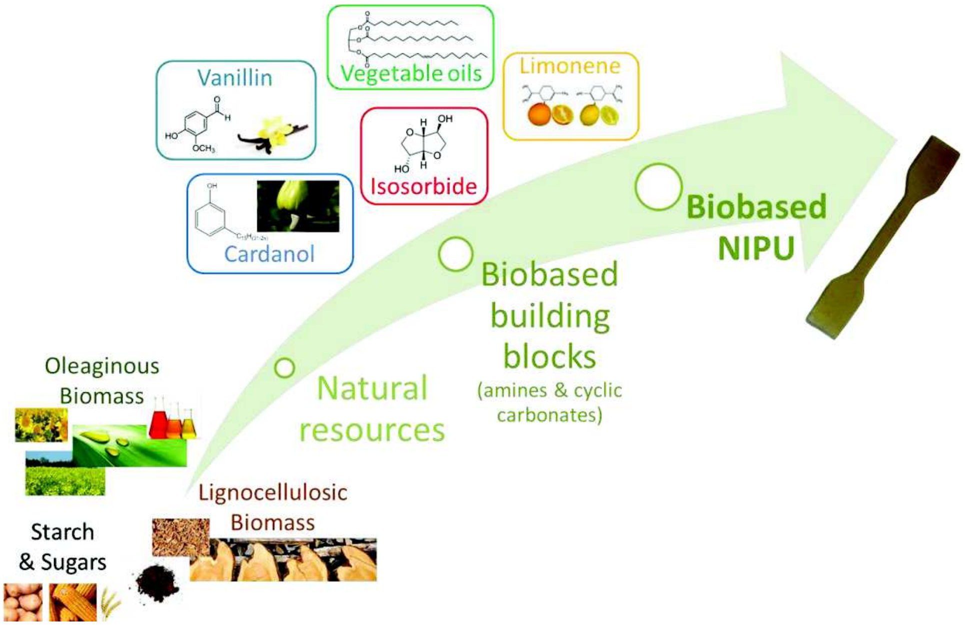
Progress in Polymer Science – Submitted article

Graphical abstract



Abstract

The world of polyurethane has considerably evolved over recent years with different and often complementary trends. After substitution of petrochemical polyols and isocyanates by their biobased equivalent, a new generation of advanced and safe polyurethanes is achieved *via* a synthesis without isocyanate. In addition to be more respectful of the environment, nonisocyanate polyurethanes (NIPUs) are also healthier. This overview presents a state of art with the convergence of both approaches, with the particular case of biobased NIPUs *i.e.*, healthy and environmental friendly materials. Novel biobased building blocks dedicated to this chemistry were also presented, leading to promising biobased NIPU materials with advanced properties. However, in all the cases, various innovative chemical strategies have already been involved including the reaction of cyclic carbonate with amines. One of the major problems still remains the low reactivity of this alternative chemistry. The slow kinetics and the low molar masses of the corresponding macromolecular structures, compared to the conventional systems based on isocyanates, limit their industrialization and commercialization. However, many efforts and researches in developing novel biobased NIPUs have resulted in significant studies in this field over the recent years.

Keywords

aminolysis, cyclic carbonate, renewable resources, nonisocyanate polyurethane.

3.1. Introduction

Crude oil is traditionally used as feedstock for the chemical industry. This strong dependence on petroleum resources is being threatened by the predictable fossil shortage and its associated high price fluctuations in the upcoming years. In addition, global warming due to carbon dioxide emissions and increasing environmental concerns lead chemical industries but also academic laboratories to develop new sustainable chemical routes.[17] Their current challenge is to substitute fossil resources by renewable ones to synthesize new promising molecules for the elaboration of sustainable materials and especially new ranges of biobased polymers.[18] Biobased means that the polymers are, either partly or fully based on biomass (*e.g.*, from vegetal, animal, mushroom resources). Biobased contents are mainly determined through the ^{14}C content, as fossil carbon resources do not contained anymore this isotope.[19]

Among biobased polymers, attention has been paid on polyurethanes (PUs), which are one of the most common polymers used nowadays in the industry, with a global market estimated at around 14,000 Kt in 2010.[20] Due to the multiplicity of their structures, and their versatile properties, they can be used in various applications. They can be found as foams (rigid or flexible) or compact materials (elastomers, thermoplastics or thermosets). The main application areas are in insulation, automotive, construction, household furniture and bedding, sports, coatings, packaging, fibers and textiles, electronics, footwear, and different appliances.[6, 21]

Nowadays and on agreement with a more sustainable development, a great number of studies have been realized in the field of biobased PUs, in the academic and industrial worlds.[22-27] Polyurethane is commonly the product of the reaction of polyols and polyisocyanates. Both polyols and polyisocyanates can be biobased. Various researches were particularly focused on biobased polyols (i) from fermentation of biomass (white biotechnologies)[28-30] or (ii) directly extracted from biomass and then chemically modified, such as the oleochemical resources.[24, 25, 31-33] Many industries (BASF, Cargill, Croda, Huntsman, Oleon) now produce their own grades of biobased polyols available in various ranges.[32] Different works on biobased isocyanates were also published but to a much lesser extent.[24, 34-37] The main raw materials are vegetable derivatives (*e.g.* soybean oil, castor oil, and oleic acid). However, isocyanates from other renewable resources such as isosorbide[38] were also obtained. Some companies are currently emerging in the industrial synthesis of biobased isocyanates such as Cognis (BASF-Germany), which produces 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane from a dimer fatty acid, and Vencorex (Joint Venture between PTT Global Chemical – Thailand, and the Perstorp Group), which commercializes an aliphatic polyisocyantae named Tolonate©. All these recent developments show that fully biobased PUs could be produced in a next future.[39]

However, biobased PUs do not mean health friendly products. In this way, the second generation of environmental friendly PUs must also be non-toxic and health friendly, with a low impact on the environment. Then conventional PUs must be modified and new perspectives must be found. A new trend is emerging with the elaboration of NonIsocyanate PolyUrethanes (NIPUs), since isocyanates are harmful and suspected to be carcinogen for humans,[12, 40-43]. A repetitive exposure to them can lead to skin irritation and incurable respiratory problems such as long-term asthma. Moreover, the synthesis of isocyanates requires the use of noxious substances such as phosgene. Since January 2009, a new European regulation was adopted, limiting the free isocyanate content in the medium.[40] This regulation should be amplified and isocyanates could be banned or strictly restricted in a close future. Thus, three answers can be brought, such as (i) the reduction of isocyanate concentration in the media, (ii) the blocking of the remaining free isocyanate groups, or (iii) the replacement of isocyanates as chemical reagents. This latter approach, called NIPU route, brings new chemical pathways and will be the main subject of this review. This overview is mainly focused on biobased NIPUs, principally synthesized *via* the aminolysis reaction. After a state of the art on NIPU synthesis, biobased building blocks for NIPU synthesis will be introduced. Then, NIPU materials and their corresponding properties will be described. Finally, the future of these advanced materials will be reported and analyzed.

3.2. Generality about NIPU synthesis

According to the literature, three main different routes to synthesize NIPUs have been reported such as (i) the AB-type azide condensation, (ii) the transurethane reaction, and (iii) the aminolysis.[44-46] These different strategies, which are either polycondensation or polyaddition reactions, will be briefly described below.

3.2.1. NIPU synthesis *via* azide condensation

The synthesis of NIPUs from azide compounds is an AB-type self-condensation between a hydroxyl and an acyl azide group. The corresponding monomer should therefore bring both of these functions.

3.2.1.1. Preparation of acyl azides

Acyl azides are most commonly prepared in excellent yield by acylation of sodium azide with acyl chlorides or carboxylic acids, previously activated with chloroformate (Figure 1-10).[47, 48]

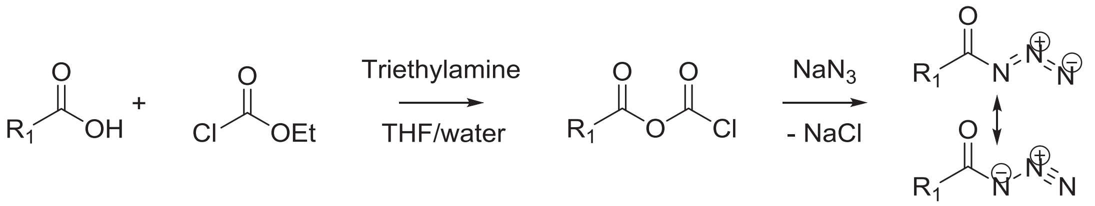


Figure 1-10. Acyl azide synthesis from carboxylic acid.

Hydrazine derivatives obtained from ester can also be converted into acyl azide *via* an oxidation reaction (Figure 1-11).

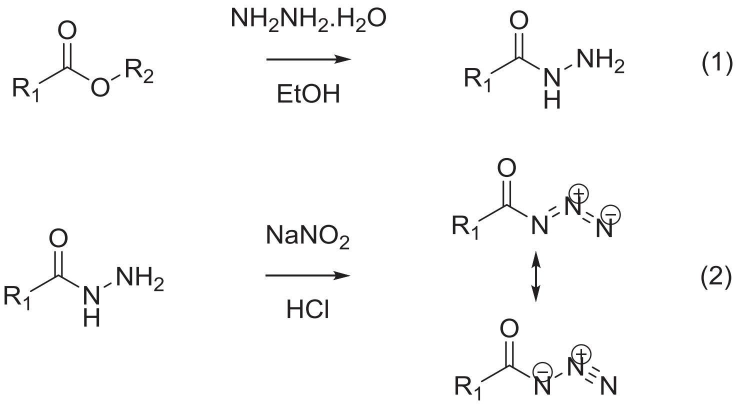


Figure 1-11. Synthesis of acyl azide from ester.

3.2.1.2. Polymerization from acyl azides

The synthesized monomers contain both hydroxyl and acyl azide functions. To carry out the polymerization, a Curtius rearrangement must be first achieved to convert the acyl azide into isocyanate (Figure 1-12). Such an arrangement requires a heating temperature from 80 to 100°C, for 10 to 24 hours.[47] Then, a AB-type self-condensation reaction between hydroxyl and isocyanate functional groups forms polyurethane. This polymerization is carried out consecutively to Curtius rearrangement. The provided heat is sufficient for the self-condensation and explains why the conversion of acyl azide to isocyanate requires a long reaction time.

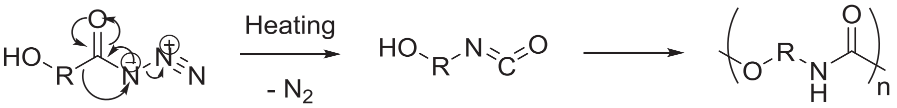


Figure 1-12. Mechanism of Curtius rearrangement followed by self-condensation stage.

Biobased NIPUs from fatty acid derivatives bearing hydroxyl moieties, synthesized by carbon double bond epoxidation or thiol-ene chemistry, were recently synthesized *via* this route and developed. The obtained NIPUs show a thermoplastic behavior with a phase-separated morphology.[47, 49]

3.2.1.3. Drawbacks of this approach

Although no isocyanate is used as starting reagent, this route has nevertheless many disadvantages either through ester or carboxylic acid pathway linked to the different steps, as shown by Table 1-2. The major inconvenient of this approach lies in the fact that the intermediate product is based on isocyanate group, in opposition with the spirit of the NIPU strategy. In addition, this method is very time and energy consuming. All these issues explain the very limited development and literature about this route to produce NIPUs.

Table 1-2. Azide condensation pathways and main drawbacks.

Acyl azide preparation		**Polymerization**
Ester pathway	Carboxylic acid pathway	
- Explosive hydrazine - Low yield for NIPUs - Long preparation time (3 days)	- Explosive sodium azide - Very low working temperature (0°C)	- High heating temperature (80 to 100°C) - Long reaction time (10 to 24 hours) **- Isocyanate as synthesis intermediate**

3.2.2. Transurethanization

The transurethane process is the second route envisaged for the synthesis of NIPUs. It is a two-step process with first the formation of diurethanes monomers (by conventional routes or aminolysis), and then the reaction with a diol in the presence of a suitable catalyst, to form the final polymer.

3.2.2.1. Diurethane synthesis

Diurethanes monomers used as reactants can be synthesized from isocyanates and alcohols but also *via* the reaction between a carbonate and an aliphatic amine in the presence of a base.[50-53] High yields are obtained (from 22 to 100% with suitable bases).[51, 52] The use of dimethyl carbonate is interesting since it leads to the formation of methanol, easily removable *in situ* during the transurethanization step.

3.2.2.2. Transurethane process

To obtain NIPUs by transurethane reaction, diols must react with diurethanes (Figure 1-13). This polycondensation reaction requires a relatively high temperature (130–150°C). Synthesized alcohols must be extracted from the reaction medium to shift the equilibrium and increase the yield till 89%.[52]

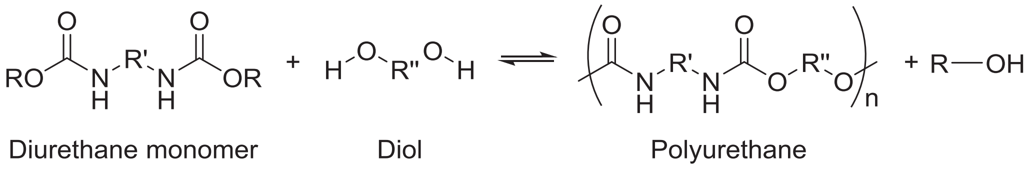


Figure 1-13. NIPUs from transurethane process.

3.2.2.3. Advantages and drawbacks

Transurethanization is a rapid reaction and the obtained NIPUs have high molar masses. However, the high reaction temperature remains a major drawback.

3.2.3. Aminolysis

One of the main routes to NIPUs is aminolysis. This reaction involves the opening of a cyclic carbonate (or cyclocarbonate) with an amine. The following discussion will be mainly focused on the characteristics of the aminolysis and the current industrial applications.

3.2.3.1. Reagents

The synthesis of cyclic carbonates and their uses first appeared more than sixty years ago.[54] Nevertheless, industrial applications have only been developed over the last fifteen years. The most common cyclic carbonates commercially available are presented on Figure 1-14. They are of great interest for the production of many products.[54] Various routes to cyclic carbonates have to be considered. The principal and current synthetic paths will be discussed in the following section. Five-membered cyclic carbonates will be mainly presented even if other cyclic carbonates (*e.g.* 6-membered and thiocarbonates) exist and can also be involved as reactants for NIPU synthesis.

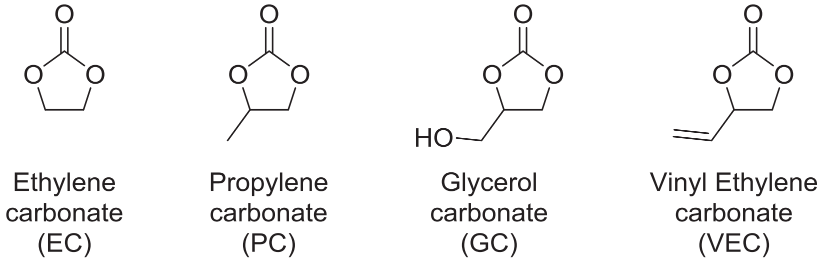


Figure 1-14. Most common cyclic carbonates.

Diamines (presenting aliphatic, cycloaliphatic or aromatic structures with various chain lengths) involved in the elaboration of NIPUs are always commercially available and will not be described in this section. Biobased intermediates will be highlighted in a dedicated paragraph below.

a) Historical synthetic paths to cyclic carbonates

Traditionally, the synthesis of cyclic carbonates was based on a chemical reaction between a diol and phosgene, or derivatives.[55, 56] The advantage of these reactions is the great reactivity of phosgene leading to high yields, even if they required additional purification steps. However, due to phosgene and its derivatives toxicity,[57] attractive alternative approaches have been considered. The most common routes involve both diols and epoxides reactants (Figure 1-15).[58]

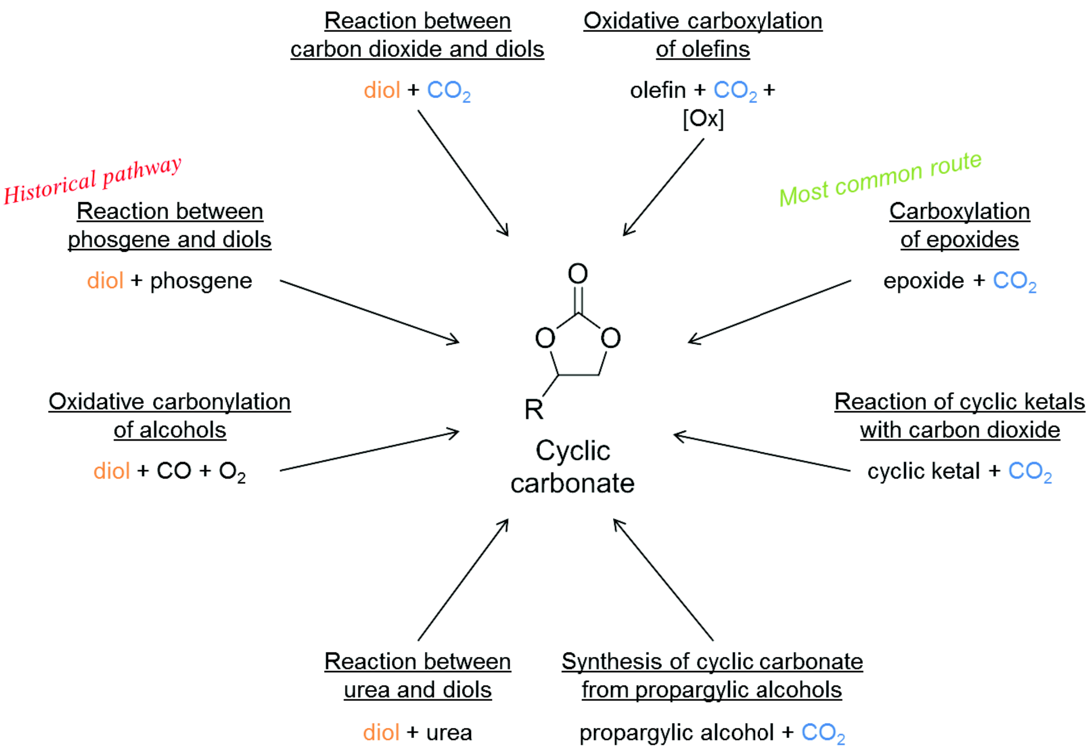


Figure 1-15. Chemical pathways to cyclic carbonate.

b) Cyclic carbonate synthesis from diols

Although less reactive than epoxides, diols can however react to form cyclic carbonates. Consequently, high temperature and pressure conditions as well as catalysts are generally required.

Oxidative carbonylation of alcohols

Diols can be converted into cyclic carbonates by an oxidative carbonylation with carbon monoxide and oxygen as oxidant reagent (Figure 1-16). The reaction is mainly promoted by palladium.[59, 60] However, copper transition metal compounds [61] can also be used. In recent years, new heterogeneous catalysts have been studied since the homogeneous catalyst systems are inefficient with issues linked to their separations and recoveries.[62]

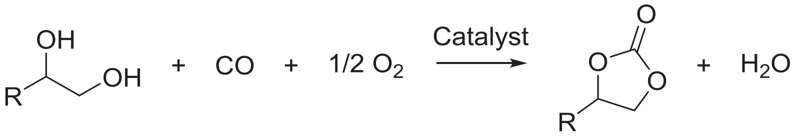


Figure 1-16. Oxidative carbonylation of diols.

Reaction between diols and urea

Cyclic carbonates can also be synthesized from urea and diols, under reduced pressures and high temperatures. It is a two-step reaction with formation of ammonia and oxazolidone, in addition to the desired cyclic carbonate.[63] Addition of a suitable metal oxide catalyst such as zinc oxide, improves the selectivity towards carbonate compounds (Figure 1-17, reactions (1) to (3)). Various diols were tested, and substituted. Six-membered ring cyclic carbonates were obtained.[64, 65] It is noticeable that the formed ammonia can be recycled by reaction with CO_2 to produce water and urea, which can also be reused (Figure 1-17, reaction (4)).

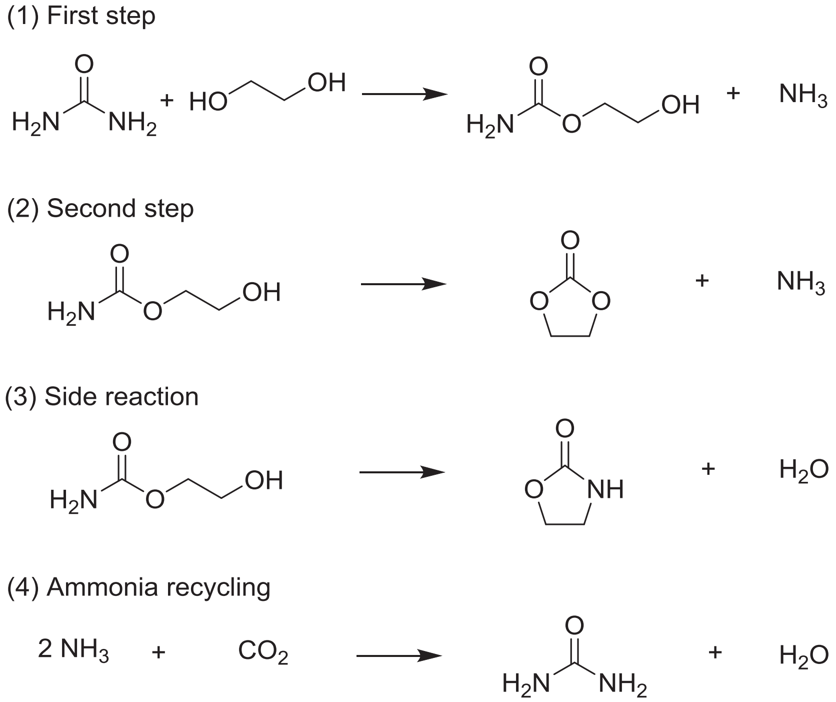


Figure 1-17. Conversion of diols into cyclic carbonate *via* urea.

c) Reactions involving carbon dioxide

Carbon dioxide (CO_2) is a sustainable resource and a naturally-occurring chemical compound.[66] CO_2 can be biobased and *e.g.*, produced from fermentation process. Furthermore, recycling waste CO_2 into a valuable chemical feedstock is also an effective and sustainable solution. Although the use of harmful phosgene and solvents were formerly required, it is now possible to produce cyclic carbonates from CO_2 and various reactants *e.g.* oxiranes and olefins.[67, 68] However, due to low reactivity, high energy or preliminary activation of the molecule is required.

Synthesis of cyclic carbonates from epoxides and CO_2[69]

The current and industrial common pathway to synthesize cyclic carbonate is the bubbling of CO_2 into oxiranes in the presence of catalysts, such as halides (mainly potassium iodide) and onium salts (tetraethyl ammonium bromide and derivatives), under high temperatures and pressures (Figures 1-18 and 1-19).

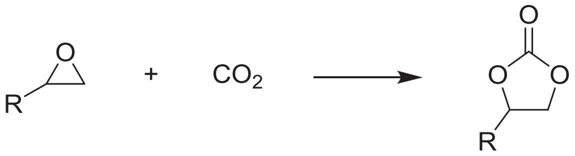


Figure 1-18. Cyclic carbonates from epoxides and CO_2.

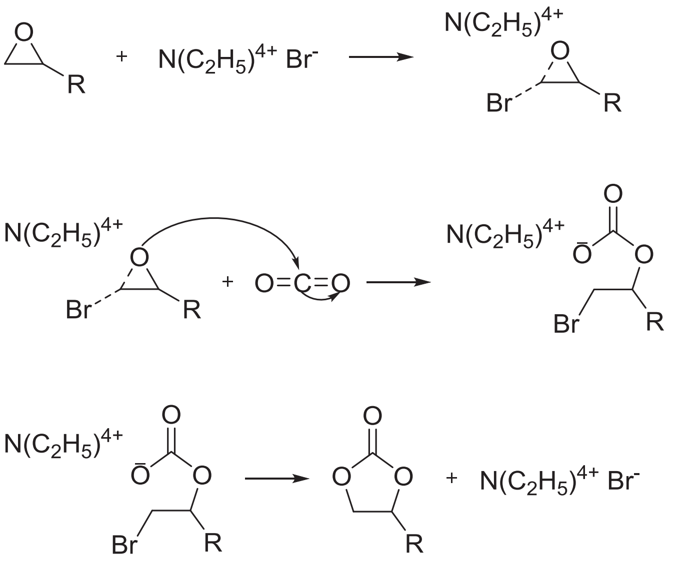


Figure 1-19. Mechanism synthesis of cyclic carbonates from epoxides.[54]

Carboxylation of epoxides was first reported in 1943 and was since well described with more and more literature, particularly about the catalysis systems.[70] A wide range of catalyst systems, both homogeneous and heterogeneous, have already been reported and reviewed.[67, 69, 71] The objectives of these various developments are increasing the catalytic activity and improving recycling. Progresses were also realized to avoid health and environmental issues by using non-halogen catalysts such as metal oxides, or waste CO_2. It appears from all these studies that the most effective catalysts combine both a Lewis-acid to activate the epoxide, and a Lewis- or Brønsted-base to initiate the CO_2 molecules.

Furthermore, due to poor solubility of CO_2 inside conventional solvent, in many cases solvent-free reactions are achieved even if cyclic carbonate can be used as solvent.

Developments on other media were also performed. New alternatives are synthesis in supercritical carbon dioxide ($scCO_2$), in ionic liquids -as solvents and catalysts-,[72-74] or both, combined. Reactions are achieved under mild temperatures and atmospheric pressures, and enable energy and economic savings. Moreover, catalyst recovery is enhanced due to phase separation between $scCO_2$ and cyclic carbonate, contrary to oxirane. Some new approaches such as microwave synthesis are also emerging.[75]

Oxidative carboxylation of olefins

Oxidative carboxylation of olefins is a direct conversion of olefins and CO_2 into cyclic carbonates, in which preliminary formation and separation of epoxides is avoided (Figure 1-20). Since 1962, with the first description of the synthesis,[76] numerous olefins were studied.[77, 78] However, styrene remains the most reported one (Table 1-3). Oxygen is the most commonly used oxidant, but syntheses with other oxidants were also developed.[77, 79, 80]

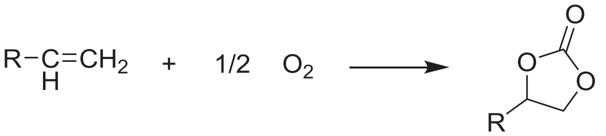


Figure 1-20. Oxidative carboxylation of olefin with oxygen as oxidant.

The conversion of styrene into corresponding cyclic carbonate was achieved using homogeneous[81] or heterogeneous catalysis.[82] Even if the heterogeneous catalyst is not deactivated after several cycles, carbonate yields were lower than for homogeneous conditions.[81] In addition to the low carbonate yield, these routes were not optimal due to poor selectivity, numerous by-products and high pressure and temperature conditions (Table 1-3). In 2004, yield and selectivity were improved in the presence of ionic liquids.[79, 80, 83] Furthermore, mild conditions and short reaction time were required.[80] Oxidative carboxylation of olefin was also performed in water with a metal-free method and hydrogen peroxide as oxidant, but high temperature and pressure were required.[77]

Table 1-3. Oxidative carboxylation of styrene *via* a one-step procedure.

Oxidant	Catalyst mode	Catalyst	Co-catalyst	Catalyst life time	Yield (%)	Selectivity	CO_2 Pressure (bar)	Temp. (°C)	Time (h)	Ref.
O_2	homogeneous	Rh	-	low	20 - 30	poor, numerous by-products	45	135	12	[81]
	hétérogeneous	Metal oxides (*e.g.* Nb_2O_5)	- $NbCl_5$	high	2 11		45	135	12	[82]
	homogeneous	Rh	TBAI	n/a	76	100	11	30	48	[78]
TBHP	ionic liquids	Ionic liquid, TBAB	-	n/a	33	n/a	150	80	6	[83]
			-		38		10	80	6	[79]
CHP			Au/SiO_2 and $ZnBr_2$		43		10	80	4	[80]
H_2O_2	homogeneous	metal-free	-	n/a	89	89	17 - 21	60	3	[77]

More recently, an efficient electrochemical method was developed, and high yields of cyclic carbonate under mild conditions and without dangerous oxidant or expensive catalysts were obtained.[84] Wu *et al.* also established a flow chemistry process valid for various olefins and based on NBS (N-bromosuccinimide) and DBU (1,8-diazabicyclo[5,4,0]undec-7-ene) as organic base, in which by-product formation was decreased as well as reaction rates and yields increased.[85]

Reaction between carbon dioxide and diols

Diols can react with CO_2 in supercritical conditions to form cyclic carbonate and water (Figure 1-21). Various catalysts such as metal oxides or organic bases were reported to promote the reaction.[86-90] All the catalytic systems present high selectivity, however yields still remain low and are, in addition to necessary water removal, the main drawback of this reaction.

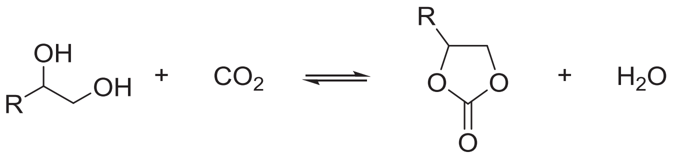


Figure 1-21. Synthesis from CO_2 and diols.

From cyclic ketal

Aresta *et al.* proposed a novel synthesis from cyclic ketals in $scCO_2$ under mild conditions assisted by transition metal catalysts.[91] In addition to cyclic carbonate, cyclohexanone is also obtained (Figure 1-22). An additional separation step is thus necessary but the molecule can be recycled for the ketal synthesis.

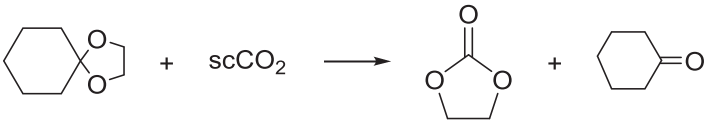


Figure 1-22. Synthesis of cyclic carbonate from cyclic ketals.

From propargyl carbonate

Cyclic carbonates have also been synthesized from propargyl alcohol derivatives and CO_2 in presence of a catalyst (Figure 1-23). Various transition metal compounds such as ruthenium,[92] cobalt,[93] palladium,[94, 95] and copper[96] were presented to promote the reaction. Phosphine complexes [97, 98] and carbene organocatalysts [99] were also efficient.

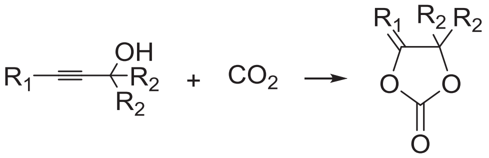


Figure 1-23. Cyclic carbonates from propargyl alcohol derivatives and CO_2.

The reaction usually achieves in organic solvents with high reaction conditions but $scCO_2$ media was reported to proceed smoothly in presence of guandine organic bases[100] or phosphines[68] as catalysts. The reaction was also carried out in ionic liquids with high yields and mild conditions.[101] More recently, polymer supported catalysts were used at low temperature and pressure conditions.[102, 103] They present an excellent stability and are easy to separate from the cyclic carbonate, which may their recycling possible. An electrochemically route at room temperature was also studied by Yuan *et al.*[104]

d) Synthesis of six- and seven-membered cyclic carbonates

In addition to standard five-membered cyclic carbonates (5CC), six-membered (6CC) or higher rings can also be synthesized. As 5CC are synthesized from epoxides and CO_2, 6CC can be obtained by reaction with oxetanes (Figure 1-24).

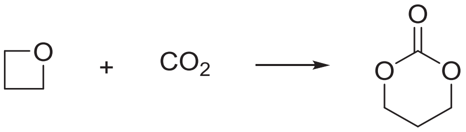


Figure 1-24. Synthesis of a cyclic carbonate from an oxetane.

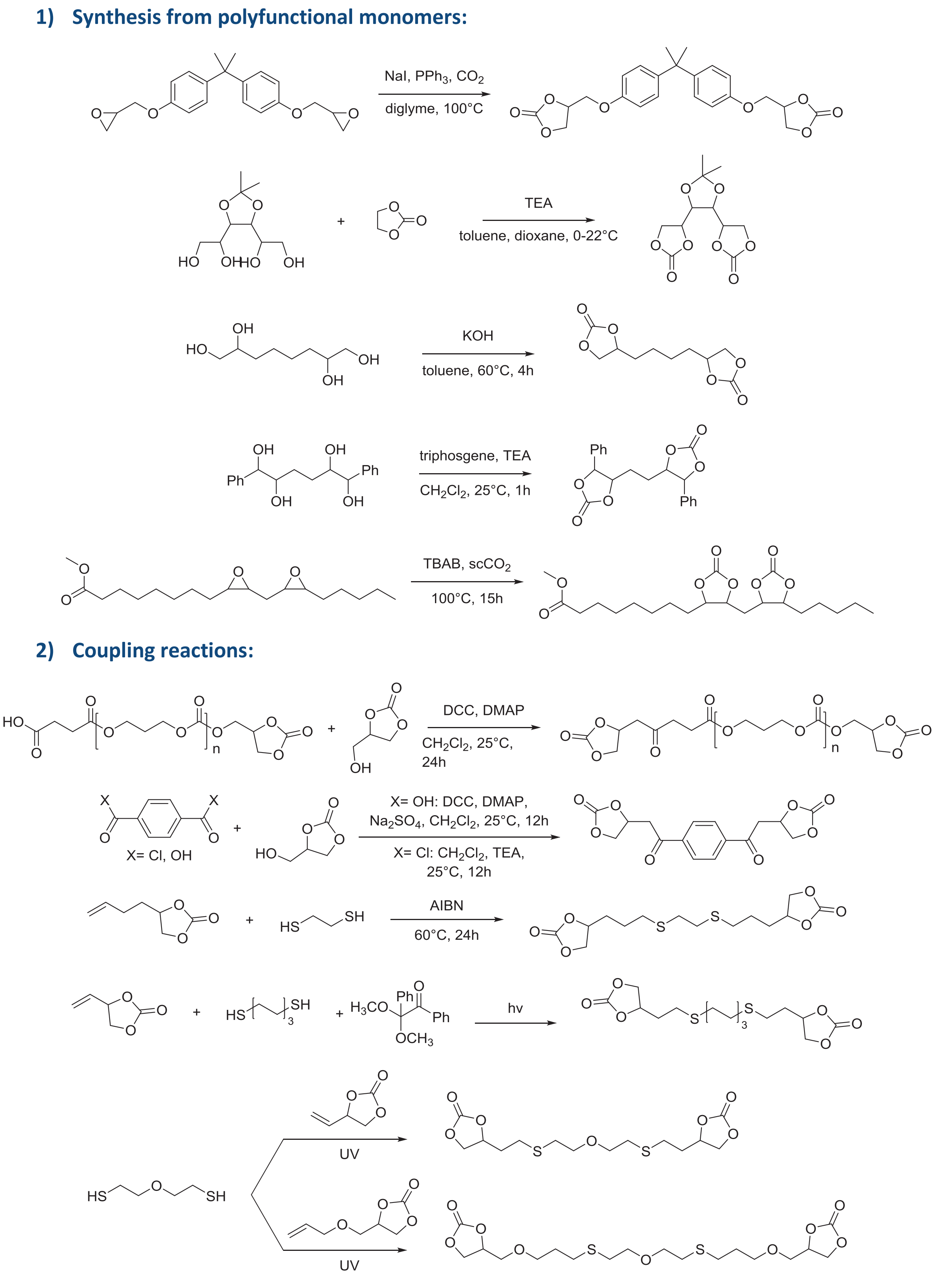
Oxethanes are four-membered cyclic ethers, and due to larger ring sizes, the latter are more stable than oxiranes. Consequently, the addition of CO_2 is less efficient. The first synthesis of

6CC from oxethane and CO_2 was reported in 1985.[105] They demonstrated that antimony catalyst yields to trimethylene carbonate at 100°C and 50 bars (P_{CO2}), in high selectivity. The yield was improved with organotin iodide catalyst with phosphine oxides.[106] Vanadium catalyst in presence of onium salt was found to promote the reaction under smooth conditions.[107] This additive combines both a Lewis acid to activate the oxetane ring and a nucleophile for ring-opening.

Besides cycloaddition from oxethanes, several routes for the synthesis of higher cyclic carbonate rings were reported. Instead of 1,2-diols involved in the synthesis of 5CC by oxidative carbonylation, 1,3-diols can also be used to obtain 6CC.[60] The main sources of carbonyl are however phosgene derivatives.[108] The most commonly procedure uses ethyl chloroformate in THF with TEA as catalyst for 2 hours a room temperature.[109] Seven-membered ring were also synthesized from 1,4-diols and triphosgene by Tomita *et al*.[110] They demonstrate that 6CC or 7CC are more reactive than conventional 5CC. However, due to a more difficult preparation they are less employed in the synthesis of NIPUs. Their main application is ring opening polymerization. A biobased seven-membered cyclic carbonate obtained from tartric acid was synthesized from 1,4-diols and triphosgene with pyridine in THF at room temperature for 6 hours.[111] Carbonate exchange reaction between alcohol and carbonate sources (phosgene, alkylene carbonate or dialkyl carbonate) in presence of a suitable catalyst is another path for cyclic carbonate synthesis.[112] Recently, Bornadel *et al.* reported such a transesterification reaction catalyzed with lipase, for a more sustainable chemistry.[113]

e) Dicyclocarbonate synthesis

Bifunctional cyclocarbonates are synthesized following the same chemical pathways as monofunctional compounds. Benyahya *et al.* reported syntheses of biscyclocarbonates commonly encountered (Figure 1-25).[114] Two main strategies can be adopted such as, (i) carbonation synthesis from epoxides or polyols with functionality of minimum two, and (ii) coupling reactions with monofunctional cyclic carbonates.



1) Synthesis from polyfunctional monomers:

2) Coupling reactions:

Figure 1-25. Various dicyclocarbonate synthesis routes. *(adapted from[114])*

Carbonation from bisepoxides or diols

Biscyclocarbonates can be obtained from the same chemical pathways than monofunctional compounds except that monomers own a bifunctionality. Thus dicyclocarbonates are obtained from polyols or from bisepoxides with CO_2.[67] This route is nowadays the main synthetic path involved, avoiding phosgene use and taking advantage of the high energy level of oxiranes.

Coupling reactions

A first coupling method for the synthesis of bicyclic carbonate is the esterification of a diacid or an acyl halide with glycerol carbonate, a cyclic carbonate having a hydroxyl function.[115, 116] This method using glycerol, a byproduct from the production of biodiesel, is very cost effective. However, this chemical pathway is more sensitive to hydrolysis reactions due to the presence of ester bonds in the chain. A new chemistry derived from thiol derivatives was developed to overcome this problem.

The reaction between vinyl cyclocarbonates and thiols is encountered in many recent studies.[58, 110, 117] The commercially available vinyl ethylene carbonate is the main precursor of this chemistry but other derivatives such as 4-[(prop-2-en-1-yloxy)methyl]-1,3-dioxolan-2-one are also encountered.[58] The products react together by radical addition activated by photoinitiation of AIBN[110] or hν decomposition of the initiator.[117] Even if no ester bond is formed, these compounds present cost and UV ageing drawbacks.

3.2.3.2. Aminolysis reaction

a) Detailed chemistry of the reaction

Aminolysis is a reaction of polyaddition. Cyclocarbonates react with amines to form urethane bonds, or more precisely hydroxyurethanes, since hydroxyl groups are also synthesized (Figure 1-26). According to the ring opening, mainly hybrid polyurethanes having both primary and secondary hydroxyl groups are formed.

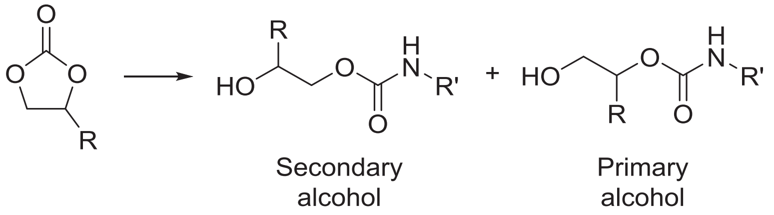


Figure 1-26. Cyclic carbonate aminolysis.

Ratio of primary vs. secondary hydroxyl groups

By orbital calculations (*ab initio* method), Steblyanko *et al.* have shown that urethane with secondary alcohol groups have a lower enthalpy of formation than primary alcohol (Figure 1-27).[118] Thus, the urethane bearing the secondary hydroxyl group is more stable. This is the major product. The secondary/primary alcohol ratio determined by ^{1}H-NMR and usually obtained is 70/30. [119] It varies depending on the used catalyst.

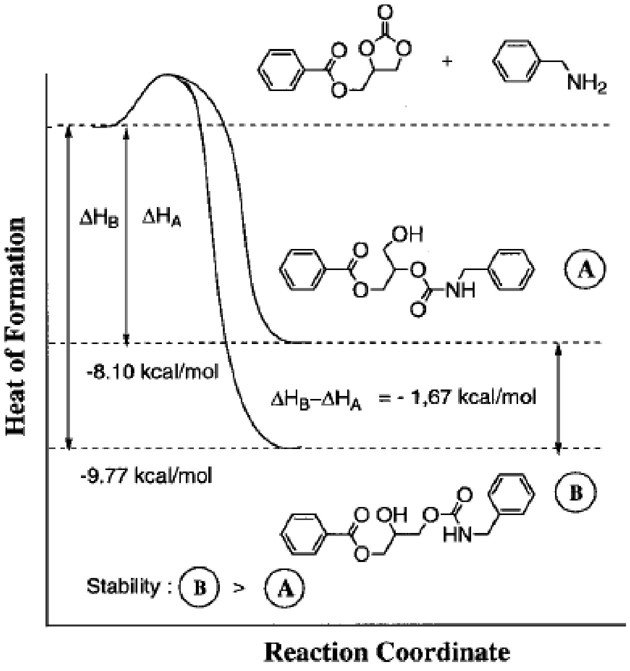


Figure 1-27. Energy profile of the addition (*via* ring opening) of cyclic carbonate with benzylamine.[118]

b) Mechanism

The reactivity between a cyclic carbonate and an amine group has been largely studied by Garipov *et al.*[120] They propose a three-step mechanism (Figure 1-28).

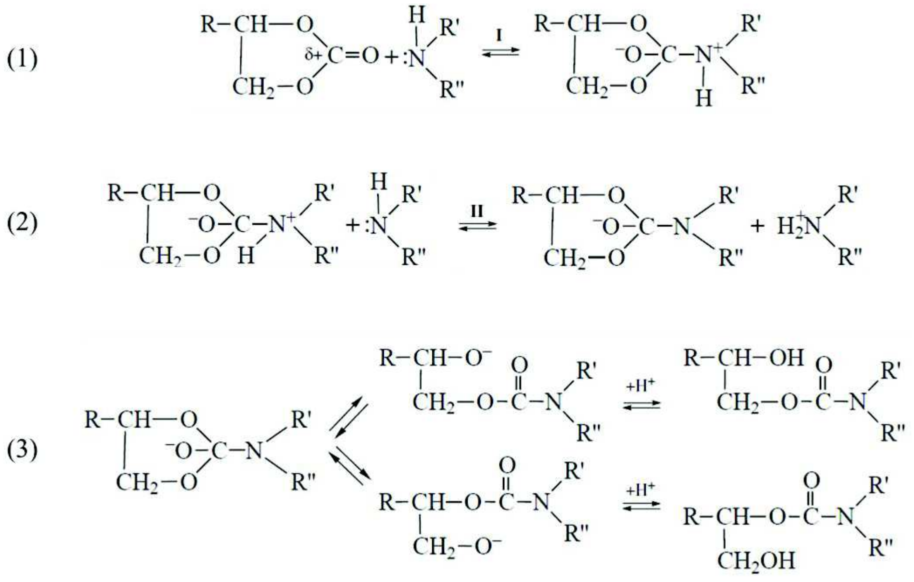


Figure 1-28. Aminolysis mechanism.[120]

The first step of the reaction is the nucleophilic attack of the amine on the cyclocarbonate carbonyl group, resulting in the formation of a tetrahedral intermediate. Then, a second amine deprotonates the tetrahedral intermediate. The last step, promoted by the strong electron withdrawing effect of the nitrogen atom, is the rupture of the carbon-oxygen bond of the cyclic carbonate, which leads to ring opening and formation of an alkoxyl ion. Then, this latter rapidly recombines with a proton to form the product of the reaction.

c) Side reactions

Formation of urea groups

At high temperatures (above 100°C), an amine molecule can react with the formed carbamate to yield a substituted urea.[121] Scheme of the reaction can be described in two stages (Figure 1-29).

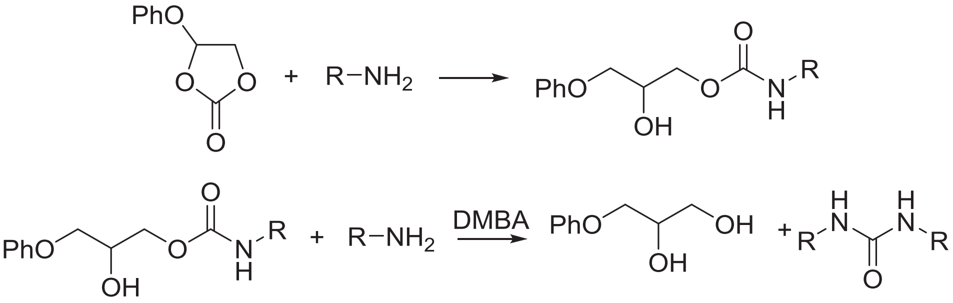


Figure 1-29. Urea group synthesis.[121]

First, cyclic carbonate reacts with amine to lead to a urethane with α or β hydroxyl groups. Then, β hydroxyl can react with a second amine to form a urea group. This second step is accelerated by tertiary amines.

Decomposition of glycerol carbonate into glycerol

The surprising presence of glycerol as by-product of an aminolysis reaction was recently highlighted.[122] Mouloungui *et al.* detected a significant formation of glycerol after the decomposition of glycerol carbonate by a hydrolysis process (Figure 1-30). They show that the glycerol yield largely depends on both the amine reactivity and the water content in the media. In organic medium, the yield of glycerol production is stable and low (approximately 10%) due to traces of water from the reactants. Secondary amines also limit the glycerol formation. On the contrary, in hydro-organic medium, water enhances the decomposition of glycerol carbonate into glycerol and reduces the hydroxyurethane yield.

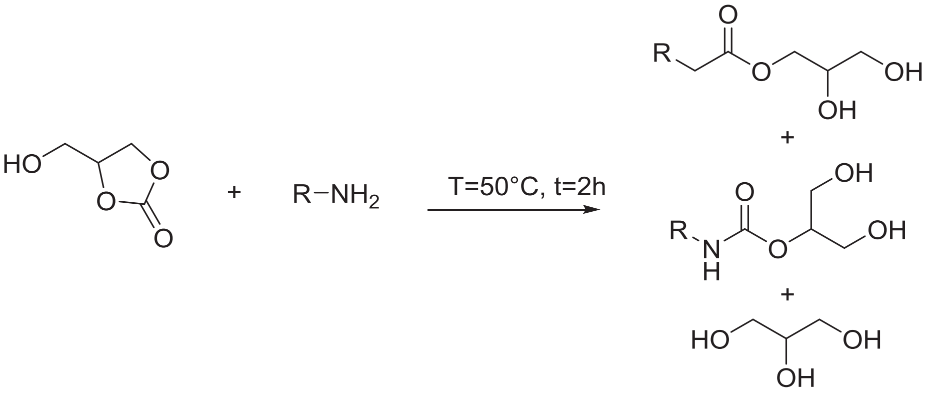


Figure 1-30. Aminolysis reaction and the corresponding chemical products.[122]

Synthesis of amide groups

If the cyclic carbonate is synthesized by reaction between carboxylic acid or derivatives and glycerol carbonate, the formed ester is then able to react with an amine to form amide groups. However, this reaction is not always evidenced. For instance, Tamami *et al.* do not detect amide group by ^{13}C-NMR and FTIR spectroscopy, at room temperature.[123] However, amide formation was confirmed at classical temperatures for aminolysis reaction (*i.e.*, from 70 to 100°C), as shown by the amide peak presence at 1636-1643 cm^{-1}. This secondary reaction is particularly highlighted in case of an amine excess regarding to cyclic carbonate.[124]

d) Parameters affecting the aminolysis

Nature of amine / Amine reactivity

The amine reactivity is governed by two main factors, which are the chemical structure and the molar mass.[125] Indeed, low molar mass amines as well as aliphatic and no substituted amines show a higher reactivity, compared to aromatic and substituted ones. Furthermore, the presence of a hydroxyl group on the amine causes an increase of its nucleophilic character and thus a higher reaction rate. Secondary amines are less reactive than primary ones, and no reaction occurs with tertiary amines.[126]

Cyclic carbonate type

It appears from several studies, including those of Tomita *et al*.,[127] that the nature of the substituents on the cyclic carbonate influences its reactivity towards diamines, as well as the secondary/primary alcohol ratio. It was shown that the reaction is accelerated with electron-withdrawing groups. Indeed, they enable to decrease the electron density on the carbon of the carbonyl bond. In addition, they allow the formation of predominant secondary hydroxyl groups. It corresponds to an increase of the acidity of the negatively charged oxygen by inductive effect.

Effect of the solvent of the reaction

Garipov *et al.* have shown that the aminolysis reaction is more favored in presence of protic solvents than with aprotic solvents.[120] However, in the literature, reactions are mainly carried out in aprotic solvents. In aprotic solvent, the reaction rate increases with increasing polarity of the medium. Furthermore, the limiting step of the reaction depends on the nature of the solvent. When the reaction is carried out in protic solvents, the limiting step is the deprotonation. On the contrary, in aprotic solvents, the reaction rate-limiting step is the nucleophilic attack of the amine on the cyclocarbonate.

Effect of the molar ratio between cyclic carbonate and amines

It was determined that systems synthesized at equimolar ratio present NIPUs with the highest properties. Indeed, at non stoichiometric ratio, secondary reactions (already discussed) can occurred and oligomers with lower molar masses, T_g, and mechanical properties are obtained.[124, 128]

e) Catalysis systems

The kinetics synthesis of NIPUs is often described as very slow.[4, 129] This is particularly due to the relatively stable nature of cyclic carbonates. To catalyze the aminolysis reaction, either electrophilicity of the carbonyl group on the cyclocarbonate (acid catalysts), or the nucleophile character of the amine (basic catalysts) can be increased.

Basic catalysts

The main basic catalysts for aminolysis found in the literature are piperazine and triethylamine. Another catalyst, triazabicyclodecene (TBD) seems also to be promising.[130] Originally used for the ring-opening polymerization of lactones, lactides and transesterifications, TBD allows to synthesize NIPUs of molar masses around 30,000 g.mol^{-1} within 24 hours, which are high values compared to the previous reported one.[131]

Other catalyst systems (salts and organo-based catalysts)

The effect of different catalysts on the kinetics of aminolysis was particularly investigated by Ochiai *et al.*[132] They examined the influence of different salts (acids and bases) on the final molar mass of the NIPUs, on the conversion rate of biscyclocarbonates and on the secondary/primary alcohol ratio in the chain. They show that whatever the catalyst, the conversion of biscyclocarbonate is increased. However, the latter is higher for salts with monovalent cations. Regarding the increase of the polymer molar mass, basic catalysts has no specific effect.[132] For acid catalysts, impact varies depending on the salt. A medium acid salt such as lithium chloride or lithium bromide could be preferred.[132] To conclude, it is better to use lithium salts than tin salts although currently predominantly used in the literature. Indeed, they are equally efficient but lithium is less harmful regarding to health and environment.

More recently, inorganic salts and organocatalysts were compared for coupling between propylene carbonate and cyclohexylamine.[133] Organocatalysts such as TBD and thiourea present higher catalytic activities (about 66% of carbonate conversion after 1 h at 25°C, and more than 80% at 100°C) compared to inorganic Lewis acids (about 53% of propylene carbonate conversion after 1 h at 25°C).

f) Advantages and drawbacks of the aminolysis reaction

Even if long reaction (several days) is required for the aminolysis reaction, this NIPU synthetic route is the most studied. Indeed, aminolysis is less restrictive and more industrially feasible than transurethane reaction and AB-type azide condensation.

The various approaches for NIPU synthesis detailed in previous parts seem to be promising alternatives to conventional PU syntheses. However, all the three paths have advantages and disadvantages. To conclude, we can say that the main obstacles are the use of (noxious) solvents to have a good control of the synthesis and thus well-defined properties of materials, and important reaction times (several days), which currently restrain industrial applications. However, synthesis temperatures are quite accessible (especially for the aminolysis: from room temperature to 100°C) and the yields are excellent (around 100%).[47, 52, 134]

g) Commercial NIPUs (or hybrid NIPUs) and their corresponding applications

Some NIPUs are already commercially available as coatings and paints, or foams. Pr. Figovsky and his team have developed a two-component product based on epoxides and hydroxyurethanes, produced from amines and cyclic carbonates.[135] This product, which is a possible substitute for current PUs, is marketed as Green Polyurethane™ by NanoTech Industries Inc. (licensor) and Hybrid Coating Technologies Inc. (licensee). It must be noticed that these NIPUs are in fact hybrid materials (also referred as HNIPUs) and combine epoxy and PU structures. Thus, these HNIPUs have superior properties to conventional PUs (particularly, better chemical, durability and wear resistance). A second type of commercial NIPU is rigid spray foam (NIPF).[136] NIPF is composed of two separate components (urea and urethane oligomers, and polyaziridine crosslinking agent), which react when they come into contact with each other. The possible given applications are insulation or structural reinforcement. None of these commercial NIPUs are biobased.

3.3. Biobased NIPUs

3.3.1. Building blocks from renewable resources

In a context of reducing crude oil consumption while preserving the environment, biorefineries emerged replacing fossil resources by renewable feedstocks to provide a large number of chemicals and polymers.[137] Different type of biomass can be used (*e.g.*, animal, vegetal, algae, mushroom). The main valorized biomass source is vegetal, mainly from forestry and crops with different types of waste or residues. After extraction, feedstocks can be mainly classified into different groups (lignocellulose, vegetable fats and oils, starch and sugars) (Figure 1-31). Herein, the potential and efficiency of biobased building blocks for NIPUs *via* aminolysis are reviewed.

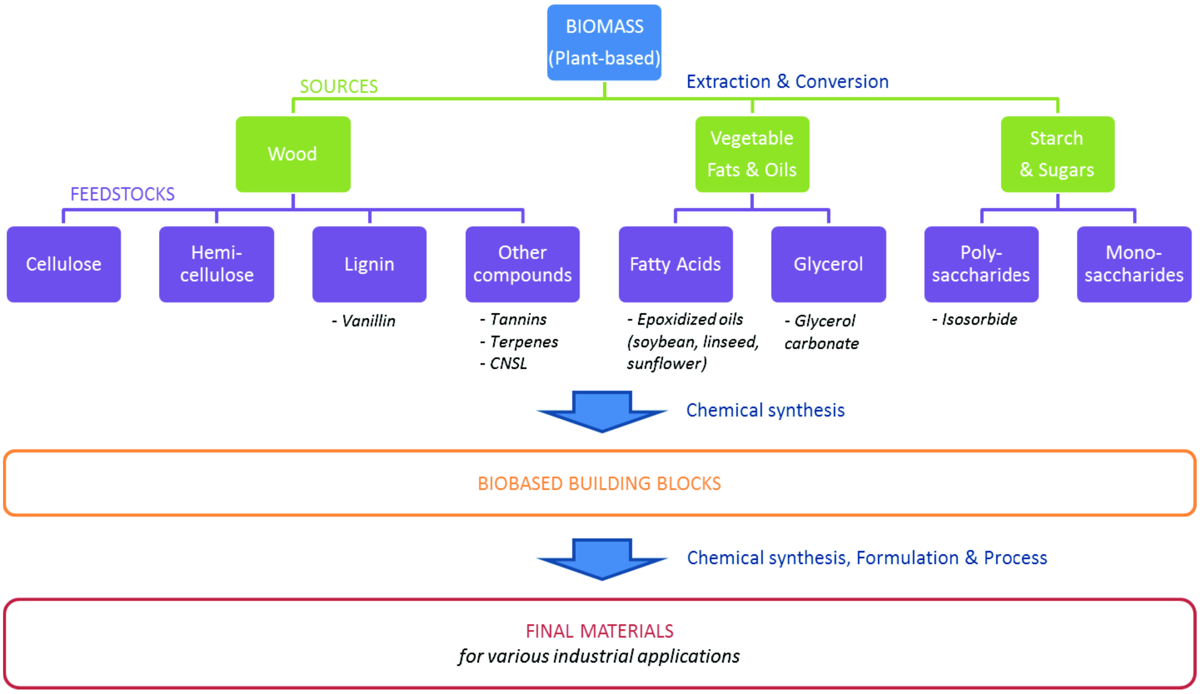


Figure 1-31. Where do biobased building blocks come from?

Various routes to cyclic carbonates have been developed concurrently with the investigations and developments on NIPUs. More and more, new cyclic carbonate molecules are biobased. The main synthetic strategy involved in their reaction is the carbonation of epoxide. Diamines used in NIPU synthesis are mainly fossil-based. However, different biobased diamines exist and are even commercialized. For instance, they are often reported as hardener in epoxy resins. In this section, we will focus on the various routes towards biobased building blocks for NIPU synthesis. Cyclic carbonates and diamines will be classified according to the origin of the corresponding renewable resources: (i) vegetable fats and oils, (ii) starch and sugars, and (iii) lignocellulosic feedstock.

3.3.1.1. Vegetable oils

Vegetable oils are mainly based on triglycerides. The composition of fatty acids in triglycerides varies and depends on the botanic source and the environment such as the season, and the growing conditions (humidity, light, soil, …).[138] In addition to their carboxylic acid end groups, fatty acids can present one or several double bonds, and can also bring hydroxyl and epoxy units, such as castor and vernonia oil, respectively.[139] A rich oleo-chemistry[32] associated with a large and global availability make this resource very attractive for the synthesis of innovative biobased monomers and building blocks.

a) Synthesis of cyclic carbonates and diamines from vegetable oils

Cyclic carbonates

All cyclic carbonates from triglyceride derivatives are synthesized from carbonation of epoxidized vegetable oils (EVO) by CO_2. EVO are molecules of interest due to their reactive oxirane sites but also their low price and readily availability. Epoxidation applied on industrial scale is carried out on double bonds of unsaturated fatty acids by an oxidizing agent, typically a peracid (*e.g.*, peracetic acid). Alternative routes have also been developed. Microwaves oven may be used for accelerating the epoxidation, thus transforming fatty acid derivatives into epoxides in a few minutes at high yield.[140] In order to work in mild conditions and improve selectivity, reactions were also performed by a chemo-enzymatic process with lipase *Candida Antartica* immobilized on various resins.[141, 142]

Epoxydized soybean oil (ESBO) and epoxidized linseed oil (ELSO) are commercially available and commonly used in a large range of applications. Various new epoxidized vegetable oils from *e.g.* cottonseed,[143] rapeseed,[144] *Lesquerella* and *Limnanthes* (Meadowfoam)[145] are also emerging. Carbonation of EVO is always performed by using CO_2, either at gaseous or supercritical state. Data on EVO carbonation process are well summarized by Miloslavskiy *et al.*[146] Even if oxiranes are highly reactive functions, their position inside the triglyceride chains can induce steric hindrance and considerably reduce the conversion of epoxy compounds into carbonates. In order to promote the reaction, TBAB is widely used as a catalyst for the synthesis of EVO but high temperature and pressure as well as several hours are still required to obtain a high conversion.[123, 124, 128, 143, 147, 148] Some progress were realized using a binary catalyst system $SnCl_4 \cdot 5H_2O$/TBAB, which combines a Lewis acid (for epoxide activation) and a Lewis base (CO_2 activation).[149] Other catalysts such as KI activated by 18-crown-6,[150] SiO_2-I,[151] or TBAB with addition of water[152] were also tested but no satisfactory result was given. Carbonation reactions are typically carried out between 60 and 180°C during 10 to 170 hours. Few papers have also reported the synthesis of cyclic carbonate vegetable oil in $scCO_2$.[153] Reaction time is more than twice reduced compared with reaction at atmospheric pressure. $ScCO_2$ improves reagent solubility and decreases viscosity. However, compared with other reactions performed with gaseous CO_2 under high pressure, no significant improvement is observed. Optimization of reaction conditions are thus required in the future to consider a large scale production. Most of the cyclic carbonates presented in the literature come from triglycerides and present functionalities higher than two and are thus not adapted to the synthesis of linear biobased NIPUs. In order to straighten out this issue, Boyer *et al.* prepared cyclic carbonates from well-defined oleic acid methyl ester.[154] They also demonstrate in this study that terminal epoxides are much more reactive than intern one, frequently encountered in the case of triglycerides carbonation. In the same way, the reactivity of intern carbonates is also reduced.

Diamines

Only few papers relate the synthesis of diamine from vegetable oils. Stemmelen *et al.* described the functionalization of grapeseed oil with amine groups involving cysteamine hydrochloride and the thiol-ene reaction.[155] Dimer fatty amines derived from the corresponding fatty acids are also remarkable amines. They result from the dimerization (Diels-Alder mechanism) of fatty acids followed by an amination reaction. Biobased dimer diamines are commercially available building blocks with 100% renewable carbon content, low viscosity, high flexibility and low T_g. These properties make them suitable for the synthesis of various biobased polymers applications.[156-158] Such diamines were recently reported by Maisonneuve *et al.* [159], and Carré *et al.*[160] in NIPU synthesis.

b) Synthesis of cyclic and biscyclocarbonates from glycerol and derivatives

Glycerol, which was identified in 2004 as a top value added chemicals from biomass by the US Department of Energy (DoE), is one of the largest bio-based wastes (*e.g.*, from the biodiesel industry).[161] It is a platform building block for various derivatives including cyclic carbonates.[161, 162] Depending which substituent is present on the carbonate ring, mainly hydroxyl or vinyl functional groups, esterification or thiol-ene coupling reactions can be envisaged to obtain bifunctionnal cyclic carbonates.

Glycerol carbonate

Glycerol carbonate (GC), a glycerol derivative, is a cheap, biodegradable and non-toxic renewable compound. This molecule has gained interest over the past 20 years for its versatile reactivity, leading to many applications. It is currently considered as a promising biobased building block.[163]

GC can result from various rather simple synthetic routes, reviewed recently by Sonnati *et al.* (Figure 1-32).[163] All the reactions were similar to conventional syntheses of cyclic carbonate.

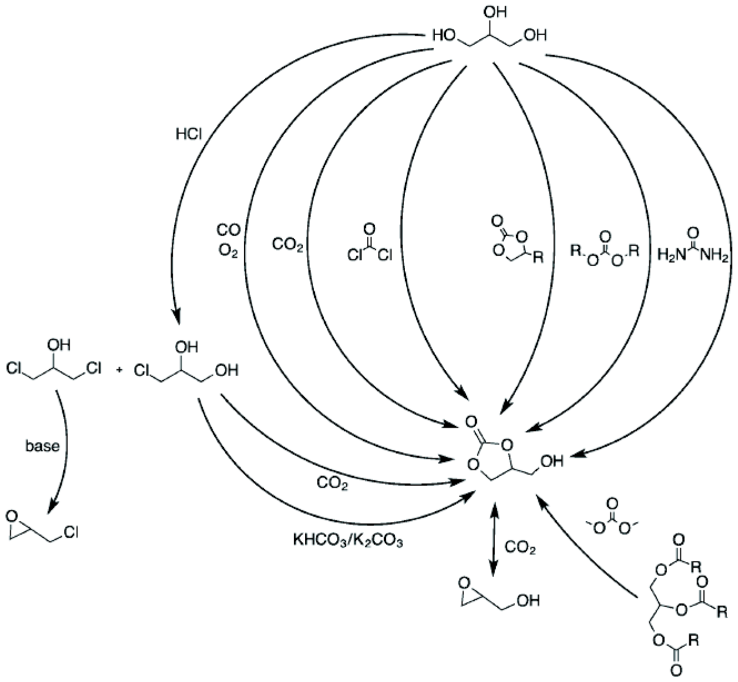


Figure 1-32. Main routes to glycerol carbonate.[163]

Reactions involving CO_2 with glycerol or epoxide are environmentally interesting because they are based on waste products from different industries. However, the uses of organic solvents and catalysts, as well as harsh temperature and pressure conditions are some strong issues for the environment. Besides, recently, Ochoa-Gomez *et al.*[164] have shown that the reaction between glycerol and CO_2 is the most promising process. However, it cannot at this time be considered for a large scale production of GC due to low CO_2 reactivity, with consequently small conversion rates. Novel routes such are enzymatic transesterification reaction of glycerol with dimethyl carbonate[165] or enzymatic coproduction of biodiesel and GC by transesterification of soybean oil and dimethylcarbonate in bulk are also emerging.[166]

In addition to its relatively straightforward synthesis, GC has a wide reactivity due to the presence on the same molecule of two units, a primary hydroxyl and a 2-oxo-1,3-dioxolane group (ODO). GC thus possesses nucleophilic and electrophilic sites. The ODO group can react with many nucleophilic compounds such as alcohols, amines, carboxylic acids, ketones, or isocyanates. The hydroxyl group of GC shows a similar reactivity to ODO group. Selectivity is thus an important parameter to avoid undesired side reactions.

Vinyl functional alkylene carbonates

Vinyl functional alkylene carbonates can also be prepared from glycerol. GCs functionalized with vinyl reactive groups have been formed by Guibe *et al.* under a Williamson ether synthesis followed by a palladium reduction (Figure 1-33).[167] Benyahya *et al.* used this protocol to further obtain a biscyclocarbonate *via* thiol-ene chemistry.[58]

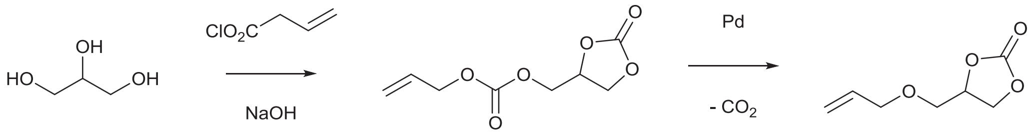


Figure 1-33. Vinyl ethylene glycerol carbonate synthesis.

GC and acryloyl chloride, in dichloromethane using triethylamine as a catalyst, lead to glycerol carbonate acrylate, another cyclic carbonate resulting from GC.[168]

3.3.1.2. Starch and sugars resources: the case of isosorbide

With two hydroxyl functional groups per molecule, isosorbide (1,4:3,6-dianhydrosorbitol) is a promising renewable plateform chemical for the synthesis of biobased polymers.[169] Furthermore, its two cycloaliphatic rings increase the rigidity of macromecular architectures. Isosorbide is commercially available from starch. However, alternative production methods have been developed from non-edible lignocellulosic biomass, without competition with food. The isosorbide production from biomass occurs in a multistep protocol.[170] First, glucose from various polysaccharides is hydrogenated to obtain sorbitol, which is then converted into isosorbide *via* a dehydration step.

Carbonate synthesis

Synthesis of epoxy and amines from isosorbide have been largely studied and developed for epoxy resins[171] and others polymers.[170] However, up to our knowledge, only a sole study reports the use of isosorbide in NIPU synthesis.[172] The authors prepared isosorbide cyclic carbonate into three steps. First, they synthesized the diglycidyl ether of isosorbide through its allylic derivative, which reacts with meta-chloroperoxybenzoic acid. Then, isosorbide diglycidyl ether oligomers are formed with an excess of epichlorohydrin in the presence of sodium hydroxide. Finally, a carbonation reaction occurs to form the desired isosorbide dicyclocarbonate, which then reacts with various diamines to obtain isosorbide-based NIPUs. Another conventional route to obtain diglycidyl ethers is using epichlorhydrin, which can be obtained from glycerol (*via e.g.* Epicerol^{TM} process, Solvay), as reactant in presence of sodium hydroxide.[173]

Amine synthesis

Even if isosorbide-derived diamine was not used in NIPU synthesis, such compounds already exist. The first diamine from isosorbide was described by Montgomery *et al.* in 1946.[174] The diamine resulted from a tosylation of isosorbide hydroxyl groups followed by a nucleophilic substitution with methyl alcoholic ammonia performed in an autoclave. Other methods starting from tosylation reaction were also reported. Thiem *et al.* successively performed azide formation and hydrogenation using palladium as a catalyst.[175] Van Es *et al.* realized a nucleophilic substitution on tosylated isosorbide with benzylamine followed by a catalytic hydrogenolysis.[176] Other isosorbide bifunctional amine derivatives were also developed. Caouthar *et al.* used fluorobenzene compounds in order to achieve first a nucleophilic aromatic substitution, and then a reduction with Raney nickel or a catalytic hydrogenation in order to obtain a diamine.[177, 178] More recently, the synthesis of diaminopropyl isosorbide was proposed in two steps involving first the reaction of isosorbide with acrylonitrile, and then hydrogenation with Raney Nickel.[179] To conclude, isosorbide is a potential chemical for NIPUs, as amine or epoxide. Subsequent epoxide carbonation techniques leading to cyclic carbonates are well-known.

3.3.1.3. Wood resources

a) Lignin

Lignin is a polymeric material, which is (with cellulose) one of the major components in structural cell walls of wood and plants. Lignin is composed of aromatic structures containing alcohols and is considered as the main aromatic renewable resource. It represents an excellent alternative feedstock for the elaboration of chemicals and polymers. Recently, lignin was used for the first time in the elaboration of NIPUs, as a polymeric agent.[180] First, urethane monomers were prepared *via* aminolysis reaction between carbonated soybean oil and an aminosilane coupling agent. Then, they were polymerized with lignin to form NIPUs. NIPUs with high biomass contents (up to 85%) were obtained. Moreover, it was observed from this study that increasing the lignin content in the material enhances the tensile strength (up to 1.4 MPa).

b) Tannins

After lignin, tannins are the most abundant source of natural aromatic compounds. Tannins are phenolic molecules mainly contained in trees and plants. As lignin, they can be used in the elaboration of NIPUs. Recently, Pizzi *et al.* reported the synthesis of NIPUs from various tannins, presenting both condensed and hydrolysable chemical structures.[181, 182] They were obtained *via* aminolysis reaction, after a preliminary carbonation of tannin with dimethylcarbonate.

c) Vanillin from lignin

Vanillin is a natural compound extracted from *Vanilla orchids* seed pods. Due to limited availability, different synthetic paths have been developed.[183, 184] Biobased vanillin can be obtained from sulfonated lignin contained in black liquor, a by-product of paper process. However, due to harsh conditions (*e.g.* severe oxidative process and intensive purification procedure), vanillin is currently mainly obtained from guaiacol, based on fossil resources.[183] Biobased vanillin and its derivatives (Figure 1-34) can be considered as aromatic platform chemicals, as they enable the synthesis of various monomers, including diamines and cyclic carbonates.[183]

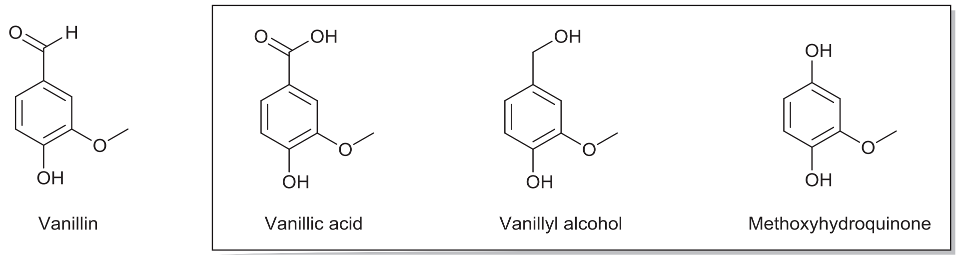


Figure 1-34. Vanillin and its derivatives.

Fache *et al.* firstly reported the synthesis of vanillin-based diamines, *via* thiol-ene addition of cysteamine hydrochloride.[183] They are also the first team to work on the elaboration of cyclic carbonate from vanillin biobased building block. The synthesis is carried out in two steps.

First, epichlorohydrin reacts with hydroxyl moieties to form an epoxide, and then addition of CO_2 induces the epoxide ring-opening to obtain the desired cyclic carbonate. Greener methods to obtain vanillin-derived epoxide were developed by Aouf *et al.* in order to replace the Bisphenol-A and the epichlorohydrin.[185] This two-step method involves alkaline allylation of hydroxyl groups followed by epoxidation of the resulting carbon double bond, either *via m*-chloroperoxybenzoic acid or *via* hydrogen peroxide with lipase as catalyst.

d) Other wood compounds

Cardanol from Cashew Nut Shell Liquid (CNSL)

CNSL is the oil contained in the shell of cashew nut (Figure 1-35). It is a promising biobased viscous liquid, largely available, which presents low toxicity and cost. The production of CNSL is around one million tons per year.[186] Furthermore, as wastes from the cashew nut industry, CNSL and its derivatives, contrary to edible vegetable oils, are not in competition with food.

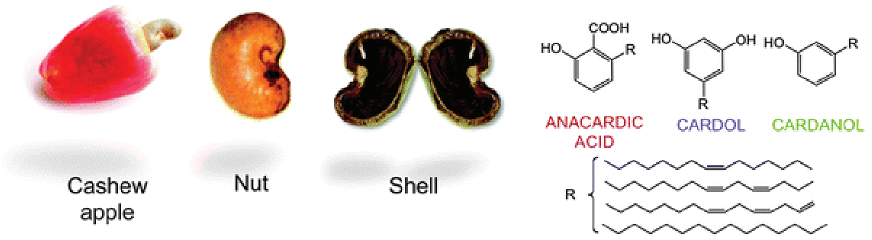


Figure 1-35. From cashew apple to cardanol.[187]

Various methods including roasting and hot vegetable oil process have been developed to extract CNSL from the nut.[188] Depending on the technique used, the chemical composition of the CNSL varies. Main constituents are anacardic acid, cardol and cardanol. They are aromatic compounds containing phenolic moieties and unsaturated carbon side chains (Figure 1-35). During the thermal treatment and the following refining distillation step, decarboxylation of anacardic acid occurs to obtain cardanol. The three reactive sites of cardanol (hydroxyl group, aromatic ring and unsaturated aliphatic chain) make it as a promising building block to substitute petroleum phenol derivatives, and as a versatile raw product for monomers and polymer synthesis.[189] For instance, cardanol is a bio-based alternative to Bisphenol-A,[171] and to polyols for polyurethanes.[190]

As far as we know, cyclic carbonate from CNSL was only reported by Kathalewar *et al.* for the synthesis of NIPU coatings.[191] Commercial NC514 epoxidized cardanol (from Cardolite) reacts with CO_2 under pressure using TBAB as catalyst.

Various chemical pathways to synthesize diamines from CNSL have been reported by Wadgaonkar *et al.*[192, 193] They all proceed through a fastidious multistep protocol. However, a cardanol-based polyamine (Phenalkamine NC540) is commercialized by Cardolite as an epoxy curing agent.[179] This chemical has been positively tested for NIPU synthesis by Mahendran *et al.*[148]

Terpenes

Terpenes are organic compounds produced by plants and trees, particularly from conifers. Limonene, a six-membered ring terpene, has gained interest for the synthesis of renewable building blocks.[194] It is an inexpensive and abundant molecule, which can be readily recovered from orange peel wastes. Limonene presents an ideal chemical structure for the synthesis of difunctional monomers (*e.g.* diamines and cyclic carbonates) with two carbon double bonds (Figure 1-36).

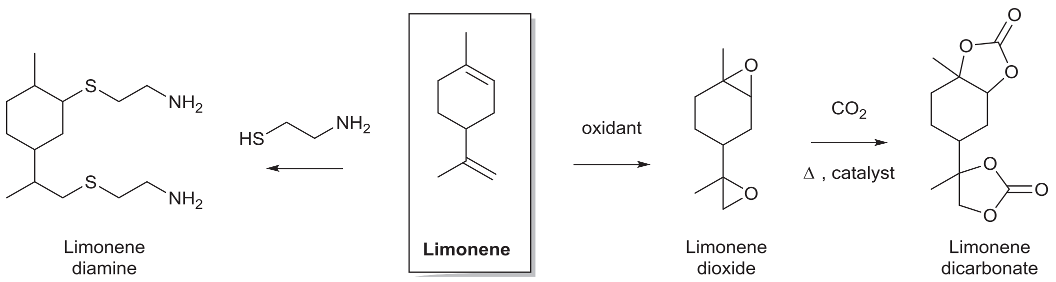


Figure 1-36. Limonene-based cyclic carbonates and diamines.

Bahr *et al.* reported the elaboration of cyclic carbonates from a commercially available limonene-based bisepoxide, originally dedicated to epoxy resin as reactive diluent, and CO_2 at 140°C under 30 bars with TBAB or silica supported iodide catalyst.[195] Even if the heterogeneous catalyst presents an easier recovery, it is less efficient and shows a lower activity.

The diamines from limonene have already been reported in 1960 but were formed from sulfuric acid and extremely poisonous hydrogen cyanide.[196] Since, a greener route from thiolene click chemistry was studied, and the addition of cystamine hydrochloride to limonene, with dimethylpropylamine as catalyst, reveals to be an effective way to obtain diamines for biobased PA and PU synthesis.[197]

3.3.2. Biobased NIPU synthesis

No particular chemical reactions were specifically elaborated for biobased NIPU synthesis. Biobased monomers, such as cyclic carbonates and diamines, are used in the same conditions than the fossil-based ones. Furthermore, no difference in term of kinetics, molar masses and secondary reactions were observed. Only the LCA, the environmental impact of the final material is modified. However, due to the specific molecular architectures brought from the biomass, the corresponding materials show specific properties.

3.3.3. Biobased NIPU properties

Till now, only few biobased NIPU materials were developed, and furthermore their properties were not often studied and reported. In this part, some trends about the "structure-properties" relationships of NIPU materials were however discussed.

3.3.3.1. Chain sizes

As fossil-based NIPUs, biobased NIPUs containing cycloaliphatic and aromatic diamines present lower molar masses than with linear diamines due to their lower reactivity.[195] NIPU derived from isosorbide BisCC show quite low molar masses and high dispersity (around 8,000 g.mol^{-1} and 4, respectively).[172] These results are nevertheless similar to those found in their related conventional NIPUs.[198]

3.3.3.2. Thermal properties

Biobased NIPUs decompose above 200°C and more generally at around 250°C, like conventional PUs.[172, 191] Similar behaviors were observed when analyses are performed under inert gas or air, indicating that no specific oxidation phenomena occurs.[172]

The structures of the diamine and the cyclic carbonate highly influence the T_g of NIPUs. In all papers, NIPUs based on linear amines own a lower T_g compared to cycloaliphatic and aromatic amines ones, which are more rigid.[124, 128, 172, 195] In addition, the length of the aliphatic carbonated chain also influences the T_g value. T_g decreases with increasing the carbon number in the diamine aliphatic chain.[151] Thus, T_g around or below 0°C can be obtained by using Jeffamine® D400 (Huntsman), a long chain polyether from oxypropylene, with primary amines end groups, which brings a high flexibility and toughness.[114, 172] This trend was however not observed by Bahr *et al.*[195]

Limonen based cyclic carbonate is one of the most rigid monomer encountered in NIPU synthesis. Thus, these NIPU systems exhibit T_g higher than 30°C whatever the diamine used.[195] Besse *et al.* also studied the influence of the number of isosorbide monomer (from one to three) inside the cyclic carbonate structure, and no noticeable difference in T_g was revealed.[172] T_g values of thermosetting NIPUs from softer vegetable oils structures are also high due to the polyfunctionality of the triglycerides (higher than 2), which leads to a strong crosslinked material. Boyer e*t al.* synthesized NIPU from well-defined fatty acid diesters in order to obtained linear NIPU materials with lower T_g.[154] With T_g around -15°C, these materials are thus more suitable for coatings applications.

3.3.3.3. Mechanical properties

Mechanical properties are strongly dependent on amine structure, and more particularly from crosslink density and hydrogen bonding between urethane, hydroxyl, and ester groups of the final macromolecular architectures. NIPUs based on rigid cycloaliphatic and aromatic diamines (*e.g.* IPDA, *m*XDA, *p*XDA) display higher tensile stress and lower elongation at break than the materials from linear aliphatic diamines such as EDA, BDA, and HMDA.[124, 128] The same behavior is also encountered when decreasing the carbonated chain length of aliphatic diamines.[124] Bahr *et al.* reported the synthesis of NIPUs from rigid limonene cyclic carbonate and polyfunctional amines.[195] They showed that increasing the amine functionality enhances Young modulus and limits the elongation at break. Furthermore, when cyclic carbonate and polyfunctional amine are both based on rigid structures, very stiff and brittle thermosetting NIPUs are obtained. In the case of NIPUs from vegetable oil derived cyclic carbonate, the mechanical properties are strongly dependent from the cyclic carbonate group content.[151] Young modulus and tensile strength increase with rising the carbonate content *i.e.* with the cyclic carbonate funtionality, contrary to the elongation at break. Thus, NIPUs from CLSO afford higher strength than those from CSBO.[151]

3.4. Conclusion and future trends

NIPUs are a new promising generation of PUs and have shown a strong and growing interest during the last years. Even if three routes have been detected: (i) AB-type azide condensation, (ii) transurethane reaction, and (iii) aminolysis, this latter reveals to be the most favorable to further developments and large production. Aminolysis reaction has been at the origin of most of NIPU studies.

Nowadays, on agreement with different environmental trends, NIPUs must also be biobased. This new class of NIPUs, which brings new macromolecular architectures, has a huge potential in various application *e.g.* building, automotive, and adhesives. Biobased NIPUs are a very recent and hot topic, then till now the number of publication is still limited. Particularly, only few potential biobased molecules have been investigated for the development of new sustainable NIPUs. First developments were concentrated on vegetable oils and their derivatives based on a rich oleo-chemistry. Now, new biobased resources receive greater attention. Indeed, contrary to linear structures of triglycerides and fatty acids, building blocks from starch, sugar or lignocellulosic biomass present aromatic or cycloaliphatic structures, that can improve the properties of NIPU materials. Furthermore, some of these molecules do not compete with food resources. Unfortunately, only some information have been published on thermal, structural, and mechanical properties of most of the corresponding polymers. A large window of investigations is still largely opened.

This review has also shown that one of the current limits of biobased NIPU development, as conventional NIPUs, still remains the low reactivity of the reaction and the lack of efficient catalysts dedicated to this new PU chemistry. Even if the chemical structures are not exactly equivalent we can compare NIPUs, which are polyhydroxyurethans, with conventional PUs. NIPUs (biobased or not) exhibit lower molar masses, slower kinetics, and thus some limited properties.

In summary, all these current developments highlight the high potential of biobased building blocks to develop innovative and performing NIPU materials in agreement with the emergent concept of sustainable development. Further improvements could be to adjust the NIPU properties with various biobased building blocks in order to fulfil the requirements for several durable applications. Answers could also emerge from investigations around post reactions with the hydroxyl moieties inherent to the aminolysis reaction.

4. Conclusion et perspectives

Ce chapitre bibliographique réalisé en préambule de nos différents travaux a dressé un état de l'art sur la synthèse de PU et notamment sur les nouvelles générations, à la fois plus respectueuses de la santé (sans isocyanate) et de l'environnement (biosourcées). Ce chapitre souligne en effet l'importance de diminuer la toxicité des synthèses de PU, liée aux isocyanates, mais également la nécessité d'incorporer dès que possible des composés biosourcés lors de l'élaboration des nouveaux matériaux NIPU. Ce chapitre a également permis de souligner la multiplicité des structures NIPU envisageables ainsi que l'influence et l'importance du choix des réactifs sur ces dernières. Bien qu'il existe plusieurs voies de synthèse de NIPU, il a été montré que la réaction d'aminolyse semble particulièrement adaptée étant donné ses conditions peu contraignantes et la faisabilité de son éventuelle industrialisation. D'autre part, le travail de recherche dédié aux « building blocks » biosourcés a montré que la gamme de composés issus de ressources renouvelables disponibles pour la synthèse de NIPU est à la fois large et variée. Ces nouveaux synthons vont permettre d'élaborer de nouvelles architectures macromoléculaires biosourcées originales dont la synthèse sera développée dans les chapitres suivants.

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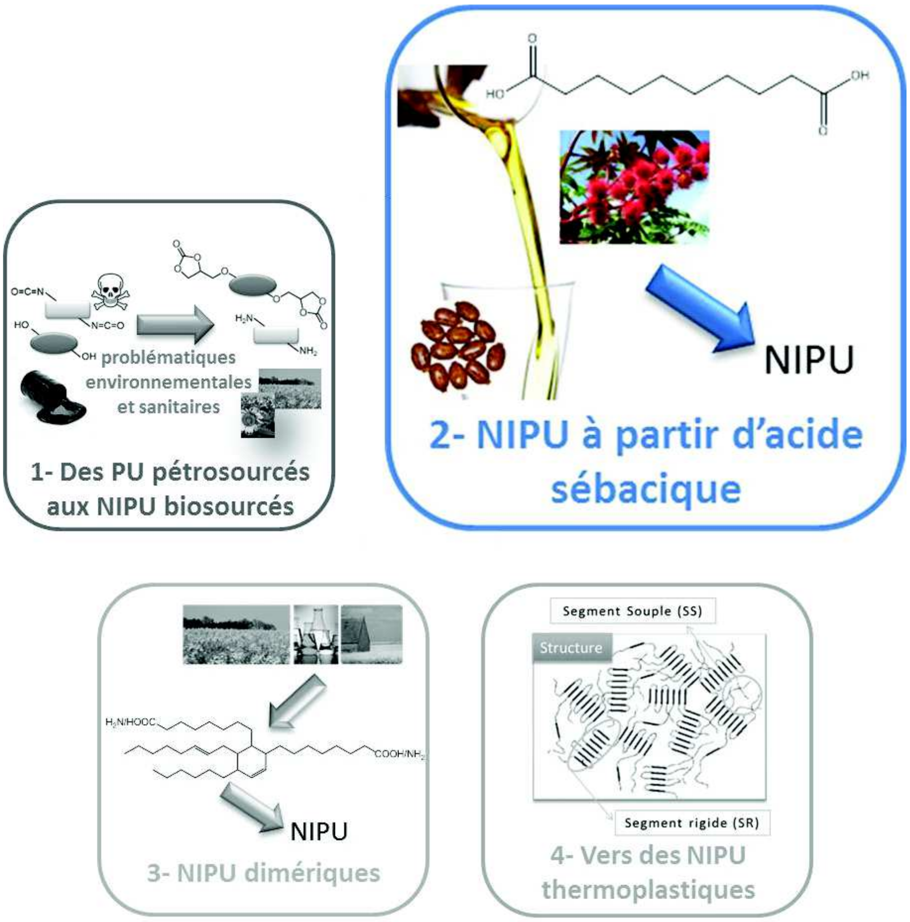
Chapitre 2

NIPU innovants issus de l'acide sébacique : Synthèse chimique et étude des propriétés



Introduction

Suite à l’étude bibliographique présentée dans le Chapitre 1, l’aminolyse semble être la voie de synthèse la plus prometteuse pour la préparation de NIPU. En effet, elle permet l’obtention de NIPU dans des conditions douces, c’est-à-dire à de faibles températures et sans utiliser de réactifs nocifs pour la santé et l’environnement, avec d’excellents rendements. Cette réaction met en jeu deux types de monomères ou synthons : des biscyclocarbonates et des diamines. Parmi les différentes voies de synthèse de biscyclocarbonates existantes, la réaction d’estérification entre un acide et le carbonate de glycérol a été retenue. Cette méthode est facilement industrialisable et permet l’obtention de produits totalement biosourcés. En effet, les acides et le carbonate de glycérol peuvent être, par exemple, issus de l’oléochimie. Le carbonate de glycérol est, de plus, une molécule bon marché et largement disponible commercialement.

Dans ce chapitre, l’acide retenu pour la synthèse du biscyclocarbonate est l’acide sébacique. Il a été choisi en tant que molécule modèle de par sa structure linéaire aliphatique relativement simple, présentant une chaine carbonée de longueur moyenne. L’acide sébacique est de plus une molécule disponible à de faibles coûts et potentiellement biosourcée. Afin d’obtenir un matériau NIPU souple, une diamine dimérique synthétisée à partir d’acide gras a été retenue. En outre, le dimère diamine est totalement biosourcé et est disponible en quantité industrielle à des prix compétitifs. Dans un souci de respect de l’environnement les diverses synthèses de NIPU ont été réalisées en masse (*i.e.* sans solvant) et sans ajout de catalyseur. La faible viscosité de la diamine a été un atout pour ces synthèses.

1. Synthèse, caractérisation et comportement de matériaux NIPU issus de l'acide sébacique et de dimères d'amine

Les travaux réalisés sur ce NIPU issu du biscyclocarbonate d'acide sébacique sont présentés sous la forme d'une publication intitulée « Original biobased nonisocyanate polyurethanes: solvent- and catalyst-free synthesis, thermal properties and rheological behavior », publiée dans *RSC Advances*.[1] L'importance du ratio entre les deux monomères ainsi que le rôle de la structure et de la fonctionalité moyenne des diamines sur les propriétés chimiques, thermiques, rhéologiques et mécaniques des NIPU obtenus ont été tout particulièrement étudiés.

Publication n°2 :

Original biobased nonisocyanate polyurethanes: solvent- and catalyst-free synthesis, thermal properties and rheological behavior

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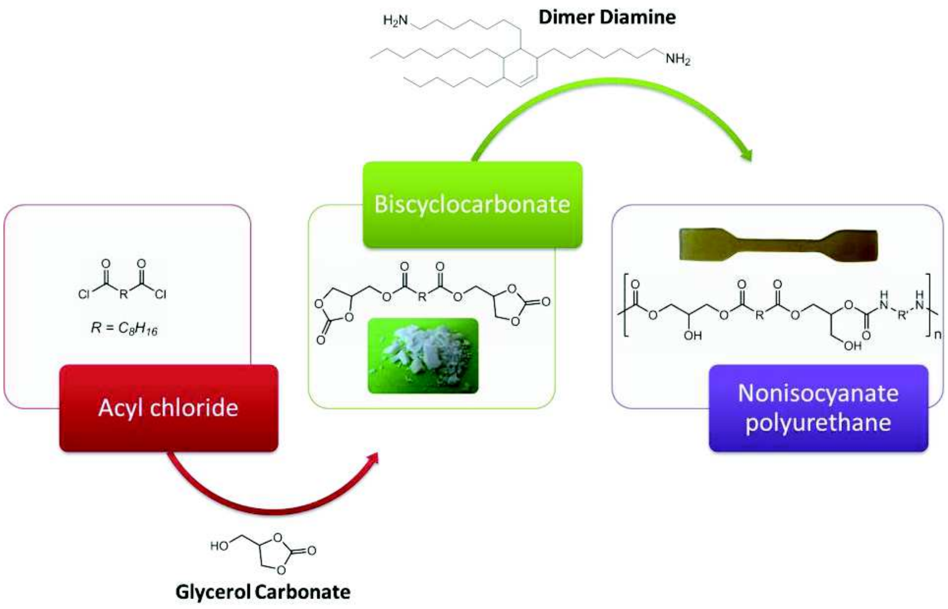
Graphical abstract



Abstract

Novel biobased NonIsocyanate PolyUrethanes (NIPUs) were synthesized from dimer-based diamines and sebacic biscyclocarbonate in bulk, and without catalyst. All synthesized NIPUs present biobased contents around 80%. Biscyclocarbonates and final NIPUs were characterized by FTIR and NMR spectroscopy. A specific study was conducted to determine the best carbonate to amine ratio. The influence on the structures and properties of NIPUs with different average amine functionalities, varying from 2.0 to 2.2, was investigated by DSC, SEC and dynamic rheological analyses. Based on FTIR analyses, it was found that the stoichiometric ratio is optimal for the NIPU synthesis to obtain the highest molar masses with appropriate kinetics. However, the results show that the molar masses (up to 22,000 g.mol^{-1}) were lower than conventional polyurethanes. A specific structuration due to a higher crosslink degree was observed when the average functionality of the dimer diamine increase. As expected, the glass transition temperature rises in this case. Crosslinked samples were synthesized with an average amine functionality of 2.15 and 2.2. A promising elastomer sample with elongation higher than 600% was then obtained.

Keywords

crosslinking, cyclic carbonate, dimer diamine, glycerol carbonate, nonisocyanate, polyurethane, renewable resources, rheological behavior, sebacic acid, solvent-free synthesis, structure-properties relationship

1.1. Introduction

Polyurethanes (PUs) are traditionally synthesized from the reaction between polyols and isocyanates.[2] The latter are nevertheless dangerous for human health. Some studies[3, 4] have clearly shown that isocyanates are harmful and potentially carcinogenic compounds. A repetitive exposure to them can lead to serious and incurable respiratory problems.[5] Moreover, the synthesis of isocyanates requires the use of noxious substances such as phosgene. These different issues can find a global answer with a new range of biobased NonIsocyanate PolyUrethanes (NIPUs), since a significant and growing attention is nowadays paid to environmental and health concerns.

Various synthetic strategies to obtain isocyanate- and phosgene-free PUs were reported the last few years.[6-9] The three most studied reactions are AB-type azide condensation,[10] transurethane polycondensation,[9, 11] and aminolysis.[12-14] PUs can indeed be prepared without isocyanate, *via* the amine-cyclocarbonate aminolysis reaction. Cyclic carbonates react with amines to form urethane, or more specifically hydroxyurethane bonds. According to the ring opening step, primary or secondary hydroxyl groups can be obtained. However, in the case of polymerization, mainly hybrid PUs having both primary and secondary alcohols are formed.[15, 16] These NIPUs are also called polyhydroxyurethanes (PHUs).

In the literature, the synthesis of NIPUs led to two major issues: (i) final low molar masses and (ii) slow kinetics, which are serious impediments to their developments. To overcome some of these drawbacks, some studies were carried out with various catalysts to enhance the reactivity of the reaction.[17, 18] In particular, the use of lithium chloride and triazabicyclodecene seems to be promising but at the moment, their efficiencies are too limited. An answer to obtain materials with high properties, and economically viable, is to use crosslinked systems to obtain high molar masses. Two strategies can be adopted. The first way is to employ polyfunctional cyclic carbonates obtained from raw triglycerides of soybean or linseed oil *via* an epoxydation/carbonation route.[19, 20] The second path is to use polyfunctional amines as curing agents, such as tris(2-aminoethyl)amine, polyethylenimine or citric acid aminoamides.[21] With such polyfunctional reagents, crosslink is then possible. Recently, Figovsky *et al.* have developed a hybrid NIPU-like coating marketed under the name Green Polyurethane$^{\text{TM}}$, which is based on cyclocarbonates and amines with epoxy functions.[22-24]

Cyclic carbonates can be synthesized by various methods[25] such as the direct esterification of carboxylic acids with glycerol carbonate. The latter appears to be a promising route in the frame of a new emerging challenge based on the use of renewable resources. Glycerol carbonate, a cheap and widely available biobased building block, can result from the reaction between carbon dioxide and glycerol, a major by-product from *e.g.*, the biodiesel industry.[26] Carboxylic acids can also be produced from biobased feedstocks and more particularly from vegetable oils. For instance, sebacic acid is industrially obtained at low cost by alkali fusion (heating with soda under oxidative conditions) at 250-280°C, from ricinoleic acid extracted from castor oil.[27] Sebacic acid is often chosen as a chemical for synthesis, since it is a biobased diacid with a 10-carbon chain length, and largely and commercially available. Then, it could be a good candidate for the synthesis of bicyclocarbonates by esterification.

Several syntheses between biscyclocarbonates and various diamines were described in the literature and the relationships between structure and reactivity were analyzed to a large extent.[28-30] Tomita *et al.* carried out studies on the reactivity of different cyclocarbonates.[29, 30] They showed that the nature of the substituent on the cyclic carbonate and the number of atoms involved on the cyclocarbonate ring have an impact on their reactivity towards diamines.

Various diamines have already been reported for NIPU synthesis. According to Diakoumakos *et al.*, the structure and the molar mass of the diamines influence their reactivity with cyclocarbonates.[28] The authors demonstrated that low molar mass aliphatic amines present the highest reactivity. However, it was also proved that secondary amines can react with cyclic carbonates.[31] As far as we know, dimer fatty amines have never been reported for NIPU synthesis and present inherent specific characteristics. Compared with conventional diamines, they are biobased building blocks with 100% renewable carbon content. Due to their structure with pending chains, the dimer diamines bring a high flexibility and a low glass transition temperature suitable for the elaboration of elastomeric polymers. Besides, the dimer diamines show a low viscosity, which is required for solvent-free synthesis. Moreover, they are commercially available. Dimer diamines are derivatives of fatty acids obtained from a dimerization process (Diels-Alder reaction). As their corresponding dimer fatty acids, they can be used as building blocks for the elaboration of several biobased macromolecular architectures.[32, 33] An example of the corresponding figure is given by Figure 2-1.

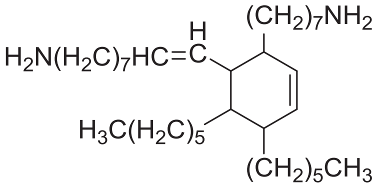


Figure 2-1. Cyclic chemical structure of dimer diamines.

In the present study, we have chosen to elaborate new biobased NIPUs *via* a green chemical pathway *i.e.*, without solvent and catalyst systems.

The aim of this study is to synthesize biobased NIPUs by bulk polymerization between sebacic biscyclocarbonate (SBBisCC) and dimer-based diamine (DDA), as illustrated in Figure 2-2, and to analyze their corresponding structure-properties relationships. In that frame, the effects of five different average amine functionalities, from 2.0 to 2.2, referred to as NIPU-fn=2.0, 2.05, 2.1, 2.15 and 2.2, respectively, were considered to modulate the crosslink degree of the samples. The chemical characterization of the NIPU systems, the effect of the carbonate:amine ratio and their corresponding physical and thermal properties were investigated. The rheological behavior of the corresponding products was also studied. Additional experiments based on specific NIPU-fn=2.15 and 2.2 were carried out to provide a better characterization and understanding of these promising biobased crosslinked materials.

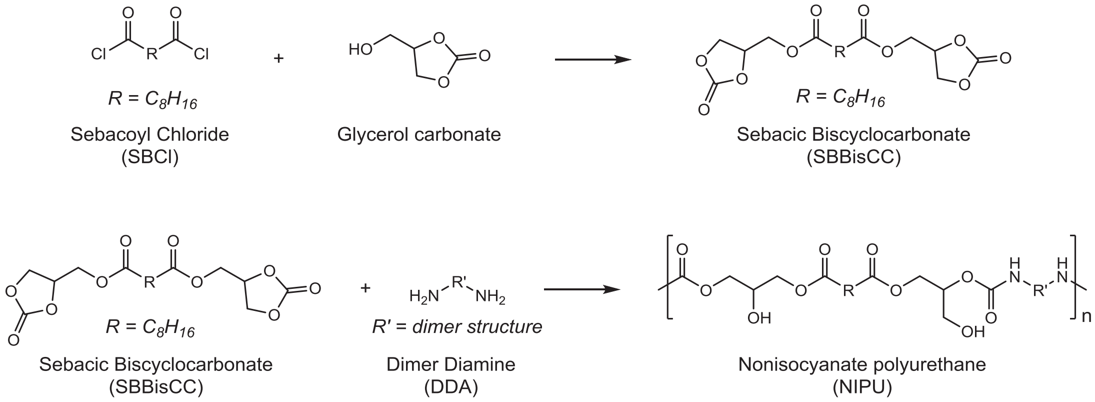


Figure 2-2. Esterification of sebacoyl chloride to yield sebacic biscyclocarbonate followed by aminolysis of sebacic biscyclocarbonate with dimer-based diamine.

1.2. Experimental part

1.2.1. Materials and chemicals

Sebacoyl chloride (97%) was purchased from Alfa Aesar (Karlsruhe, Germany). Glycerol carbonate (Jeffsol GC, 93%) was obtained from Huntsman (Everberg, Belgium). Dimer diamines (DDA) commercially available under the trade name Priamine were kindly supplied by CRODA (Goole, England). DDA are C36-biobased molecules obtained from the dimer fatty acid (Figure 2-1).

Two grades of DDA, hereinafter referred to as DDA1 and DDA2, were used alone or mixed together to adjust a precise average amine functionality. DDA1 has an average functionality of 2.2 (dimer content = 75%) and DDA2 of 2.0 (dimer content >99%), respectively. They present an amine value (AV) of 198 and 204 mg KOH per g, respectively, with glass transition temperatures lower than -50°C. At room temperature, DDA1 is an amber, viscous liquid and DDA2 is a yellowish, slightly viscous liquid. All chemicals were used as received without any purification.

1.2.2. Syntheses

1.2.2.1. Synthesis of sebacic biscyclocarbonate (SBBisCC)

The sebacic biscyclocarbonate was synthesized following the pathway given by Figure 2-2. The glycerol carbonate (20 g, 170 mmol) was mixed with freshly distilled dichloromethane (60 mL) and triethylamine (8.6 g, 85 mmol) under a light stream of inert gas. The flask was cooled in an ice water bath. Sebacoyl chloride (18.5 g, 77.3 mmol) was added dropwise to the stirred reaction mixture.

After an overnight reaction, triethylamine hydrochloride $NEt_3 \cdot HCl$ was taken out by filtration, and the organic phase was washed with a 5 wt% HCl solution and water, to eliminate the excess of glycerol carbonate. The solution was then dried with anhydrous sodium sulphate. Solvent was removed under vacuum to yield 22-23 g (71-77%) of white powder.

The structure of SBBisCC was determined and confirmed by ^{1}H- (Figure 2-3) and ^{13}C-NMR spectra (Figure 2-S1 in the ESI†). On the FTIR spectrum, the characteristic peaks of the ester and cyclocarbonate functions were 1740 cm^{-1} and 1796 cm^{-1}, respectively (Figure 2-S2 in the ESI†).

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 1.32 (8H, *s*, -OCO-CH_2-CH_2-C*H*$_2$-), 1.64 (4H, *t*, *J* = 7.1 Hz, -OCO-CH_2-C*H*$_2$-CH_2-), 2.38 (4H, *t*, J = 7.5 Hz, -OCO-C*H*$_2$-CH_2-CH_2-), 4.15; 4.55 (8H, m*;* *t*, *J* = 8.6 Hz, -OCOO-C*H*$_2$-CH-C*H*$_2$-O-) and 4.9 (2H, *m*, -OCOO-CH_2-C*H*-CH_2-O-).

^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): 24.7 ($OCO\text{-}CH_2\text{-}\mathit{C}H_2\text{-}CH_2\text{-}$), 28.9 ($OCO\text{-}CH_2\text{-}CH_2\text{-}\mathit{C}H_2\text{-}$), 33.8 ($OCO\text{-}\mathit{C}H_2\text{-}CH_2\text{-}CH_2\text{-}$), 62.8 ($\text{-}OCOO\text{-}CH_2\text{-}CH\text{-}\mathit{C}H_2\text{-}O\text{-}$), 66.0 ($\text{-}OCOO\text{-}\mathit{C}H_2\text{-}CH\text{-}CH_2\text{-}O\text{-}$), 73.8 ($\text{-}OCOO\text{-}CH_2\text{-}\mathit{C}H\text{-}CH_2\text{-}O\text{-}$), 154.4 ($\text{-}O\mathit{C}OO\text{-}$ from the cyclocarbonate ring) and 173.2 ($\text{-}O\mathit{C}O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}$).

FTIR-ATR (cm^{-1}): 1740 (-COO-) and 1796 (-OCOO-).

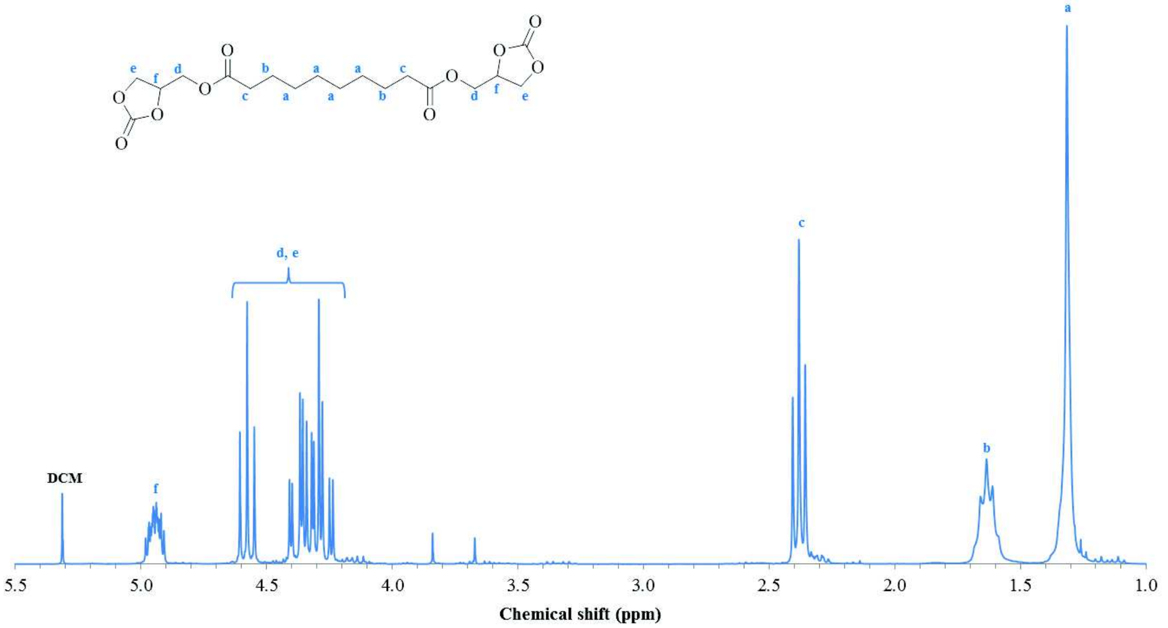


Figure 2-3. ^{1}H-NMR of SBBisCC.

1.2.2.2. Synthesis of NIPUs

In a 100 mL reactor equipped with a mechanical stirrer, sebacic biscyclocarbonate (20 g, 49.7 mmol) and diamine, or a mix of both diamines, were added at a molar stoichiometric ratio, according to the second chemical equation given by Figure 2-2. The reaction took place in bulk without catalyst, at a temperature of 75°C, and under inert gas flow to avoid the amine carbonation during the synthesis. After two hours under stirring, the viscous mixture was spread on a plate covered with a Teflon® sheet and heated in an oven under vacuum at 75°C for ninety-four hours. The product was obtained as a yellow or brown solid depending on the DDA used.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm, Figure 2-4): 0.88 (6H_m from DDA dangling chains, *s*, -$\mathit{CH_3}$), 1.20-1.40 (4H_f and H_c from DDA structure, *m*, -$\mathit{CH_2}$-), 1.50 (4H_b, *s*, -$\mathit{CH_2}$-), 1.63 (4H_e, *s*, -$\mathit{CH_2}$-), 2.36 (4H_d, *t*, J = 7.41 Hz, -$\mathit{CH_2}$-), 3.18 (4H_a, *m*, -$\mathit{CH_2}$-), 3.63 (0.6H_g, *m*, -$\mathit{CH_2}$-), 3.72 (0.6H_i, *m*, -CH_2-), 4.07 (0.7H_k, *m*, -CH=), 4.10-4.36 (2.8$H_{j,l}$, *m*, -CH_2-) and 5.00 (0.3H_h, m, -CH=).

^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm, Figure 2-S3 in the ESI†): 14.2 (-CH_3), 22.7 and 28.9-32.0 (-OCO-CH_2-CH_2-CH_2- and -CH_2 from DDA structure), 24.8 (-OCO-CH_2-CH_2-CH_2-), 26.8 (-OCO-NH-CH_2-CH_2), 33.8 (-OCO-CH_2-CH_2-CH_2-), 41.3 (-OCO-NH-CH_2-CH_2-R-), 62.5 (-COO-CH_2-CH-CH_2-OH), 63.2 (-COO-CH_2-CH-CH_2-OH), 65.1 (-NH-COO-CH_2-CHOH-CH_2-), 66.0 (-NH-COO-CH_2-CHOH-CH_2-), 68.6 (-NH-COO-CH_2-CHOH-CH_2-), 70.7 (-COO-CH_2-CH-CH_2-OH), 156.8 (OCONH) and 174.0 (-OCO-CH_2-CH_2-CH_2-).

FTIR-ATR (cm^{-1}, Figure 2-S4 in the ESI†): 1247 (=CO stretching, s), 1536 (-NH bending, m), 1701 (-C=O stretching of urethane and ester, s, broad) and 3335 (-NH and –OH stretching, respectively m and s, broad).

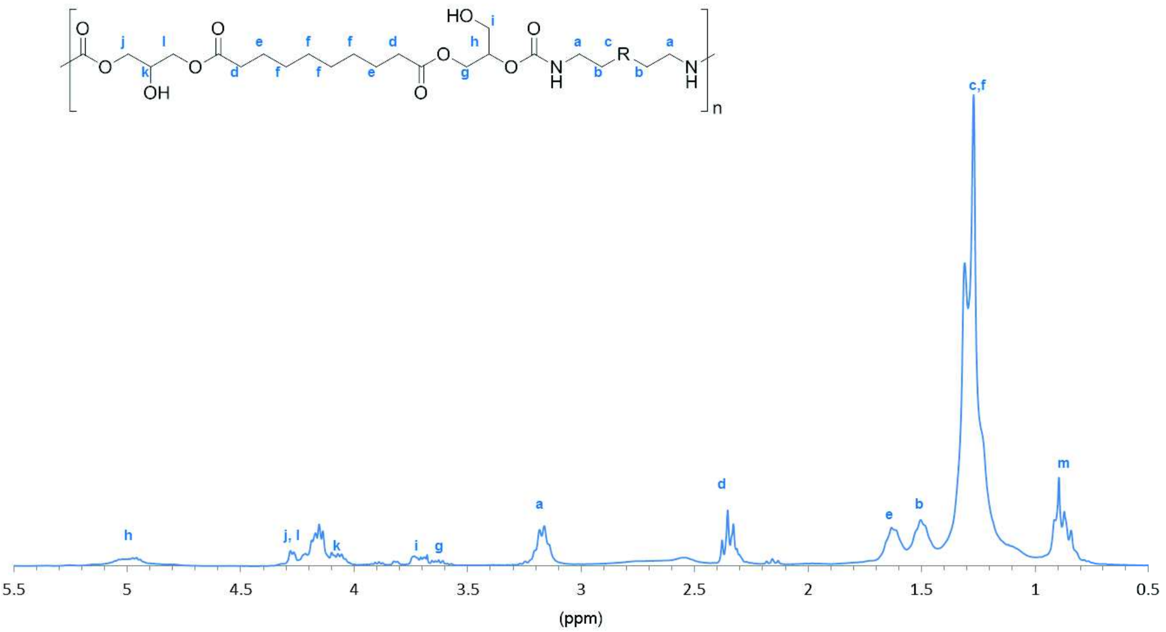


Figure 2-4. ^{1}H-NMR of NIPU-fn=2.0.

1.2.3. General characterization techniques

Infrared spectroscopy was achieved with a Fourier transformed infrared spectrometer Nicolet 380 (Thermo Electron Corporation) working in reflection mode and equipped with an ATR diamond module (FTIR-ATR). The FTIR-ATR spectra were collected at a resolution of 4 cm^{-1} and with 64 scans per run.

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Ascend^{TM} 400 spectrometer at 400 MHz and 100 MHz respectively. Chloroform-d_6 was used as a solvent.

Thermal degradation was studied by thermogravimetric analyses (TGA). Measurements were conducted under dry nitrogen (flow rate = 25 mL.min^{-1}) using a Hi-Res TGA Q5000 apparatus from TA Instruments. The samples (3–5 mg placed in an aluminium pan) were heated up to 650°C at 10°C.min^{-1}. The characteristic degradation temperatures are the temperatures at the maxima of the derivative thermogram (DTG) curves (T_{max}).

The main characteristic temperatures were determined by differential scanning calorimetry (DSC Q200, *TA Instruments*) under nitrogen flow. The samples (2–5 mg) were heated until 175°C with a heating rate of 10°C.min^{-1} (first heating scan), then cooled to -80°C at 5°C.min^{-1} and finally re-heated to 175°C at a heating rate of 10°C.min^{-1} (second heating scan). The glass transition temperatures (T_g) were determined as midpoints of the change in slop of the baseline. These values were obtained from the second heating scan in order to erase the previous thermal history of the samples during the first scan.

The number average molar mass (M_n), the weight average molar mass (M_w) and the dispersity (Đ) of the resulting samples were determined by Size Exclusion Chromatography (SEC), using Malvern Instrument apparatus (Viscotek RImax). This device was equipped with a guard column 10 mm (8 µm) and three 300 mm columns (50, 150 and 500 Å). Refractive index (RI) and ultra-violet (UV) detectors were used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL.min^{-1}. The apparatus was calibrated with linear polystyrene standard from 162 to 20,000 g.mol^{-1}.

Dynamic rheological analyses (DRA) of final materials were performed by using a strain-controlled rheometer (ARES, Rheometric Scientific) equipped with parallel-plate geometries. The oscillatory measurements were carried out on 8 and 25 mm diameter plates, with 2 mm thickness. The following tests were conducted: (i) dynamic strain sweep to estimate the viscoelastic region of the samples, (ii) isofrequency dynamic temperature sweep test from 0 up to 160°C at a frequency of 1 Hz. Changes in the viscous and elastic, or storage, modulus (G'' and G', respectively) were registered, and the corresponding tan $\delta = G''/G'$ were determined.

Dynamic mechanical thermal analyses (DMTA) were performed on polymers (samples with dimensions around 23 x 4 x 1 mm) with RSA-II apparatus from TA Instruments equipped with a liquid-nitrogen cooling system. Experiments were recorded on films with traction mode at a maximum strain from 0.03 to 2% and a frequency of 1 Hz. The samples were heated from -50 to 200°C at a heating rate of 2°C.min^{-1}.

Uniaxial tensile tests were achieved using an Instron machine (type 5567, serie H1592). The experiments were performed at room temperature, using a crosshead speed of 100 mm.min^{-1} and a load cell of 5 kN sensitivity. After adjusting the parameters, experiments were carried out at least 3 times for each sample. Young's modulus (E), tensile strength at break (σ_{max}) and elongation at break (ε_{max}) were determined.

1.3. Results and discussion

1.3.1. NIPU synthesis and chemical characterizations

A first study based on the analysis of the SBBisCC:DDA ratio was conducted to determine the optimal ratio for the NIPU synthesis. FTIR spectroscopy was used to highlight specific changes in hydroxyl and carbonyl vibrations, which provide direct evidence of reactions between cyclocarbonate and amine reagents. FTIR spectra of NIPUs show distinctive absorption bands of the urethane group at 3300-3400 cm^{-1}, 1700 cm^{-1} (merged with the ester absorption peak), 1535 cm^{-1} and 1245 cm^{-1}, respectively (Figure 2-5). The absorption band at 3300-3400 cm^{-1} is also assigned to the hydroxyl group resulting from the carbonate opening. Hydroxyl and urethane groups are shown for all samples, which confirms the expected structure of NIPUs, also known as polyhydroxyurethanes (PHUs). The peak at 1790 cm^{-1} is assigned to the unreacted SBBisCC carbonyl and the absorption peak of the amide group resulting from the aminolysis of ester groups appears at 1650 cm^{-1}. The samples prepared with a carbonate:amine ratio of 1.1:1 present a significant amount of unreacted SBBisCC. The amide peak is hardly noticeable, indicating that the ester group aminolysis is not significant. Samples formed at a stoichiometric ratio display neither BisCC nor distinct amide absorption peaks, suggesting that the carbonate conversion to urethane is quite complete. Only few secondary reactions could occur. At a ratio 1:1.1, the amide absorption peak becomes stronger, highlighting the aminolysis of the ester groups. These results show the importance of a stoichiometric ratio to achieve a complete reaction and minimize the secondary reaction of ester aminolysis, which induces chains cleavage, according to the reaction given by Figure 2-6. This result is in good agreement with previous observations from Javni *et al.*[19, 34]

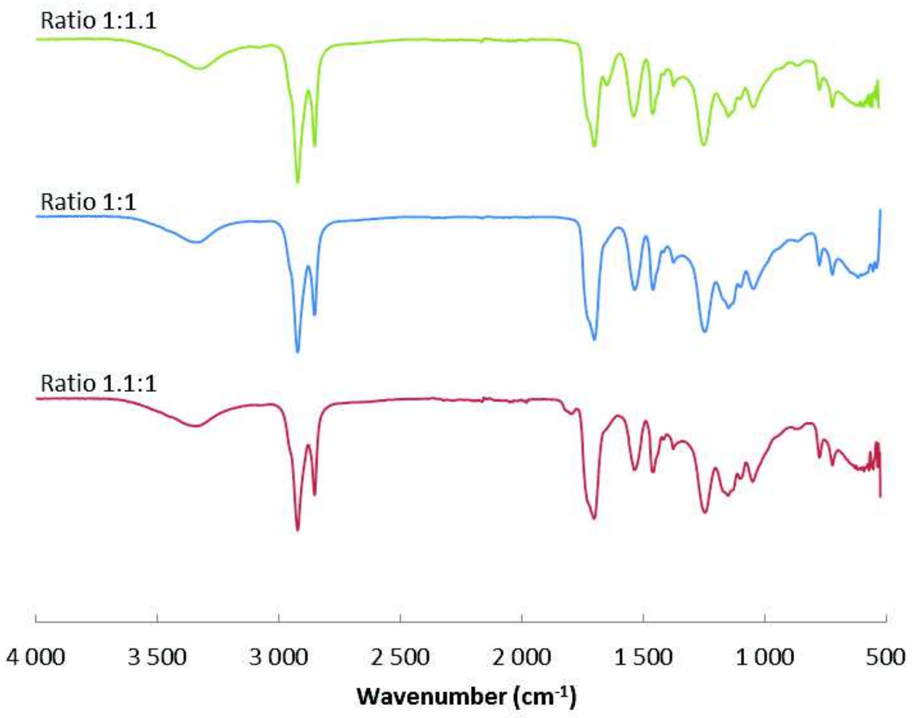


Figure 2-5. FTIR spectra of NIPU-fn=2.0 at different carbonate:amine ratios.

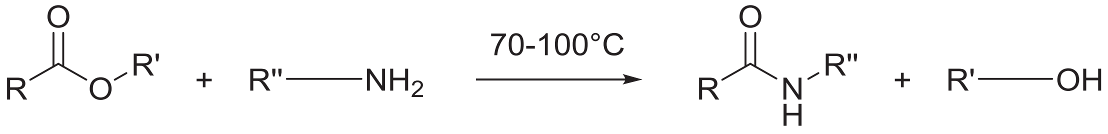


Figure 2-6. Aminolysis of ester as side-reaction.

The number average molar masses (M_n) and the dispersity (Đ) of NIPU samples are summarized in Table 2-1, except for NIPU-fn=2.15 and 2.2, which were not soluble in THF.

Table 2-1. Average molar masses of NIPUs.

NIPU sample	M_n (g.mol^{-1})	M_w (g.mol^{-1})	Đ
NIPU-fn=2.0	6,000	20,000	3.1
NIPU-fn=2.05	9,000	22,000	2.4
NIPU-fn=2.1*	7,000	18,000	2.5
NIPU-fn=2.15	Not soluble in common solvents		
NIPU-fn=2.2	Not soluble in common solvents		

* Partially soluble.

Compared with conventional PUs obtained *via* the classic isocyanate-alcohol route,[35, 36] the molar masses and Đ obtained for the NIPU samples are quite lower and higher, respectively. This is due to the limited reactivity of the cyclocarbonate towards diamines, the existence of secondary reactions, such as the ester aminolysis, as well as the diamine, which also presents a high Đ. However, molar masses are comparable to other NIPU systems,[8, 37] and high Đ are also observed in PUs formed with polyisocyanates and dimer derivatives.[33] A significant decrease of the molar mass is observed for NIPU-fn=2.1. Owing to an average amine functionality above 2.0, a part of the sample is crosslinked and thus not soluble. Consequently, only the soluble fraction with the lowest masses is analyzed.

1.3.2. NIPU thermal properties

The thermal properties of NIPUs were investigated by TGA and DSC to better understand the structure and the behavior of the NIPUs. The corresponding results are summarized in Tables 2-2 and 2-3, respectively.

TGA was used to investigate the influence of the average amine functionality on the thermal stability of the resulting synthesized polymers. Conventional PUs are known to have a relatively low thermal stability, mainly because of the urethane bond reversibility.[38] In their study, Saunders *et al.* presented a three-stage degradation mechanism of the urethane bond.[39] The first degradation step consists in the dissociation to isocyanate and alcohol. Then, the formation of primary amine and olefin occurs. Finally, the third degradation step is the formation of secondary amine. As demonstrated by Javni *et al.*, these three reactions may proceed simultaneously.[40] TG curves (Figure 2-7) indicate that thermal decomposition of NIPUs starts at 200°C, after a slight mass decrease between 0 and 150°C due to the vaporization of residual and linked water molecules. The thermal stability of these NIPUs is similar to other NIPUs from the literature,[41, 42] but lower than those of conventional dimer-based PUs, which decompose above 300°C.[43, 44]

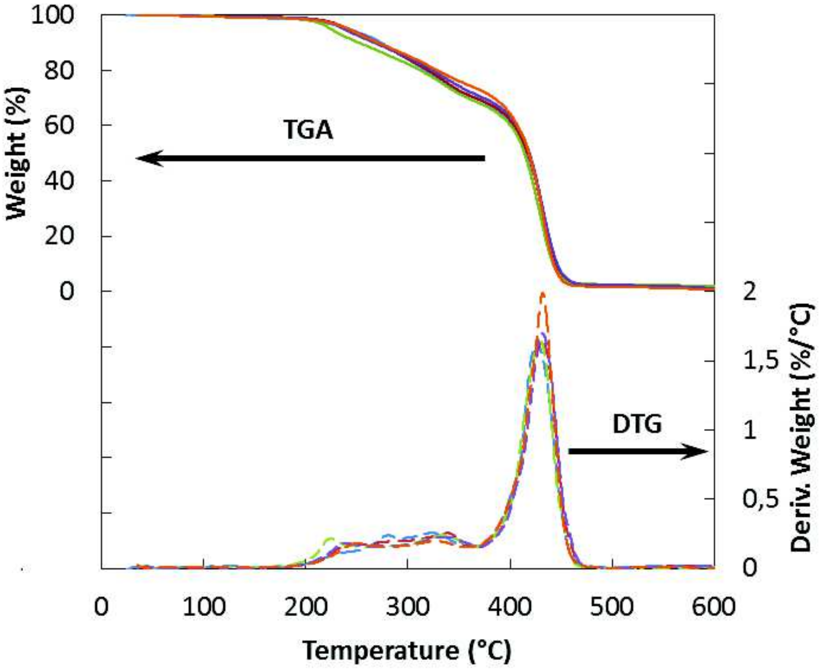


Figure 2-7. TGA (solid line) and DTG (dotted line) curves of NIPUs under nitrogen. NIPU- fn=2.0 (blue), fn=2.05 (red), fn=2.1 (green), fn=2.15 (purple), fn=2.2 (orange).

It can be observed that the different NIPU materials show quite similar three-step degradation behaviors (Table 2-2). This result is not surprising considering that the PU structures are based on equivalent biscyclocarbonate and diamine building blocks. The two first degradation stages could be attributed to the degradation of the urethane linkages such as the ester bonds,[45] which follows an irreversible mechanism starting from around 200°C. The last degradation, which is more notable, could be attributed to the decomposition of the carbonated chains. For all samples, no difference between oxidative and inert atmosphere was noticed. Oxidation has no impact on thermal degradation.

Table 2-2. Main degradation temperatures for the different NIPU samples.

Samples	**1st degradation stage**		**2nd degradation stage**		**3rd degradation stage**	
	%deg	T_{max} (°C)	%deg	T_{max} (°C)	%deg	T_{max} (°C)
NIPU-fn=2.0	15	279	15	326	70	426
NIPU-fn=2.05	8	235	22	339	69	432
NIPU-fn=2.1	11	223	20	334	67	430
NIPU-fn=2.15	10	236	19	336	70	432
NIPU-fn=2.2	11	249	14	327	74	432

In the temperature domain explored by DSC, NIPUs are not degraded (Table 2-2). Furthermore, neither endothermic nor exothermic phenomena were observed, indicating that all NIPU samples are fully amorphous. Their glass transition temperatures, T_g, are around -20°C, between -23 and -14°C (Table 2-3). DDA shows a hydrocarbonated cycle with pendant aliphatic chains, which raise free volume and then increase the chains mobility. Such a particular structure is thus responsible of the low T_g observed for all NIPU samples. Equivalent T_g values are classically obtained for PUs based on polyisocyanates or NIPUs with dimer structures or pendant aliphatic fatty acid chains.[33, 37] Furthermore, we can notice that the T_g increases with the average functionality of the amine and thus with the crosslink degree of the polymers. The NIPU-fn=2.15 and more especially the NIPU-fn=2.2 samples differentiate from the others since their respective T_g are higher. Nevertheless, this trend is attenuated by two opposite behaviors. On the one hand, when increasing the average amine functionality, DDA masses should be enhanced to maintain a stoichiometric ratio. This means that when increasing the average amine functionality, the global T_g decreases. One the other hand, it is well known that the denser is the formed network, the less mobile are the polymer chains and thus the higher is the T_g. These last results show the effect of the monomer functionality on the final macromolecular architecture.

Table 2-3. Thermal properties of NIPU samples.

Samples	**T_g (°C)**
NIPU-fn=2.0	-23
NIPU-fn=2.05	-21
NIPU-fn=2.1	-22
NIPU-fn=2.15	-19
NIPU-fn=2.2	-14

1.3.3. Rheological behavior of NIPU materials

To obtain additional and complementary information about architecture and organisation of the NIPUs, rheological analyses were carried out. Figures 2-8 and 2-9 show the results of the dynamic rheological analyses of NIPU samples.

We can notice that the behavior of the NIPUS varies according to the amine functionality. Between 80 and 120°C, a rubbery plateau is observed for the NIPU samples with amine functionalities superior or equal to 2.15. This plateau shows a particular structuration of the polymer due to crosslinking points. In these cases, thermosets were obtained. Furthermore, the rubbery plateau of NIPU-fn=2.2 is higher and longer than the one of NIPU-fn=2.15, which indicates that the crosslink density is higher. The storage modulus of NIPU-fn=2.2 approximately equals to 10^4 Pa at 100°C, which is lower than conventional thermosets whose moduli stay constant at about 10^6 Pa.[46] Below an average amine functionality of 2.15, the storage modulus (G') drops when increasing the temperature. The materials flow and thus are poorly or not structured. This phenomenon is highlighted at low average amine functionalities.

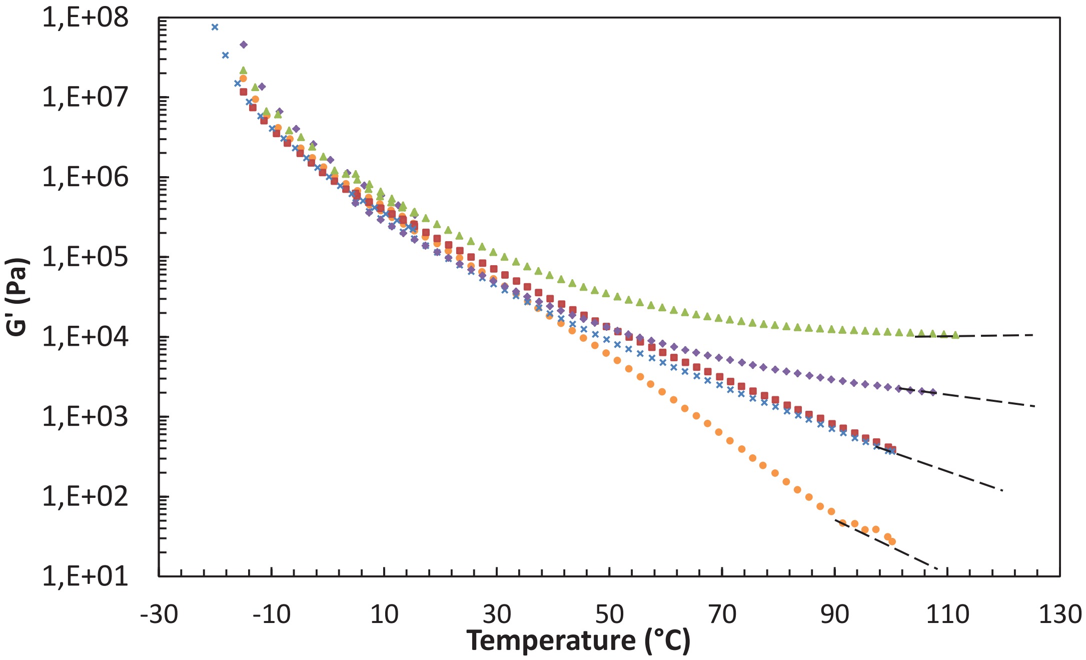


Figure 2-8. Dynamic rheological analyses of NIPU samples.
Influence of the average amine functionality on the storage modulus.
NIPU-fn=2.0 (●), 2.05 (■), 2.1 (x), 2.15 (♦), and 2.2 (▲).

The tangent delta (tan δ) is also a relevant factor to evaluate the flow of the polymers. If this factor is lower than 1, no flow appears. Figure 2-9 confirms the previous interpretations. For the NIPU-fn=2.0, 2.05 and 2.1 samples, this factor quickly increases from the room temperature to become higher than 1. These evolutions highlight the flow and the low structuration of these samples. For the other samples with higher average amine functionalities, the loss factor remains constant on a wider domain, and mainly lower than 1. Furthermore, the presence of a rubbery plateau for each NIPU sample reveals an elastomeric behavior for these materials.

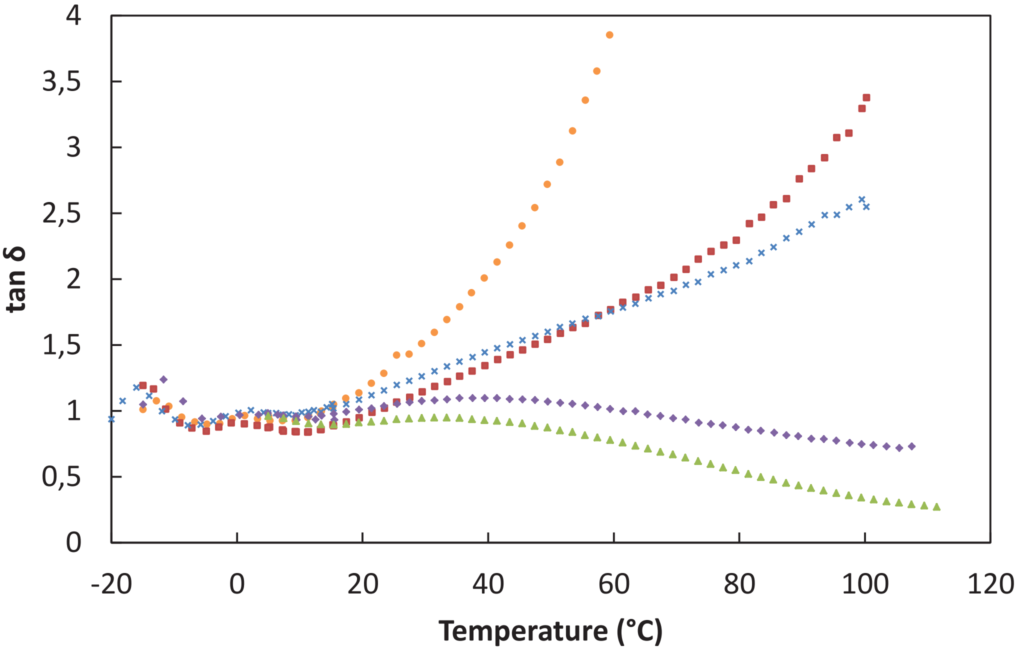


Figure 2-9. Dynamic rheological analyses of NIPU samples.
Influence of the average amine functionality on the tangent delta.
NIPU-fn=2.0 (●), 2.05 (■), 2.1 (x), 2.15 (♦), and 2.2 (▲).

1.3.4. Particular cases: crosslinked materials

Considering the specific behavior of the samples with a high average amine functionality (2.15 and 2.2), additional experiments were carried out for these materials in order to obtain further information on their morphologies and properties.

Dynamic mechanical analyses were performed on samples to complete the dynamic rheological analyses at low temperatures. Furthermore, it is also possible to evaluate the storage and the loss moduli, represented on Figure 2-10. For both samples, a glassy plateau is observed from -80 to -40°C followed by a broad transition. The alpha relaxation temperature (T_α) can be estimated at the maximum of the loss modulus curve (Table 2-4). The samples reach then a rubbery state, due to the presence of crosslinking.

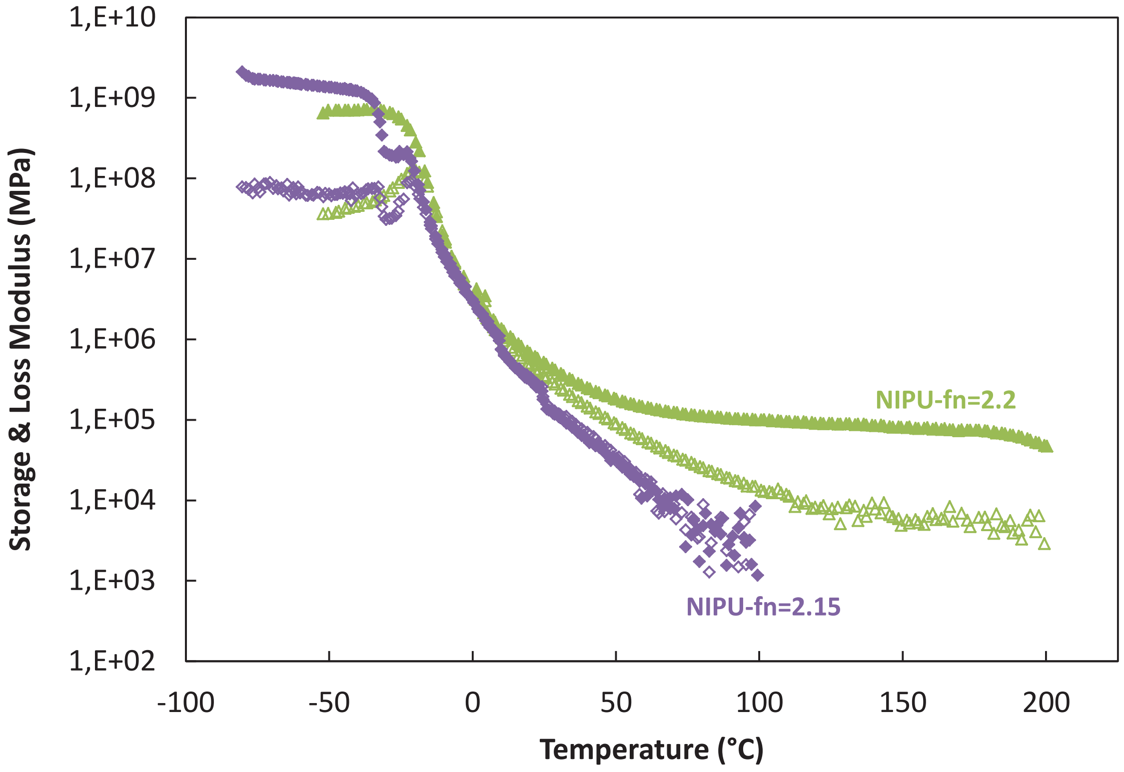


Figure 2-10. DMTA curves of NIPU-fn=2.2: E'(▲) - E''(△) and 2.15: E'(◆) - E''(◇).

The crosslink density, the degree of swelling and the gel content were determined for each crosslinked system *i.e.* for NIPU-fn=2.15 and 2.2 samples.

The crosslink density (ν_e) can be obtained from Equation 1 which is derived from the rubber elasticity theory[47] where, R is the gas constant (8.31 $J.mol^{-1}.K^{-1}$) and T is the temperature in Kelvin.

$$\nu_e = \frac{E}{3\,R\,T} \qquad (1)$$

Since the elastic modulus (E) can be associated to the storage modulus (E') at temperatures well above T_g, E can be substituted by E' in Equation 1 to determine ν_e (in the rubbery region at T_α + 40°C). Thus, the plateau of the elastic modulus in the rubbery state obtained from DMTA curves can be used to evaluate the crosslink density of NIPU materials. Table 2-4 summarizes values of the crosslink density determined from Equation 1. As expected, the crosslink density increases with the amine functionality. It is thus possible to modulate NIPU properties. The higher crosslink density is obtained with an average amine functionality of 2.2. However, the values are quite low compared to conventional systems.[48, 49]

Table 2-4. Main characteristic values for crosslinked NIPUs.

Samples	**T_α [a/] (°C)**	**T_α + 40 (°C)**	**E' [b/] at T_α + 40 (Pa)**	**ν_e [c/] (mol.m^{-3})**	**G [d/] (%)**	**Q [e/]**
NIPU-fn=2.15	-26	15	5.67 10^5	79	21	1.4
NIPU-fn=2.2	-20	20	6.58 10^5	90	70	1.6

a/ Alpha relaxation temperature determined from DMTA. b/ Storage modulus. c/ Crosslink density. d/ Gel content. e/ Degree of swelling.

The equilibrium degree of swelling (Q) was calculated from the swelling of NIPU in chloroform, using Equation 2. Where, W_P is the weight of dry polymer, W_S the weight of the solvent at equilibrium, d_P the density of the polymer and d_S the density of the solvent.

$$Q = \frac{W_P/d_P + W_S/d_S}{W_P/d_P} \tag{2}$$

The percentage of gel content (G) was determined from Equation 3. Where, W_{P0} is the initial sample weight.

$$G = \frac{W_P}{W_{P0}} * 100 \tag{3}$$

All these results confirm that the NIPU synthesized with the diamine of an average functionality of 2.2 is the highest crosslinked system with the highest gel content (Table 2-4). Compared with conventional PUs, which are fully crosslinked at a functionality of 2.2, NIPU-fn=2.2 contains 30% of soluble fraction. This result is due to the secondary reactions.

Finally, uniaxial tensile tests were performed on the highest crosslinked NIPU, NIPU-fn=2.2, in order to estimate its mechanical performances. Young's modulus E = 0.4 ± 0.1 MPa, tensile strength at break σ_{max} = 0.6 ± 0.2 MPa and elongation at break ε_{max} = 630 ± 80% were determined from the corresponding stress-strain curve. In the literature, PUs based on poliisocyanate with dimer fatty acids have similar elasticity and higher modulus.[44] However, NIPUs with a crosslink network often present a very low elasticity, far from an elastomeric behavior.[6] With an elongation at break higher than 600%, NIPU synthesized from DDA1 and SBBisCC reveals to be a promising soft material with high elastomeric properties.

1.4. Conclusions

A solvent-free and catalyst-free method for preparing polyurethanes (PUs) without harmful isocyanate was developed. All NIPUs synthesized present biobased contents around 80% (based on ^{14}C). Sebacic biscyclocarbonate and biobased dimer diamines (DDA) were used as building blocks for the synthesis of new biobased nonisocyanate polyurethanes (NIPUs). The resulting properties and behaviors were investigated.

All obtained NIPUs are amorphous and show a low T_g suitable for a wide range of applications. Various average amine functionalities of DDA were used to determine the structure-properties relationships of the NIPUs. Thermal and rheological analyses revealed that the modulation of the properties is possible through the control of the average amine functionalities of DDA. It was observed that the NIPU behavior is linked to the crosslink degree, which can be adjusted. NIPU with the highest crosslinking displays high elasticity. This corresponding NIPU with original macromolecular architecture is a promising elastomer with a great potential to replace some conventional soft PUs in the future. These results clearly show the possibility to use such biobased architectures to design novel environmental and health friendly PUs with high performances.

Acknowledgements

The authors thank the Alsace Region, the urban community of Strasbourg, SOPRÉMA and PSA Peugeot Citroën for their financial supports. Croda and Huntsman are also acknowledged for having kindly provided dimer diamines and glycerol carbonate, respectively. The authors would like to acknowledge Prof. Jean-Pierre Pascault (IMP-INSA Lyon, France) and Dr. Sébastien Gallet (ICPEES Strasbourg, France) for helpful discussions.

1.5. Supporting information

1.5.1. Characterization of sebacic biscyclocarbonate (SBBisCC)

Additional chemical characterizations were performed on SBBisCC in order to fully determine its structure.

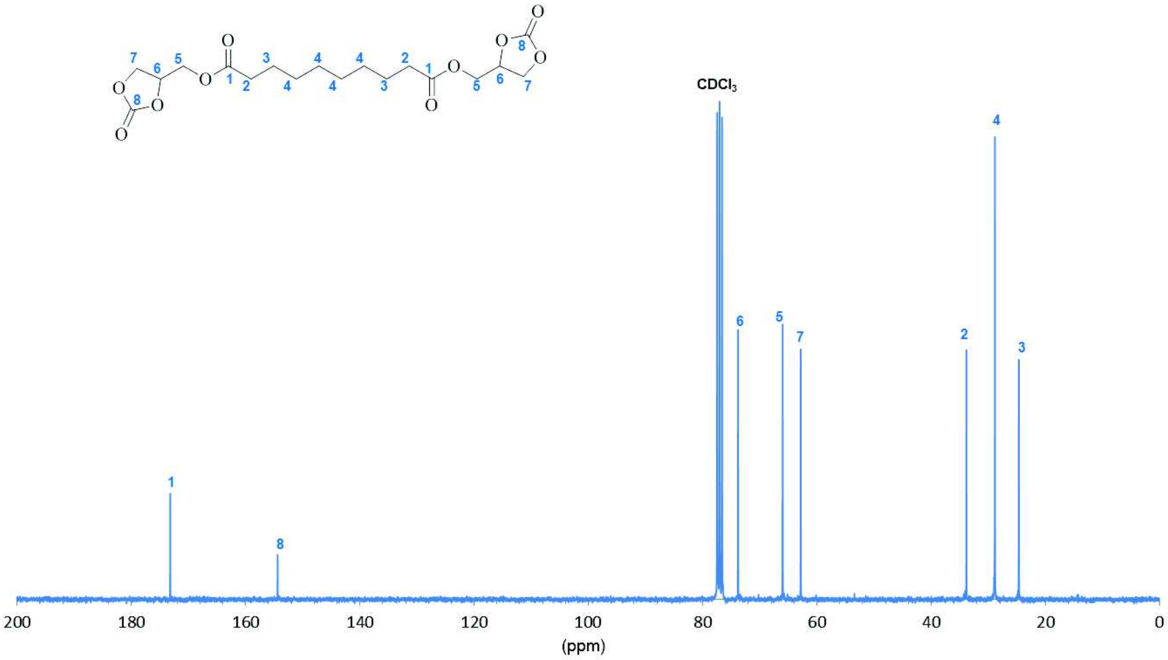


Figure 2-S1. ^{13}C-NMR of SBBisCC.

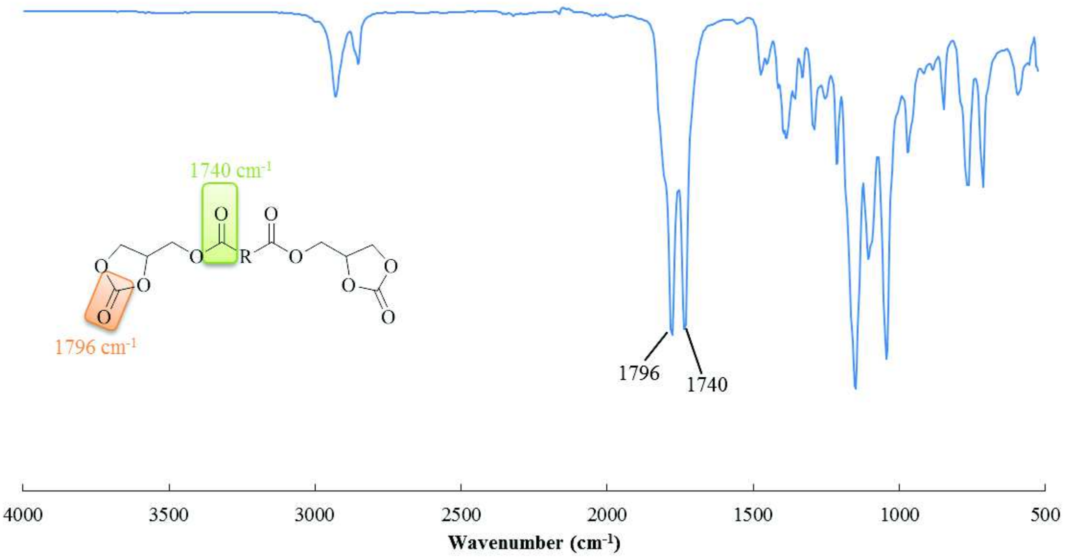


Figure 2-S2. FTIR spectra of SBBisCC.

1.5.2. Characterization of nonisocyanate polyurethane

Additional chemical characterizations were performed on NIPU-fn=2.0 in order to fully determine its structure. Same peaks were observed for the other amine average functionalities.

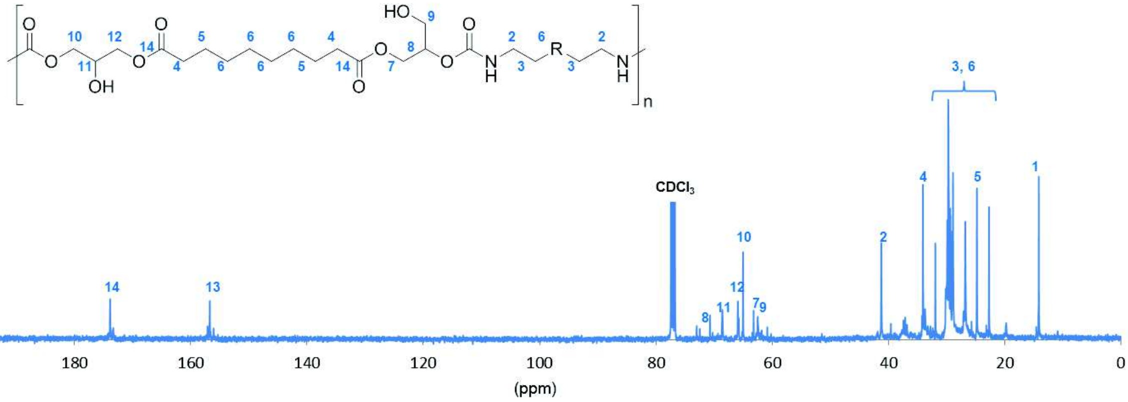


Figure 2-S3. ^{13}C-NMR of NIPU-fn=2.0.

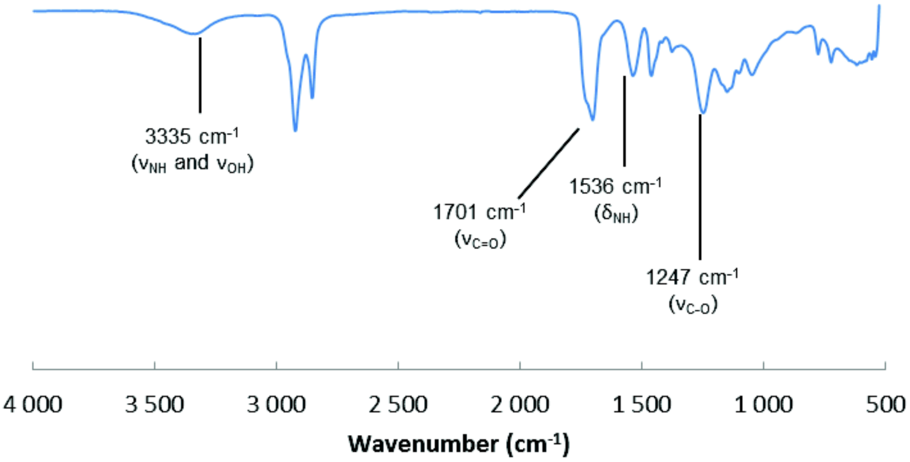


Figure 2-S4. FTIR spectra of NIPU-fn=2.0.

2. Conclusions et perspectives

Dans ce chapitre, une synthèse sans solvant et sans catalyse a été développée. Différents NIPU ont été synthétisés à partir d'acide sébacique et de dimère diamines. Ils présentent une teneur importante en biosourcé : environ 80%.

Une première étude a montré qu'un des paramètres importants pour obtenir les chaînes les plus longues et pour limiter les réactions secondaires est de sélectionner un ratio molaire stœchiométrique entre les deux monomères. Les masses molaires restent cependant relativement faibles comparées aux PU conventionnels, mais sont comparables à celles des autres systèmes NIPU rencontrés dans la littérature.

Dans un second temps, une étude de l'influence de la fonctionnalité moyenne de la diamine sur les propriétés thermiques et sur le comportement rhéologique des matériaux obtenus a été menée. En conclusion, en variant cette fonctionnalité, il est possible de moduler le degré de réticulation des NIPU et par conséquence leurs propriétés finales. La réticulation a permis de pallier à la faible réactivité de la réaction pour obtenir des matériaux avec des propriétés intéressantes pour un grand nombre d'applications potentielles. Le caractère élastomère et la très faible température de transition vitreuse de ces matériaux semblent tout particulièrement favorable à des applications de coating ou d'enduction. Toutefois, des essais supplémentaires de mise en œuvre monocomposant ou bicomposants seraient nécessaires à leur développement. Un autre point à étudier serait lié à la diminution de la fraction soluble, qui reste encore trop élevée comparée à des systèmes thermodurcissables classiques. Une solution serait d'augmenter la fonctionnalité du biscyclocarbonate en utilisant par exemple l'acide citrique qui est trifonctionnel et, de plus, biosourcé.

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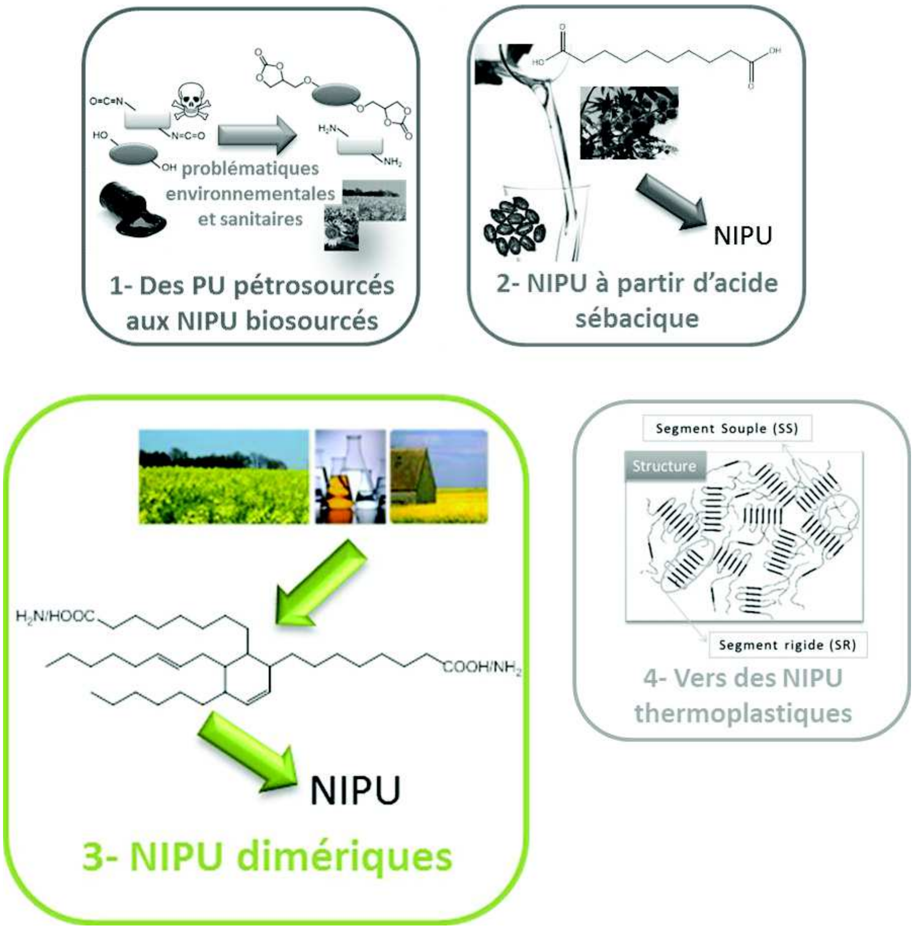
Chapitre 3

NIPU dimériques : Synthèse, caractérisation et comparaison à d'autres systèmes



Introduction

L'étude réalisée et présentée dans le Chapitre 2 a permis de développer une voie de synthèse de NIPU viable, sans solvant et sans catalyseur. C'est à dire en accord avec les différentes règles de base de la chimie verte.[1] À travers l'emploi d'une dimère diamine, le Chapitre 2 a également montré le fort potentiel lié à l'utilisation d'une structure biosourcée dimérique, issue d'acides gras, pour moduler les propriétés du matériau NIPU final.

L'objectif de ce nouveau chapitre est de proposer une synthèse de NIPU 100% biosourcés et issus de dimères d'acides gras, ce qui d'après l'analyse de la littérature (*cf.* Chapitre 1) n'avait encore jamais été réalisé. Dans cette optique, un nouveau biscyclocarbonate issu de dimères d'acide gras et totalement biosourcé a donc été élaboré. Afin de comprendre l'influence des structures dimériques sur les propriétés des NIPU, une première étude a permis de comparer des NIPU totalement dimériques avec des NIPU issu de « building blocks » (ou synthons) linéaires. Lors d'une seconde étude, le potentiel de ces NIPU dimériques a été évalué *via* une comparaison avec des PU conventionnels issus de structures similaires.

1. Les dimères d'acide gras et leurs dérivés, des synthons prometteurs pour la synthèse de NIPU

La troisième publication présentée dans ce chapitre est intitulée « Solvent- and catalyst-free synthesis of fully biobased nonisocyanate polyurethanes, from two dimer fatty acids. Effect of the macromolecular architectures », et soumise à *Green Chemistry*. Dans un premier temps, cette publication présente la synthèse et la caractérisation d'un biscyclocarbonate issu de dimères d'acides gras et de ses intermédiaires. Dans un second temps, l'intégration de ce synthon dans la synthèse de NIPU dimériques, entièrement biosourcés et réalisés en suivant les principes de la chimie verte est rapportée. Afin d'évaluer l'impact de ces synthons dimériques et le potentiel de ces nouveaux NIPU, diverses comparaisons avec (i) des NIPU présentant des structures linéaires, et (ii) des PU conventionnels dimériques sont ensuite abordées.

Publication n°3 :

Solvent- and catalyst-free synthesis of fully biobased nonisocyanate polyurethanes, from two dimer fatty acids. Effect of the macromolecular architecture.

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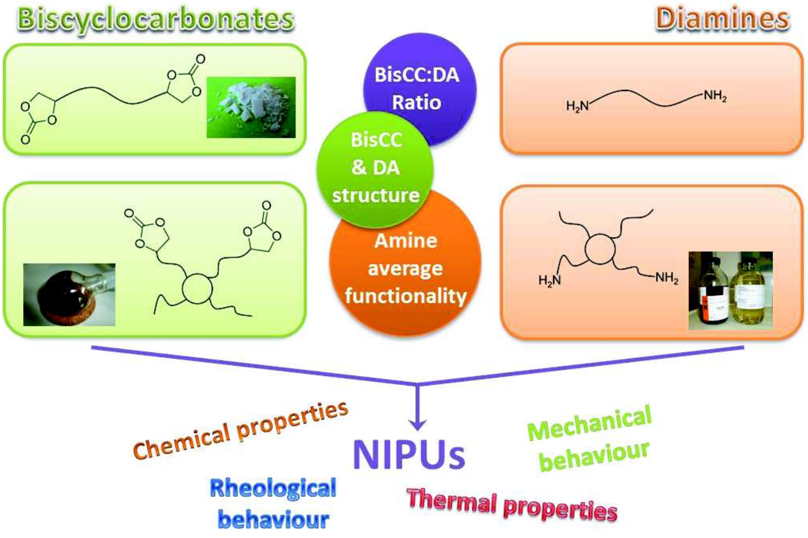
Green Chemistry – Submitted article

Graphical abstract



Abstract

A biscyclocarbonate based on a dimer fatty acid was successfully synthesized. The chemical structures of this original cyclic carbonate and its intermediates were determined by FTIR and NMR analyses. This cyclic carbonate reacts then with a dimer-based diamine to give a fully biobased nonisocyanate polyurethane (NIPU), without solvent and catalyst. Different macromolecular architectures were obtained. The influence of the cyclic carbonate:amine ratio, and the effect of the amine average functionality were investigated by chemical, thermal and rheological analyses, respectively. These parameters strongly impact the final NIPU properties. Comparisons with NIPUs based on linear structures show the effect of the architecture brought by the dimer-based building blocks on the resulting NIPU properties. To evaluate the real potential of these novel materials, NIPUs were also compared to conventional polyurethanes with equivalent architectures.

Keywords

dimer fatty acids, glycerol carbonate, nonisocyanate, polyurethanes, renewable resources, solvent-free synthesis

1.1. Introduction

Currently, literature shows more and more scientific papers about biobased PUs. In most of the cases only polyols are biobased, since the isocyanates stay fossil-based.[2-5] However, to increase the renewable carbon content of the PUs, some scientists have developed *e.g.*, vegetable oil-based isocyanates,[6-9] to produce fully biobased PUs.[10] Although several very promising molecules have been developed, a simple substitution with biobased products cannot solve the arising problems linked to the use of harmful and potentially carcinogenic isocyanates. A repetitive exposure to them can lead to serious and incurable respiratory problems.[11] Moreover, the synthesis of isocyanates requires the use of noxious substances such as phosgene. The current trend, linked also to the evolution of national and international regulations, is thus to move from petrochemical PUs to promising biobased ones, without isocyanates.[3] Nowadays, a significant attention is paid to environmental and health concerns with a new range of polyurethanes called NonIsocyanate PolyUrethanes (NIPUs). One of the main ways to obtain NIPUs is the aminolysis synthesis. *Via* the amine-cyclocarbonate reaction, NIPUs can be prepared without the use of toxic isocyanate.[3, 12, 13] These NIPUs are also called polyhydroxyurethanes (PHUs), since they present some hydroxyl groups due to the cyclic carbonate ring opening.[14]

Cyclic dicarbonates can be synthesized by various methods,[15] such as the direct esterification of dicarboxylic acids with glycerol carbonate, a promising route in the frame of a new emerging challenge based on renewable resources. Glycerol carbonate, a cheap and widely available biobased building block, can result from the reaction between carbon dioxide and glycerol, a major by-product from *e.g.*, the oleochemistry and the biodiesel industry.[16]

Diamines and the corresponding dicarboxylic acids can be produced from biobased feedstocks, and more particularly from vegetable oils. In addition to linear fatty diacids obtained from *e.g.* oxidative cleavage (ozonolysis, alkali fusion, …),[17, 18] methoxycarbonylation,[19] metathesis[20] or microbial oxidation,[21] dimer fatty acids (DFAs) can also be produced by dimerization of unsaturated fatty acids (Diels-Alder reaction), derived from vegetable oils such as *e.g.* rapeseed and soybean oils. An example of the corresponding chemical structures is given by Figure 3-1. In addition to diacids and due to specific process conditions (200-250°C under pressure in presence of catalysts), monoacids and triacids could also result from this reaction. Distillation and hydrogenation steps can be performed depending on the desired purity and final structures. Dimer diamines (DDAs) can result from the synthesis of DFAs with ammonia followed by a reduction reaction.[22] DFAs and DDAs are promising biobased (100% renewable carbon content) building blocks for the elaboration of new durable and biobased macromolecular architectures. And, thanks to their unique structures with long carbon pending chains, they bring to the polymers some specific behaviors such as high flexibility and low glass transition temperature. Furthermore, they show a low viscosity, which is required for solvent-free synthesis.

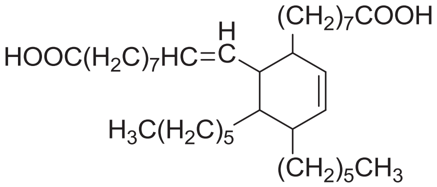


Figure 3-1. Cyclic chemical structure of dimer fatty acids.

In the literature, several papers have highlighted the influence of the chemical structures of cyclic carbonates and the diamines on their respective reactivity for NIPU synthesis.[23-27] The main key parameters of the cyclic carbonate reactivity are the presence and the nature of substituents, as well as the number of atoms of the cyclic carbonate ring.[14, 24, 28] It was already demonstrated that cyclic carbonates with larger rings sizes present the highest reactivity towards amines, with an increase of the reaction rate[23] and the molar masses.[24] Although, it seems that the corresponding cyclic carbonates are responsible of more secondary reactions.[29] Furthermore, reactivity is also enhanced when the substituent of the cyclic carbonate is a stronger electron-withdrawing group.[28] Concerning diamines, highest reactivity with cyclic carbonate was observed for lower mass aliphatic amines.[25] The type of diamine also plays a key role in the aminolysis reaction, since primary amines are reactive towards cyclic carbonates, whereas tertiary amines do not react. Recently, it was shown that secondary amines can also react in some conditions with carbonates.[26] Furthermore, less hindered and more nucleophilic amines display the highest reactivity.[27] Contrary to the effect of the structure on the reactivity reported by several groups,[25, 26, 28] the influence of monomers structures on NIPU properties has not yet been studied.

The aim of this study is to synthesize novel and fully biobased NIPUs *via* a green chemistry process, without solvent and catalyst. Therefore, our investigations were focused on the use of DFAs and DDAs, from vegetable oils. Furthermore, comparisons with NIPUs containing linear structures were realized to show the influence of the specific dimer architectures on the resulting NIPU properties. In order to evaluate the real potential of these novel isocyanate-free PUs, comparison with conventional PUs based on similar macromolecular architectures were also performed. Besides and as far as we know, PU synthesis has never been reported from two different dimers fatty acid derivatives, polyols and polyisocyanates, respectively.

1.2. Experimental part

1.2.1. Materials

Radiacid 0970, a dimer fatty acid (DFA) was provided by Oleon (Ertvelde, Belgium). Table 3-1 shows its respective composition in monomer, dimer and trimer. Thionyl chloride (≥99%), ethyl acetate (≥99%) and dichloromethane (DCM, ≥99%) were purchased from Sigma-Aldrich. Glycerol carbonate (Jeffsol GC, 93%) was obtained from Huntsman (Everberg, Belgium). Dimer-based diol (DOH) and dimer-based diamines (DDAs) were kindly supplied by Croda (Goole, England), under the trade name Pripol 2033 and Priamine, respectively. Two grades of DDA, hereinafter referred to as DDA2.2 and DDA2.0, were used neat or mixed together to obtain a precise average amine functionality. DDA2.2 and DDA2.0 have an average functionality of 2.2 and 2.0, respectively. Dimer and trimer contents are reported in Table 3-1. These latter present an amine value (AV) of 198 and 204 mg KOH per g, respectively, with glass transition temperatures lower than -50°C. At room temperature, DDA2.2 is a viscous ambered liquid, and DDA2.0 is a yellowish, slightly viscous liquid. Diaminooctane (DA8, >98%) and sebacoyl chloride (SBCl, 97%) were purchased from Alfa Aesar, and triethylamine from Carlo Erba, respectively. 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, commercialized under the trade name DDI 1410 (>98%), was kindly supplied by Cognis-BASF. Hexamethylene diisocyanate (HDI, >99.5%) was provided by Vencorex (Waalwijk, Netherlands). All chemicals were used as received without any purification, except DCM, which was purified with a drying solvent station. Table 3-1 presents an overview of the compositions of the different dimeric materials.

Table 3-1. Summary of the dimeric materials used and their corresponding contents.

Samples	Monomer content (wt%)	Dimer content (wt%)	Trimer content (wt%)
Radiacid 0970 (DFA)	0.7	96.7	2.6
Priamine 1071 (DDA2.2)	*trace amount*	75	25
Priamine 1075 (DDA2.0)	*trace amount*	> 99	< 1
Pripol 2033 (DOH)	0.5	98.6	0.9
DDI 1410	*trace amount*	≥ 98	< 2

Data obtained from suppliers.

1.2.2. Synthesis

1.2.2.1. Synthesis of biscyclocarbonate (BisCC)

Two types of BisCC, referred to as SBBisCC and DBisCC, were synthesized. They present linear and dimer structures, respectively.

Sebacic biscyclocarbonate (SBBisCC) was directly synthesized by esterification of sebacoyl chloride using glycerol carbonate (GC) according to a previously reported procedure.[30]

Dimer biscyclocarbonate (DBisCC) was obtained by esterification of a dimer fatty acid (DFA) with GC. In order to improve the reactivity of DFA, a preliminary halogenation reaction of the compound has been carried out. DBisCC was thus synthesized in two steps following the general pathway given in Figure 3-2.

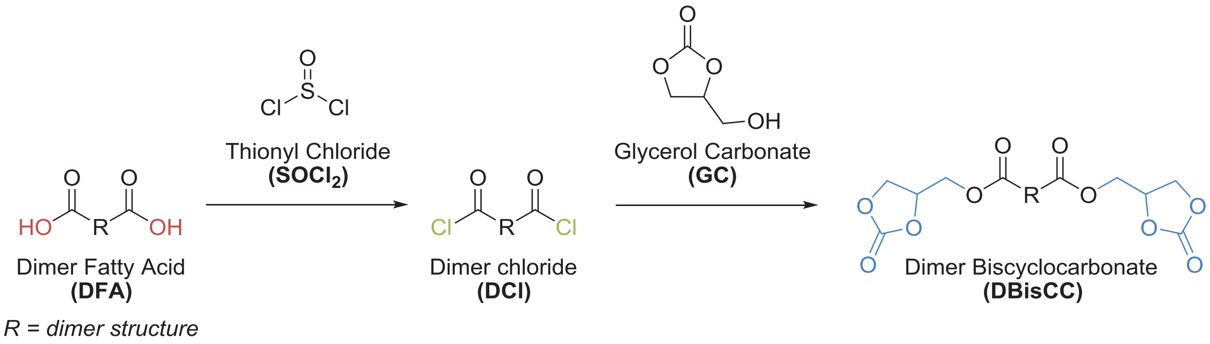


Figure 3-2. Reaction scheme for the synthesis of DBisCC.

Halogenation step. In a three-necked 250 mL round-bottomed flask equipped with a magnetic stirrer, DFA (20.0 g, 35 mmol) was dissolved into ethyl acetate (100 mL) under a nitrogen flow at a temperature of 35°C. An excess of thionyl chloride (16.7 g, 140 mmol) was then added drop by drop through the stirred reaction mixture, which was finally heated at 35°C during 4 hours. The formed hydrogen chloride was trapped in a wash-bottle containing an aqueous sodium hydroxide solution connected to the flask *via* an outlet. The solvent and the excess of thionyl chloride were then distilled out from the reactive mixture. Dimer chloride (DCl) was obtained in a yield of 21.3 g (100%), as a brown viscous product. The halogenation reaction was confirmed by IR and NMR analyses.

FTIR-ATR (cm^{-1}, Figure 3-3): 1798 (C=O chloride group).

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm, Figure 3-4): 0.85-0.90 (6H, m, -C*H*$_3$), 1.26 (38H, s, -C*H*$_2$-), 1.65-1.76 (4H, m, -C*H*$_2$-CH_2-COCl), 2.88 (4H, t, *J* = 7.4 Hz, -C*H*$_2$-COCl), 4.97-5.44, 6.69-7.12 (0.93H, m, -C*H*=C*H*-).

^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm, see Figure 3-S4 in the ESI†): 14.3 (-CH_3), 22.8 (-*C*H_2-CH_3), 25.2 (-*C*H_2-CH_2-COCl), 28.6-29.9 (-*C*H_2-), 47.3 (-*C*H_2-COCl), 174.0 (-*C*OCl).

Esterification step. The esterification synthesis was carried out in a three-necked 250 mL round-bottomed flask. Glycerol carbonate (15.5 g, 131.3 mmol) and triethylamine (13.3 g, 131.4 mmol) were successively introduced in the flask and mixed under an inert gas flow with 50 mL of freshly dried dichloromethane. DCl (20 g, 32.8 mmol) was then added drop by drop to the stirred reaction mixture, cooled in an ice water bath. The reaction was then conducted overnight at room temperature under agitation with a continuous nitrogen stream. The formed triethylamine hydrochloride $EtN_3 \cdot HCl$ was then taken out by filtration and the organic phase was washed with a 5 wt% HCl solution and water, to eliminate the excess of glycerol carbonate. The solution was finally dried with anhydrous sodium sulphate and solvent was removed under vacuum to yield 25.2 g (99.5%) of DBisCC, a brown viscous liquid. The biscyclocarbonate structure was confirmed by IR and NMR analyses.

FTIR-ATR (cm^{-1}, Figure 3-3): 1740 (C=O ester group), 1797 (C=O cyclocarbonate group).

^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm, Figure 3-4): 0.81-0.90 (6H, m, -C*H*$_3$), 1.25 (38H, s, -C*H*$_2$-), 1.56-1.66 (4H, m, -C*H*$_2$-CH_2-COO-), 2.36 (4H, t, *J* = 7.6 Hz, -CH_2-C*H*$_2$-COO-), 4.22-

4.39, 4.55 (8H, m, t, J = 8.6 Hz, -OCOO-CH_2-CH-CH_2-O-), 4.88-4.96 (2H, m, -OCOO-CH$_2$-CH-CH$_2$-O-), 5.00-5.45, 6.69-7.12 (0.82H, m, -CH=CH-).

^{13}C-NMR (100 MHz, CDCl$_3$, δ, ppm, see Figure 3-S5 in the ESI†): 14.3 (-CH$_3$), 22.8 (-CH$_2$-CH$_3$), 24.9 (-CH$_2$-CH$_2$-COO-), 29.1-30.2 (-CH$_2$-), 34.0 (-CH$_2$-COO-), 62.9 (-OCOO-CH$_2$-CH-CH$_2$-O-), 66.1 (-OCOO-CH$_2$-CH-CH$_2$-O-), 73.9 (-OCOO-CH$_2$-CH-CH$_2$-O-), 154.5 (-OCOO-), 173.4 (-COO-).

1.2.2.2. Synthesis of NIPUs

Two NIPU families, referred to as LNIPUs and DNIPUs, were synthesized. They were obtained from linear SBBisCC and dimeric DBisCC, respectively. The formulations of all NIPU samples are summarized in Table 3-2, with the corresponding designations.

Table 3-2. Designation and formulation of the different NIPU samples.

Sample	**NIPU family**	**BisCC**	**Diamine**	**Corresponding quantities for NIPU synthesis**[a]		
				BisCC	**Diamine**	
					DDA2.0	***DDA2.2***
LNIPU-DA8	LNIPU	SBBisCC	DA8	20.0 (49.7)	7.2 (49.7)	-
LNIPU-DDA2.0			DDA2.0		27.3 (49.7)	-
LNIPU-DDA2.05			DDA2.05		20.5 (37.3)	7.7 (12.4)
LNIPU-DDA2.1			DDA2.1		13.7 (24.9)	15.5 (24.9)
LNIPU-DDA2.15			DDA2.15		6.8 (12.4)	23.2 (37.3)
LNIPU-DDA2.2			DDA2.2		-	31.0 (49.7)
DNIPU-DA8	DNIPU	DBisCC	DA8	20.0 (25.9)	3.7 (25.9)	-
DNIPU-DDA2.0			DDA2.0		14.2 (25.9)	-
DNIPU-DDA2.05			DDA2.05		10.7 (19.4)	4.1 (6.5)
DNIPU-DDA2.1			DDA2.1		7.1 (13.0)	8.1 (13.0)
DNIPU-DDA2.15			DDA2.15		3.6 (6.5)	12.1 (19.4)
DNIPU-DDA2.2			DDA2.2		-	16.1 (25.9)

[a]Initial formulations for the synthesis of the different NIPUs, in g. The molar masses (in mmol) are given between brackets.

Linear aliphatic NIPUs, referred to as LNIPUs, were prepared in bulk and without catalyst at 75°C. SBBisCC and various diamines were added at a molar stoichiometric ratio, according to a methodology already reported.[30]

Dimer-based NIPUs (DNIPUs) were obtained *via* the aminolysis reaction between a BisCC and a diamine. A general synthesis was carried out as follows (Monomer ratios are given in Table 3-2). In a 100 mL reactor equipped with a mechanical stirrer, DBisCC (20.0 g, 25.9 mmol) and diamine were added at a molar stoichiometric ratio. The reaction took place in bulk and without catalyst under inert gas flow at a temperature of 75°C. After two hours under stirring, the viscous mixture was spread on a polytetrafluoroethylene-based sheet and heated in an oven under vacuum at 75°C for ninety-four hours. The product was obtained as a yellow or brown solid depending on the diamine used.

1.2.2.3. Synthesis of conventional PUs

Two PU families, referred to as LPUs and DPUs, were synthesized. They were respectively obtained from linear (HDI) or dimeric (DDI 1410) isocyanate, and two types of polyols following the ensuing general protocol. The formulations of all PU samples are summarized in Table 3-3.

The typical procedure for the synthesis was carried out as follows. Isocyanate and polyol (Table 3-3 for corresponding quantities) were charged in a 100 mL reactor equipped with a mechanical stirrer. The NCO:OH molar ratio was calculated on the basis of the hydroxyl index (I_{OH}) of the polyol and the NCO content (*NCO%*) of the isocyanate, preliminary determined (Titration methods given in the ESI†). A molar ratio equals to 1.05 was used for all syntheses. This 5 mol% excess of isocyanate was used to compensate the by-reaction due to the estimated residual water brought by the dried polyols. The main reaction took place in bulk without catalyst, at a temperature of 75°C, and under a dry nitrogen gas flow to prevent the reaction of the isocyanate groups with air moisture. After two hours under stirring, the viscous mixture was spread on a polytetrafluoroethylene-based sheet and heated in an oven under vacuum at 75°C for ninety-four hours. The product was obtained as a yellow or colorless solid depending on the raw materials used.

Table 3-3. Designation and formulation of the different conventional PU samples.

Sample	PU Family	isocyanate	polyol	PU formulation[a]	
				isocyanate	polyol
LPU-DOH	LPU	HDI	DOH	5.1 (60.3)	15 (57.4)
DPU-OH8	DPU	DDI 1410	OH8	20.0 (61.1)	4.3 (58.2)
DPU-DOH			DOH	20.0 (61.1)	15.2 (58.2)

[a] Initial composition (in g) of the different synthesized NIPUs. The molar masses (in mmol) are given between brackets.

1.2.3. Measurements

Infrared spectroscopy was achieved with a Fourier transformed infrared spectrometer Nicolet 380 (*Thermo Electron Corporation*) working in Reflection Mode and equipped with an ATR diamond module (FTIR-ATR). The FTIR-ATR spectra were collected at a resolution of 4 cm^{-1} and with 64 scans per run.

^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker* Ascend$^{\mathrm{TM}}$ 400 spectrometer at 300 MHz and 100 MHz respectively. Chloroform-d_6 was used as a solvent.

DOSY NMR spectra were recorded on a *Bruker* Avance 400 MHz using a QNP 5 mm gradient probe. The temperature was regulated at 300 K, and the NMR tube was not spun. The diffusion NMR experiments were performed with a pulsed-gradient stimulated echo sequence, using a bipolar gradient.[31] The samples were prepared by dissolution in deuterated water (D_2O) at a concentration of about 10 mg.mL^{-1}. Sequence delays were $\Delta = 150$ ms (diffusion delay), $\tau = 0.4$ ms (after gradient recovery delay), and Te = 2.6 ms (LED recovery delay). Additional information are available in the ESI†.

Thermal degradations were studied by thermogravimetric analyses (TGA). Measurements were conducted under inert gas (flow rate = 25 mL.min^{-1}) using a Hi-Res TGA Q5000 apparatus from *TA Instruments*. The samples (3–5 mg placed in an aluminum pan) were heated up to 600°C at 10°C.min^{-1}. The characteristic degradation temperatures are the temperatures at the maximum of the derivative thermogram (DTG) curve (T_{max}) and at which the sample weight equals 98%, 50% and 2% of the initial one ($T_{98\%}$, $T_{50\%}$ and $T_{2\%}$).

The main characteristic temperatures were determined by differential scanning calorimetry (DSC Q200, *TA Instruments*), under nitrogen flow. The samples (2–5 mg) were heated until 175°C with a heating rate of 10°C.min^{-1} (first heating scan), then cooled to −80°C at 5°C.min^{-1} and finally re-heated to 175°C at a heating rate of 10°C.min^{-1} (second heating scan). The glass transition temperature (T_g) was determined as midpoint of the change in slop of the baseline, from the second heating scan in order to erase the previous thermal history of the samples during the first scan.

The number-average molar mass (M_n), the mass-average molar mass (M_w) and the dispersity (Đ) of the resulting samples were determined by Size Exclusion Chromatography (SEC), using Malvern Instrument apparatus (Viscotek RImax). This device was equipped with a guard column 10 mm (8 µm) and three 300 mm columns (50, 150 and 500 Å). Refractive index (RI) and ultra-violet (UV) detectors were used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL.min^{-1}. The apparatus was calibrated with linear polystyrene standard from 162 to 20,000 g.mol^{-1}.

Swelling ratio (SR) was calculated by Equation 1, where, W_S is the weight of the solvent at equilibrium and W_D is the weight of dry polymer after swelling.

$$SR\ (\%) = \frac{W_S - W_D}{W_D} * 100 \tag{1}$$

The gel content was determined for each system from Equation 2, where, W_{P0} is the initial sample weight.

$$G = \frac{W_P}{W_{P0}} * 100 \tag{2}$$

Dynamic rheological analyses (DRA) of the final materials were performed with a strain-controlled rheometer (ARES, Rheometric Scientific), equipped with parallel-plate geometries. The oscillatory measurements were carried out on a 25 mm diameter plate, with 2 mm thickness. The following tests were conducted: (i) dynamic strain sweep to estimate the viscoelastic region of the samples, (ii) isofrequency dynamic temperature sweep test from 0 up to 160°C at a frequency of 1 Hz. Changes in the viscous and storage modulus (G'' and G', respectively) were registered. The corresponding tan δ = G''/G' were determined.

Uniaxial tensile tests were achieved using an Instron machine (5567 type, H1592 serie). The experiments were performed on tensile specimens (size: 25 x 4 x 1 mm) at room temperature, using a crosshead speed of 100 mm.min^{-1} and a load cell of 5 kN sensitivity. After adjusting the parameters, experiments were carried out at least 3 times for each sample. Young's modulus (E), tensile strength at break (σ_{max}) and elongation at break (ε_{max}) were determined.

1.3. Results and discussion

The results are presented in five sections. First, DFA raw material has been characterized to clearly define its chemical structure. Afterwards, intermediate products DCl and DBisCC were analyzed to confirm the chemical modifications of DFA. The properties of DNIPUs are then presented and compared with NIPU materials based on more classical linear structures. The last part is dedicated to the comparison of the obtained NIPUs with conventional PUs.

1.3.1. DFA characterization

The main characteristics of DFA, obtained from dimerization of rapeseed fatty acids, are reported in Table 3-4. FTIR and ^{1}H-NMR results are presented in Figures 3-3 and 3-4, respectively (Figure 3-S1 in the ESI† for ^{13}C-NMR analysis and corresponding signal attributions). After dimerization and purification, partial hydrogenation was performed to reduce the double bond content and to improve the long-term stability and the ageing of this building block. The number of residual double bonds was quantified by ^{1}H-NMR analysis. Table 3-4 shows that DFA has a low number of double bonds per molecule, which is equal to 0.15. Determination of molar masses by SEC is based on a calibration with equivalent PS molar masses, not perfectly adapted for the analysis of such molecules. The corresponding values are higher than expected. Nevertheless, the SEC chromatogram of DFA (Figure 3-S2 in the ESI†) displays a well define double peak, which corresponds to dimer and trimer molecules, with a higher content of dimer structures. All these results are in good agreement with the data given by the supplier.

Diffusion ordered spectroscopy, also called DOSY NMR spectroscopy, was performed to deeply analyze the chemical structure of DFA raw material without any preliminary physical separation (Figure 3-S3 in the ESI†).[32] All spots of the DFA samples are perfectly aligned suggesting a unique Đ coefficient. The product presents a low dispersity. It is not easily possible to distinguish acyclic from cyclic structures but we can confirm the cyclic content value, on agreement with data from the supplier (75% linear, 25% cyclic).

Table 3-4. Analysis results performed on DFA raw product.

SEC analysis	*Peak #1*		*Peak #2*	
	M_n *(g.mol^{-1})*	808	M_n *(g.mol^{-1})*	1304
	M_w *(g.mol^{-1})*	827	M_w *(g.mol^{-1})*	1331
	Đ (=M_w/M_n)	1.02	Đ (=M_w/M_n)	1.02
	% area	93	% area	7
^{1}H-NMR analysis	Double bonds number per molecule			0.15
DOSY NMR analysis	Dispersity			low
Titration	Acid value *(mg KOH/g)*			219.8

1.3.2. Synthesis and characterization of DBisCC

The DBisCC was designed to react afterwards *via* aminolysis reaction. DBisCC was obtained from GC and DFA. The structure of all the corresponding intermediates were analyzed and confirmed by FTIR and NMR spectroscopies (Figures 3-3 and 3-4).

In the first step, halogenation of DFA with thionyl chloride yields DCl. FTIR spectra of DFA displays an absorption peak at 1707 cm^{-1} assigned to the carbonyl group and a broad band from 2400 to 3400 cm^{-1}, corresponding to the OH of the carboxylic acid groups. The halogenation of DFA was confirmed by the disappearance of the OH band around 3000 cm^{-1}, such as the shift of the carbonyl group peak from 1707 to 1798 cm^{-1} due to the formation of more withdrawing chloride groups. ^{1}H-NMR analysis and more particularly the deshielding effect (from 2.35 to 2.88 ppm) of the methylene group attached to the carboxylic acid also confirm the halogenation (Figure 3-4).

The esterification reaction of DCl with GC leads to the synthesis of DBisCC and results in modification in the carbonyl groups region, observed through FTIR. Whereas carbonyl peak related to chloride groups disappears in favour of the ester carbonyl group peak at 1740 cm^{-1}, an additional peak at 1797 cm^{-1} confirms the presence of carbonate groups (Figure 3-3). The esterification reaction was also confirmed by NMR analysis results, presented in Figure 3-4. The methylene group linked to the chloride function shifts from 2.88 to 2.36 ppm, due to the formation of the ester, a less electronegative group. Furthermore, some peaks assigned to the cyclic carbonate group appear in the region 4.2-5.0 ppm. Carbon double bonds are still present, as shown by their signals at around 5.3 and 6.8 ppm.

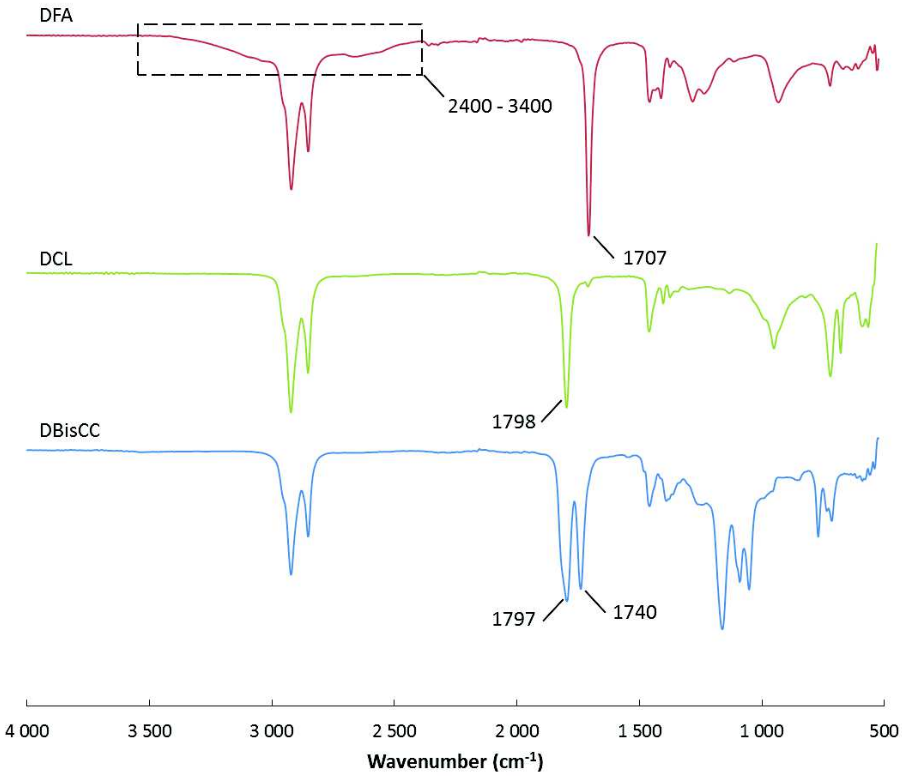


Figure 3-3. FTIR spectra of intermediates based on DFA.

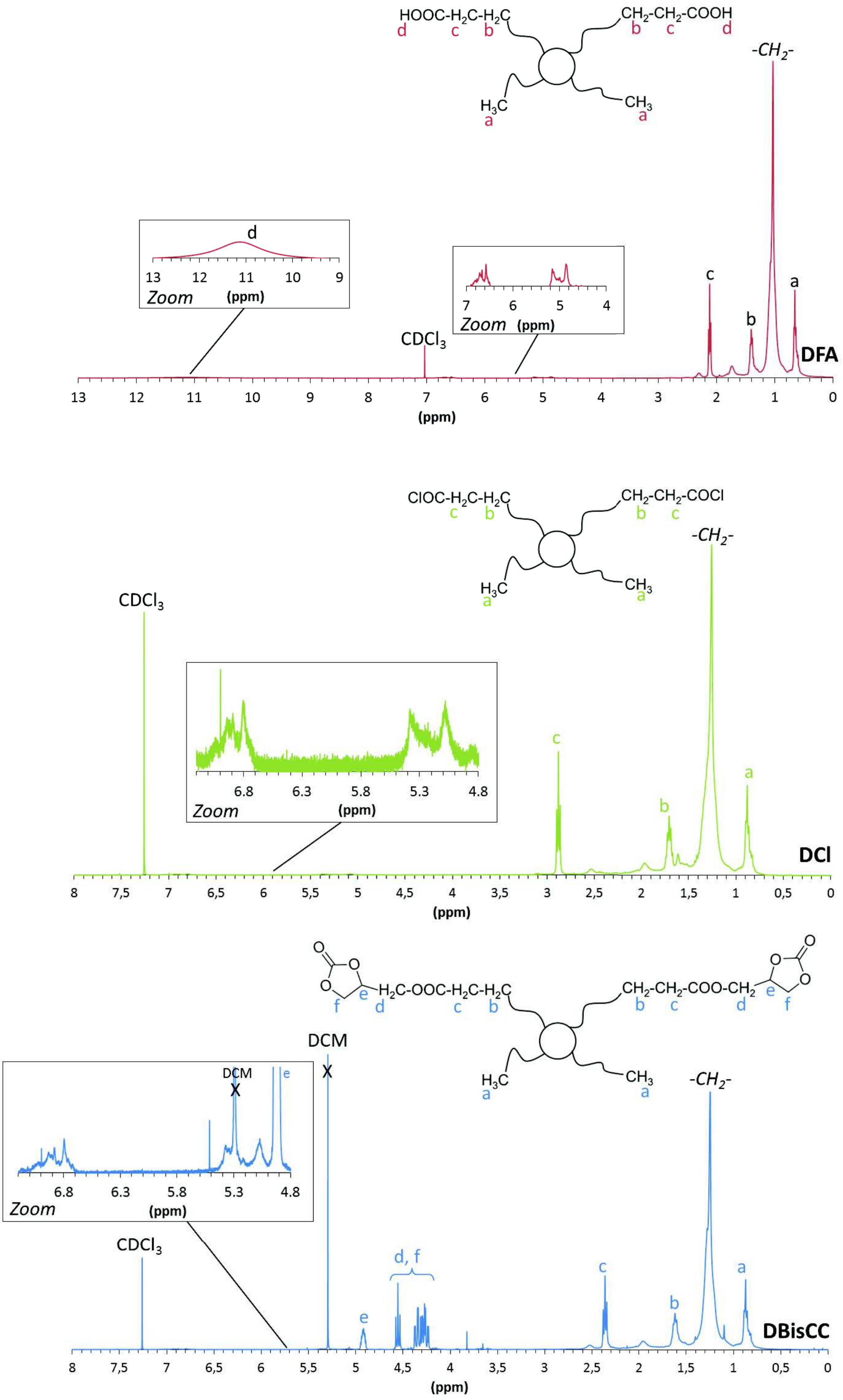


Figure 3-4. ^{1}H-NMR spectrum of intermediates based on DFA.

1.3.3. DNIPU characterization

1.3.3.1 Effect of the DBisCC:diamine molar ratio

A first study was performed to determine the optimal ratio for the NIPU synthesis. Figure 3-5 shows storage modulus (G') and loss factor (tan δ) as function of temperature for DNIPU-DDA2.0 based on different DBisCC:diamine molar ratios, in a large temperature range from 5 to 130°C. Two main behaviors were observed:

(i) For a stoichiometric ratio, a short rubbery plateau is visible on the storage modulus curve, which shows a particular structuration, due to a network formation. The maximum loss factor value, lower than one, corroborates this result.

(ii) For a non-stoichiometric ratio, G' moduli drop and tan δ quickly rise, meaning that the materials flow and do not have a specific structuration. Shorter chains are formed. With an excess of amine, secondary reactions with ester linkage can occur with a decrease of the chains length, as mentioned by Javni *et al.*[33, 34] Resulting amide linkages were confirmed by FTIR analysis (see Figure 3-S6 in the ESI†) and were already noticed for other NIPU materials.[30]

All things considered, stoichiometric ratio was selected for the further studies.

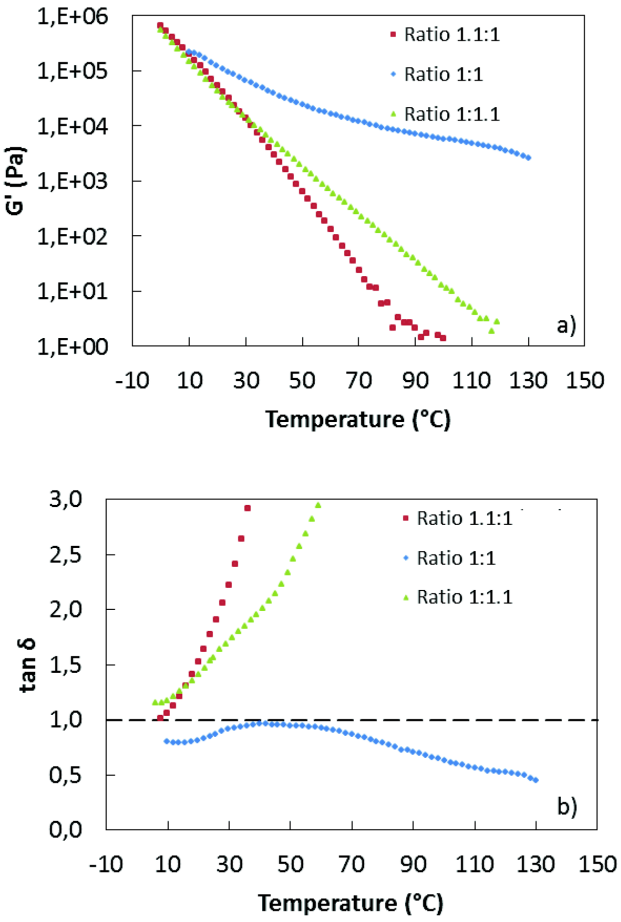


Figure 3-5. Dynamic rheological analysis curves of DNIPU-DDA2.0 based on various molar ratios.
DNIPU-1.1:1 ratio (■),DNIPU-1:1 ratio (●), DNIPU-1:1.1 ratio (▲).
a) storage modulus, G’ ; b) loss factor, tan δ.

1.3.3.2. Effect of the average amine functionality

DNIPUs were synthesized from dimer bis(cyclic carbonates), varying their average amine functionalities from 2.0 to 2.2. They are referred to as DNIPU-DDA2.0, 2.05, 2.1, 2.15 and 2.2, respectively. Chemical characterizations of these materials were performed to define their structures, and to analyze the influence of the average amine functionality on their structures and on the corresponding thermal and rheological properties.

The characteristic peaks of DNIPUs were observed by FTIR analysis (Figure 3-S7 in the ESI†). Except for DNIPU-DDA2.05, DNIPU samples are not soluble in common solvents. They are mainly thermoset polymers and form polymeric gels. The results obtained from swelling data of DNIPU samples in tetrahydrofuran are summarized in Table 3-5. Except DNIPU-DDA2.05, all polymers are crosslinked. However, their gel values are quite low and

DNIPUs contain about 30% of soluble fractions, compared with few percent for the conventional PUs.[35] This difference can be explained by chain cleavages due to secondary reactions between amines and ester links.[33, 34] High SR values indicate low crosslinking degrees. One can remark that as a trend, SR decreases when the amine average functionality increases.

Table 3-5. Gel content and degree of swelling of DNIPU thermosets.

Samples	**G (%)**	**SR (%)**
DNIPU-DDA2.0	75	2000
DNIPU-DDA2.05	*soluble*	*soluble*
DNIPU-DDA2.1	70	1970
DNIPU-DDA2.15	67	1740
DNIPU-DDA2.2	66	1450

Table 3-6 shows T_g of the synthesized DNIPUs. All T_g are quite low (around -20°C) compared to those of conventional NIPUs,[3] due to the dimer structures with pending aliphatic chains, which increase the free volume and consecutively chains mobility. Amine average functionality does not seem to influence significantly the T_g value. DNIPUs have rather low crosslinking degree, which can be approached through the inverse of the SR value (Table 3-5). Thus, these corresponding variations are too low to have a significant impact on the T_g values.

Table 3-6. DSC data of DNIPU samples.

Samples	**T_g (°C)**
DNIPU-DDA2.0	-20
DNIPU-DDA2.05	-21
DNIPU-DDA2.1	-21
DNIPU-DDA2.15	-20
DNIPU-DDA2.2	-19

The thermal degradation of DNIPUs and their monomers was investigated *via* TGA (Figure 3-6 and Table 3-S1 in the ESI†). As their corresponding dimer acids and derivatives, all DNIPUs display an excellent thermal stability with degradation temperatures higher than 444°C (Table 3-S1 in the ESI†). DDA2.0 shows a well-defined degradation step, whereas DDA2.2 presents a broader transition towards higher temperatures. This is due to the higher trimer content with DDA2.2, forming a crosslinked network, increasing the thermal resistance. The thermal decomposition of conventional PUs is usually a multi-stage process including the decomposition of urethane bonds and the degradation of the corresponding carbonated chains.[36] The degradation of the DNIPUs starts at around 250°C and presents two main steps. The large temperature range, from around 250 to 400°C indicates that the first degradation step is a combination of various degradation processes. It could be assigned to both urethane and ester linkages decomposition.[37] The last degradation step (between 400 and 500°C), which is more noticeable, could be attributed to the degradation of the carbonated segments. More details are given below, to compare PU and NIPU thermal degradations.

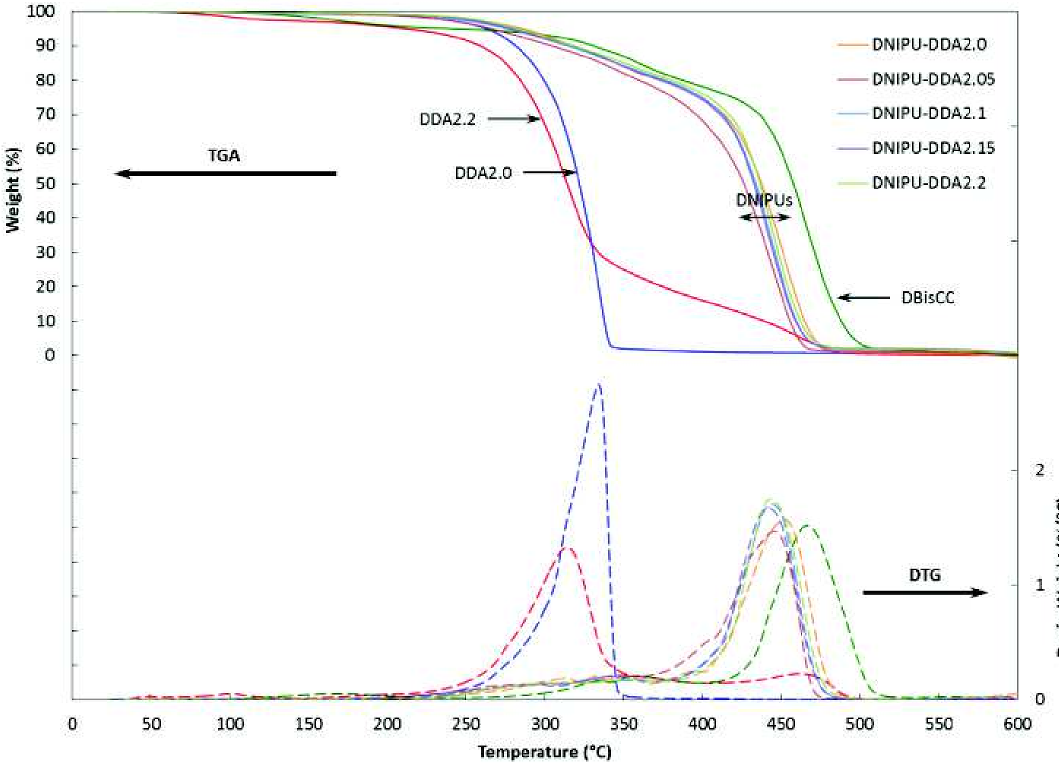


Figure 3-6. TGA (solid line) and DTG (dotted line) curves of DNIPUs and their monomers under nitrogen.

Table 3-S1 in the ESI† demonstrates that the amine average functionality seems to have a small influence on the thermal degradation of DNIPUs. DNIPU-DDA2.05, based on a non-crosslinked structure, is more thermal sensitive. The corresponding degradation slightly begins before those of the other DNIPUs. Considering the $T_{2\%}$ values, higher temperatures are shown when the amine average functionality increases. This should be due to a higher trimer contents in the initial compounds and then in the macromolecular architectures. The TGA analysis also confirms that in the temperature domain explored by DSC, DNIPUs are not degraded.

Rheological analyses were performed in order to obtain further information on the morphology of these DNIPUs. Figure 3-7 displays the temperature dependence on the storage moduli (G') of the DNIPUs. The curves from Figure 3-7 indicate that the rheological behavior of DNIPUs is influenced by the average amine functionality. Except for DNIPU-DDA2.05, whose storage modulus falls when increasing the temperature, all the samples present a rubbery plateau at a temperature higher than 80°C (Figure 3-7). This plateau confirms their crosslink states. Two main behaviors are thus highlighted, with a transition at an average amine functionality between 2.05 and 2.1. For crosslinked DNIPUs, the rubbery plateau becomes higher and longer with increasing the average amine functionality, which confirms the rising trend of the crosslinking density (approached from the previous SR ratio calculations). It should be noted that DNIPU-DDA2.0 is a particular case and shows a rubbery plateau despite its low amine average functionality. Table 3-5 shows that the gel content value found for DNIPU-DDA2.0 is the highest among all DNIPU samples. This means that in this case, secondary reactions are lower and the molar masses higher compared to the other DNIPU samples with higher amine average functionalities. This could explain the better structuration of DNIPU-DDA2.0.

All these results confirm that tailoring the properties of these DNIPU systems is possible *via* a modulation of the average amine functionality.

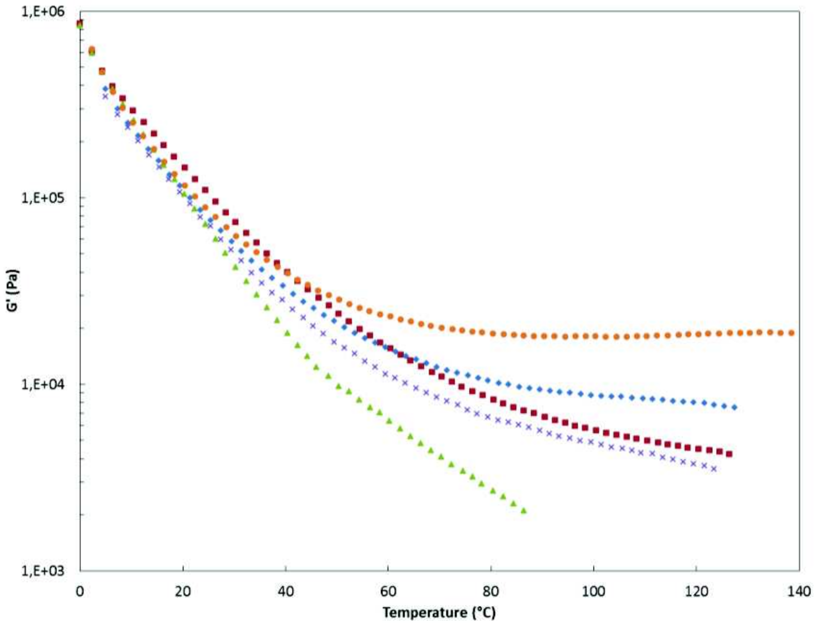


Figure 3-7. Dynamic rheological curves of DNIPU samples, evolution of storage modulus (G').
DNIPU-DDA2.0 (■), DNIPU-DDA2.05 (▲), DNIPU-DDA2.1 (×),DNIPU-DDA2.15 (♦), and DNIPU-DDA2.2 (●).

1.3.3.3. Analysis of the mechanical properties of DNIPU-DDA2.0

Considering DNIPU-DDA2.0, additional tests were achieved to determine the mechanical behavior of this particular system. The stress-strain curves of DNIPU-DDA2.0 samples obtained from uniaxial tensile tests is typical of an elastomeric behavior with a high elongation at break, $\varepsilon_{max} = 1280 \pm 10\%$ (Figure 3-S8 in the ESI†). This high elongation is explained by a specific structuration, linked to a low crosslink density. However, the ultimate tensile strength, $\sigma_{max} = 0.5 \pm 0.1$ MPa, is quite low compared to the great majority of common elastomers.[38] The Young modulus $E = 0.20 \pm 0.03$ MPa was also determined from the stress-strain curves. This low value is typical of very soft elastomers.

1.3.4. Analysis of the relationships between the chemical structure of the building blocks (dimeric *vs.* linear) and the properties of the corresponding NIPUs

To analyze the “chemical structure-properties” relationships, different NIPUs have been synthesized from dimer or more conventional linear building blocks. DNIPU-DDA2.0 and LNIPU-DDA2.0 have been synthesized from two different biscyclocarbonates, dimeric DBisCC or linear LBisCC, respectively, with dimer diamine DDA2.0. In addition, DNIPU-DDA2.0 and DNIPU-DA8 have been synthesized from the same dimer biscyclocarbonate and two different diamines, the dimer DDA2.0 or the linear DA8, respectively. Analyses have been performed on these two NIPU families to investigate the influence of cyclic carbonate and amine structures (dimer *vs.* linear structures), on some final material properties.

Figure 3-8 displays the TGA and DTGA curves of DNIPU samples under nitrogen atmosphere. It can be observed that the building block structures of the cyclic carbonate and amine strongly affect the thermal degradation.

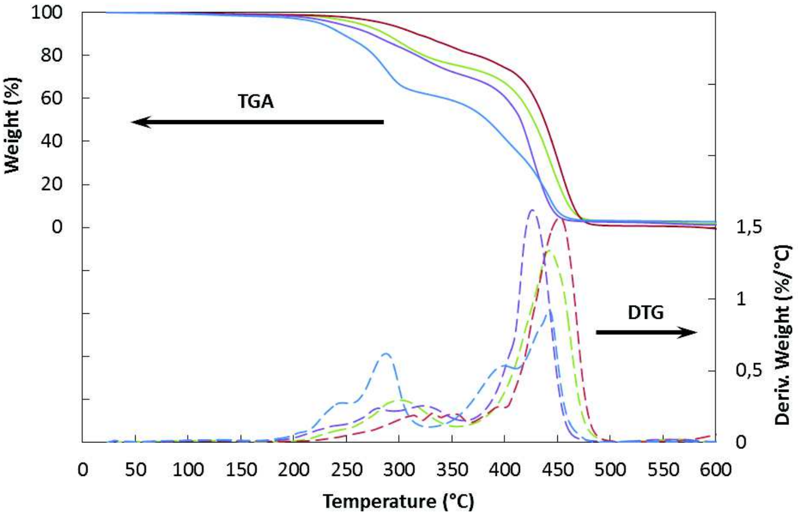


Figure 3-8. TGA (solid line) and DTG (dotted line) curves of NIPU samples. DNIPU-DDA2.0 (in red), DNIPU-DA8 (in green), LNIPU-DDA2.0 (in purple), and LNIPU-DA8 (in blue).

As it can be observed from Table 3-7, the $T_{98\%}$ value of DNIPU-DDA2.0 is 40°C higher than the $T_{98\%}$ value of LNIPU-DDA2.0. NIPUs synthesized with DBisCC present a higher thermal stability than those which are obtained from linear LBisCC. This higher resistance is due to, (i) the cyclic structures of DBisCC, and (ii) the presence of trimers, which both enhance the thermal degradation. The same effect is also observed for NIPUs obtained with BisCC and linear or dimer diamine. For instance, DNIPU-DDA2.0 presents a higher thermal stability with a $T_{98\%}$ value about 20°C higher than DNIPU-DA8's one (Table 3-7). The difference of thermal stability is thus less noticeable for diamines structures compared to cyclic carbonates. This could be explained by the effect of the trimer content, which is higher for DBisCC (about 3%) than for DDA2.0 (less than 1%), whereas it is quite the same for both linear and dimeric diamines. Furthermore, the more the purity of building blocks is low, the broader is the DTG curve with no distinctive peak between 200 and 400°C. This large range is caused by the diversity in the dimer structures of DDA2.0 (acyclic, monocyclic, and bicyclic) in addition to the effect of the trimers. Each of these particular structures presents its own degradation temperatures and steps.

Table 3-7. NIPU characteristic temperatures obtained from TGA and DSC.

Samples	**$T_{98\%}$ (°C)**	**$T_{50\%}$ (°C)**	**$T_{2\%}$ (°C)**	**T_{max} (°C)**	**T_g (°C)**	**T_m (°C)**
DNIPU-DDA2.0	245	437	479	452	-20	-
DNIPU-DA8	226	427	573	442	-16	41
LNIPU-DDA2.0	206	415	548	426	-23	-
LNIPU-DA8	178	383	600	442	-17	38

TGA results show that in the temperature range explored by DSC, NIPUs are not degraded (Table 3-7). As for the case of biscyclocarbonate (previously presented), the amine chemical structure does not significantly affect the T_g values of the NIPUs (Table 3-7). All NIPUs present a low T_g at around -20°C. However, when DA8 is used as a building block, the T_g is slightly higher due to a decrease of the mobility, and a melting temperature appears. Semi-crystalline polymers are thus obtained with linear diamines.

Dynamic rheological analyses brought complementary information about the macromolecular architecture of the different NIPUs. Figures 3-9 and 3-10 show the influence of the NIPU structure on the storage modulus such as on the tangent delta. They highlight two different behaviors. Linear LNIPUs flow when increasing the temperature, whereas DNIPUs present a rubbery plateau indicating a certain structuration (Figure 3-9). This structuration could be due to the presence of a trimer content of 3%, which is enough to induce a crosslinking responsible of a network formation. However, as shown before, the crosslinking density is low and the value of the storage modulus on the rubbery plateau is lower than for conventional thermoset polymers.[38] As it appears on Figure 3-10 and from 0 to 120°C, only DNIPU-DDA2.0 sample presents an alpha relaxation temperature, determined at maximum of tangent delta. The maximum of tangent delta is lower than 1. The elastic part is always higher than the viscous one. This sample shows the highest structuration.

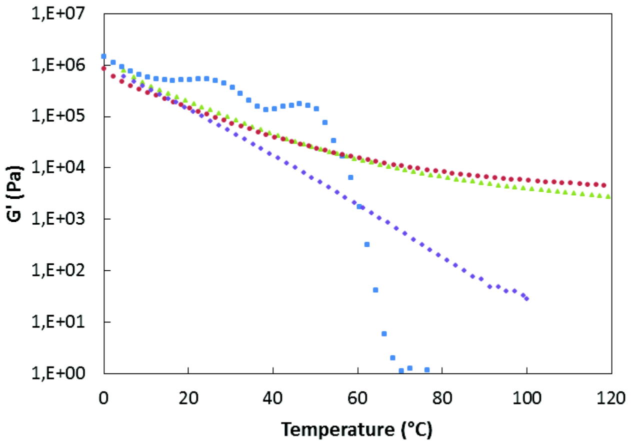


Figure 3-9. Dynamic rheological analyses of NIPU samples.
Influence of the building block structure on the storage modulus.
DNIPU-DDA2.0 (●), DNIPU-DA8 (▲), LNIPU-DDA2.0 (♦), and LNIPU-DA8 (■).

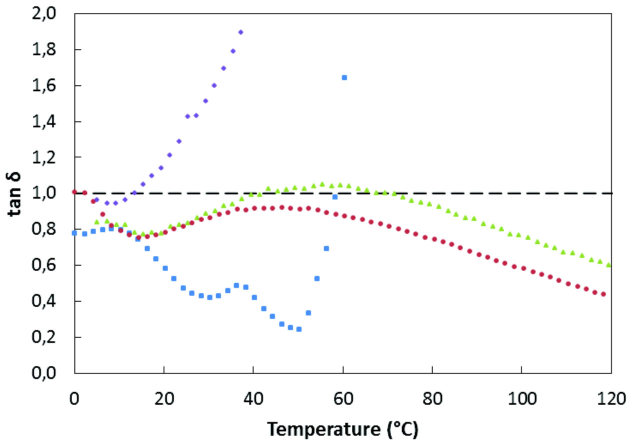


Figure 3-10. Dynamic rheological analyses of NIPU samples.
Influence of the building block structure on the tangent delta.
DNIPU-DDA2.0 (●), DNIPU-DA8 (▲), LNIPU-DDA2.0 (♦), and LNIPU-DA8 (■).

1.3.5. Comparison between NIPUs and conventional PUs based on equivalent structures

Conventional PUs were synthesized with both dimer and linear polyols and isocyanates to enable a comparison with analogous NIPUs. It should be noticed that even with equivalent building blocks, the chemical structures of the NIPUs and PUs differ with the presence of OH groups (PHUs). These OH functions increase the number of hydrogen bonds such as the possibility to cause potential post-reactions.

SEC results are presented in Table 3-8. As expected, PUs present higher molar masses than NIPUs, caused by the limited reactivity of cyclic carbonates towards diamines such as the existence of secondary reactions like ester aminolysis. Compared to DPUs, DNIPUs are not soluble in common solvents, probably due to the trimer building blocks in the corresponding macromolecular architectures. Besides, the hydrogen bonds, linked to the OH groups in NIPUs, could also limit the DNIPU solubility in some common solvents.

Table 3-8. SEC results of NIPUs and PUs.

Samples	**M_n ($g.mol^{-1}$)**	**M_w ($g.mol^{-1}$)**	**Đ**
DNIPU-DDA2.0	*Not soluble in common solvent*		
DNIPU-DA8	*Not soluble in common solvent*		
LNIPU-DDA2.0	6,000	20,000	3.1
DPU-DOH	36,000	89,500	2.5
DPU-OH8	35,000	73,500	2.1
LPU-DOH	17,400	33,000	1.9

Table 3-9 shows the thermal analysis results of the PUs. $T_{98\%}$ value indicates that all PUs have a higher thermal stability than their corresponding NIPUs (Table 3-7). Due to the isocyanate higher reactivity, longer chains are formed, and then the thermal degradation starts at higher temperatures. Like for NIPUs, the fully dimer-based PU presents the best thermal resistance. This phenomenon highlights again the effect brings by the dimer structure on the thermal resistance.

Table 3-9. PU characteristic temperatures obtained from TGA and DSC characterizations.

Samples	**$T_{98\%}$ (°C)**	**$T_{50\%}$ (°C)**	**$T_{2\%}$ (°C)**	**T_{max} (°C)**	**T_g (°C)**	**T_m (°C)**
DPU-DOH	350	422	505	419	-25	-
DPU-OH8	341	398	426	406	-12	55
LPU-DOH	340	413	514	394	-18	63

Except, DPU-DOH sample, which is a fully amorphous polymer with a low T_g similar to NIPUs, PUs have a 10°C higher T_g than those of NIPUs (Tables 3-7 and 3-9). Furthermore, DPU-OH8 and LPU-DOH present a melting temperature and are semi-crystalline structures. The highest molar masses give a better structuration of the samples and linear monomers can play their conventional role in the reorganization of these systems.

1.4. Conclusions

A two-step method for the elaboration of a dimer-based cyclic carbonate was developed. This cyclic carbonate and its derivatives were then characterized and subsequently used as building blocks for NIPU synthesis. Fully biobased NIPUs, from dimer cyclic carbonate and dimer diamine were synthesized and characterized. The importance of a stoichiometric ratio and the influence of the amine average functionality were highlighted. When increasing the amine average functionality, a crosslinked network is formed. NIPUs with various macromolecular architectures were also designed and the effect of the chemical structure of the building block on their thermal, rheological and mechanical properties was investigated. It was shown that the dimer structure affects the NIPU properties, and particularly increases the thermal stability of the corresponding polymers. But the key factor linked to the properties of these polymers is the dimer composition. A small percentage of trimers inside biscyclocarbonate or diamine seems to increase the crosslinking and brings a specific structuration. However, even if NIPUs show high performance materials, lower properties than conventional PUs based on equivalent dimer structures were obtained. The main reasons for such differences are the low reactivity of the aminolysis reaction compared to the conventional reaction based on isocyanate. Thus, lower molar masses were obtained for NIPUs compared to PUs. Nevertheles, it was demonstrated that NIPUs based on crosslinks with the elaboration of a specific network can partially fill in these gaps.

Acknowledgements

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1.5. Supporting information

1.5.1. Titration methods

In order to calculate the NCO:OH molar ratio required for PU synthesis, preliminary titrations were realized to determine the hydroxyl index (I_{OH}) of the polyol and the NCO content (*NCO%*) of the isocyanate.

1.5.1.1. Hydroxyl index determination (I_{OH})

I_{OH} is a key parameter in the characterization of polyols. This value is the amount of potassium hydroxide (KOH), in milligrams, equivalent to the number of OH groups in 1 g of polyol.

I_{OH} was determined by the standard esterification method using phthalic anhydride. Polyol (1 g) and the reactive solution (20.0 mL, phtalic anhydride 1 M in pyridine) were heated at 130°C for 45 minutes, and then cooled to room temperature. Pyridine (30 mL) was then added, followed by water (30 mL). The solution was then titrated with a 1 M sodium hydroxide (NaOH) solution.

Hydroxyl index (I_{OH}), in mg KOH/g, was determined from Equation S1 where, V_b and V_{eq} are the volumes in milliliter of the NaOH titration solution required respectively for blank and polyol sample titrations, C is the NaOH solution concentration in mol.L^{-1}, and w_P is the polyol weight in grams.

$$I_{OH} = \frac{(V_b - V_{eq}) * C * 56.1}{w_P} \qquad \text{(S1)}$$

1.5.1.2. NCO content determination (*NCO%*)

NCO% is a key parameter in the characterization of isocyanates. This value is the percent by mass of the NCO groups present in the sample. *NCO%* was determined by indirect titration of dibutylamine in excess with a hydrochloric acid (HCl) solution.

In a flask, isocyanate (1 g), toluene (30 mL) and a 1 M solution of dibutylamine (20.0 mL) were added. This flask was closed and then stirred during 15 minutes at room temperature. Methanol (30 mL) was then added. The solution was finally titrated with a 1 M HCl solution. A blank sample without isocyanate was also titrated in order to determine the total quantity of dibutylamine introduced. *NCO%* was determined according to Equation S2 where, V_b and V_{eq} are the volumes in milliliter of the HCl titration solution required respectively for blank and isocyanate sample titrations, C is the HCl solution concentration in mol.L^{-1}, and w_P is the isocyanate weight in grams.

$$NCO\% = \frac{(V_b - V_{eq}) * C * 4.2}{w_P} \tag{S2}$$

1.5.2. DFA chemical characterization

1.5.2.1. FTIR, ^{1}H- and ^{13}C-NMR analyses

Chemical characterizations were performed on DFA in order to define its chemical structure. FTIR and ^{1}H-NMR analyses are presented in Figures 3-3 and 3-4. Additional ^{13}C-NMR spectrum (Figure 3-S1) and the attribution of DFA signals for each of these analyses can be found below.

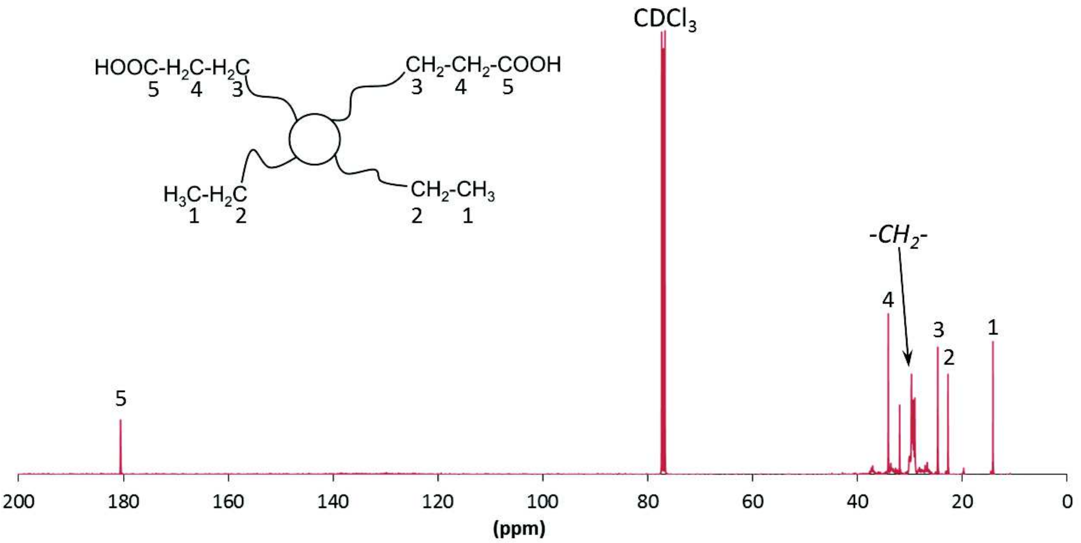

Figure 3-S1. ^{13}C-NMR spectrum of DFA.

^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 0.85-0.93 (6H, m, -C*H*$_3$), 1.26 (38H, s, -C*H*$_2$-), 1.58-1.68 (4H, m, -C*H*$_2$-CH_2-COOH), 2.35 (4H, t, *J* = 7.4 Hz, -C*H*$_2$-COOH), 5.01-5.46, 6.69-7.08 (0.31H, m, -C*H*=C*H*-), 11.36 (2H, s, -COO*H*-).

^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): 14.3 (-*C*H$_3$), 22.8 (-*C*H$_2$-CH_3), 24.9 (-*C*H$_2$-CH_2-COOH), 29.2-30.3 (-*C*H$_2$-), 34.3 (-*C*H$_2$-COOH), 180.7 (-*C*OCl).

FTIR-ATR (cm^{-1}): 1707 (C=O carbonyl group).

1.5.2.2. SEC analysis of DFA

SEC analysis was achieved to evaluate the average molar mass of DFA and observe its dispersity (Figure 3-S2).

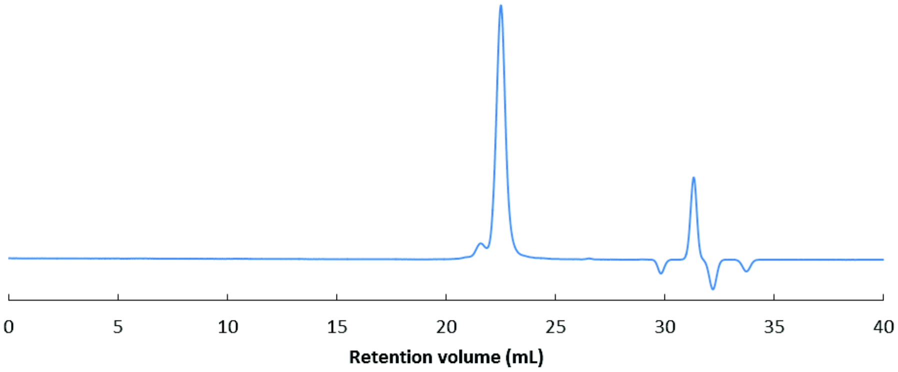

Figure 3-S2. SEC chromatogram of DFA obtained with RI detector (PS standard calibration).

1.5.2.3. DOSY NMR analysis of DFA

Molecules are differentiated according to their self-diffusion coefficient (D), related to their hydrodynamic radius. NMR spectra of molecules presenting sufficiently different sizes can be isolated. DOSY is a two-dimensional (2D) NMR experiment with a frequency dimension (^{1}H-NMR chemical shifts) and a dimension related to a D coefficient. D measurement is based on the use of magnetic field gradients. This results in a 2D map displaying spots, which correlate each NMR signal to a D coefficient. It is thus possible to isolate the NMR spectrum of each compound of the mixture. D measurement is based on the use of magnetic field gradients.

DOSY spectra were generated by using the program NMRNotebook and the DOSY Module from NMRTEC (NMRNotebook, *http://www.nmrtec.com/software/nmrnotebook*) using inverse Laplace Transform (M. A. Delsuc and T. E. Malliavin, *Anal. Chem.*, 1998, 70, 2146-2148) driven by Maximum Entropy, to build the diffusion dimension. For each data set, 8192 complex points were collected for each 20 experiments in which the gradient strength was linearly incremented from 0.5 to 45 G.cm^{-1}. The gradient duration δ/2 was adjusted to observe a near complete signal loss at 45 G.cm^{-1}. A 1 s recycle delay was used between scans. The number of scan was set to 64. The total experiment time, including a 20 min temperature equilibration step, is close to two hours. For each data set, the spectral axis was processed with sine-bell, and Fourier transform was applied in order to obtain 4096 real points. A spline baseline correction was finally applied. The columns (axis of varying gradient) of the datasets were then processed for Inverse Laplace transform using the Inverse Laplace Technique using the NMRNotebook software (NMRTEC-France). The DOSY reconstruction was performed with 256 points in the diffusion dimension and a maximum of 100,000 MaxEnt iterations.

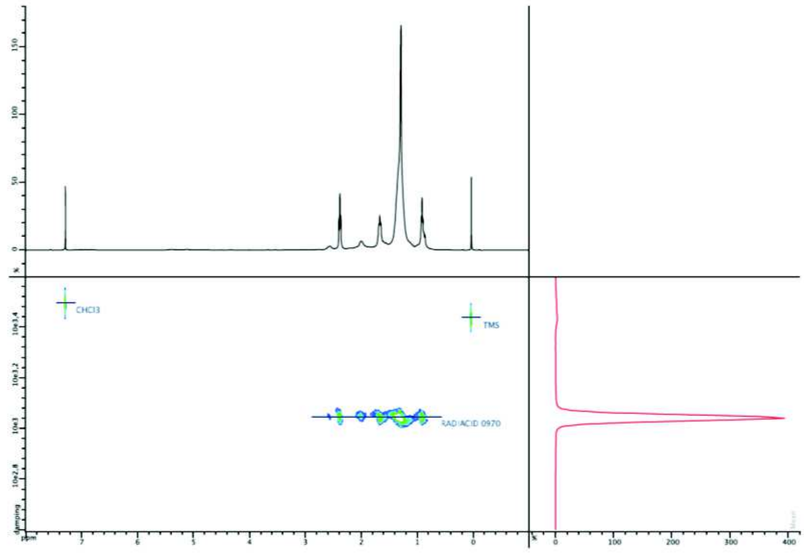

Figure 3-S3. DOSY NMR spectra of DFA in $CDCl_3$.

1.5.3. Characterization of intermediates based on DFA

In order to complete ^{1}H-NMR analyses, ^{13}C-NMR analyses were also performed on DFA intermediates (Figures 3-S4 and 3-S5).

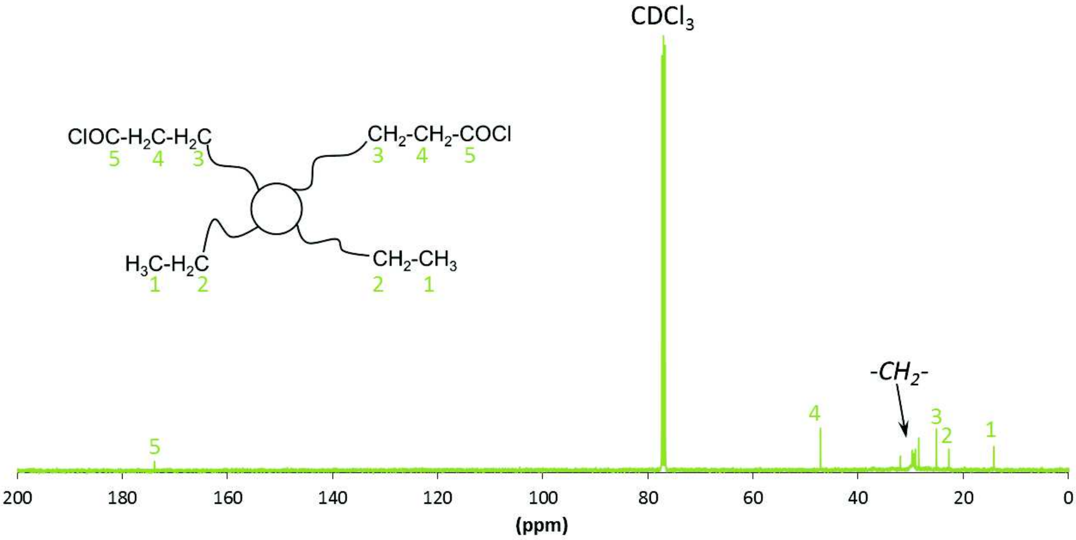

Figure 3-S4. ^{13}C-NMR spectrum of DCl.

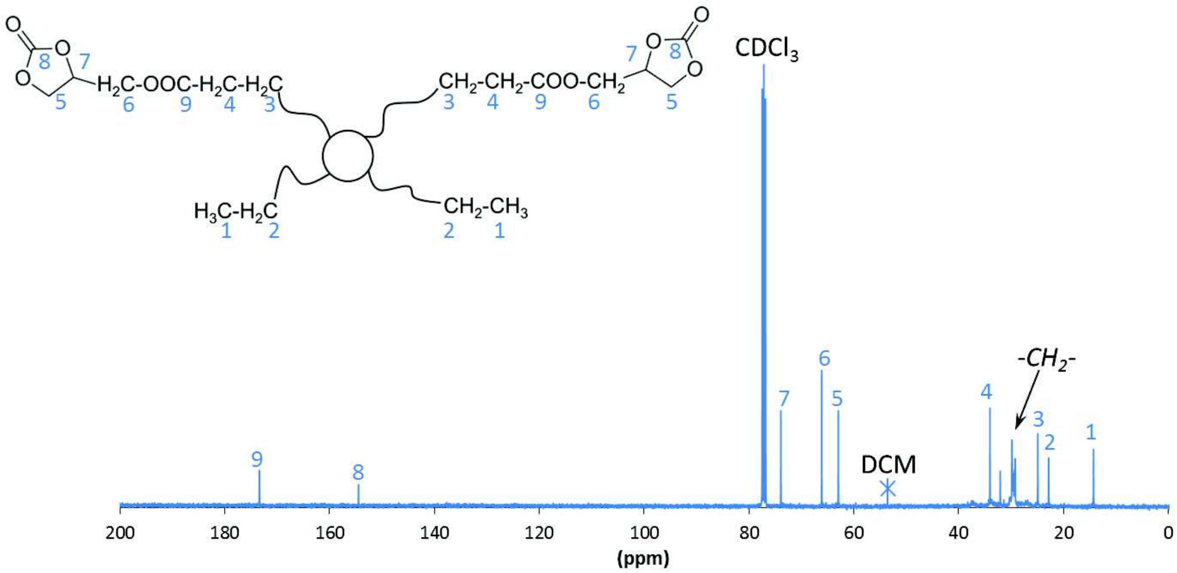

Figure 3-S5. ^{13}C-NMR spectrum of DBisCC.

1.5.4. Synthesis and characterization of DNIPU

1.5.4.1. Effect of the DBisCC:diamine molar ratio

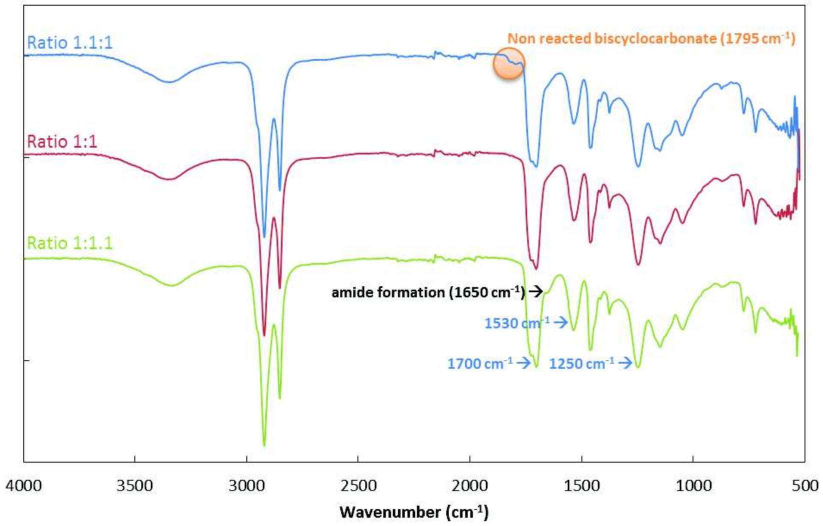

Figure 3-S6. FTIR spectra of DNIPU-DDA2.0 at different carbonate:amine ratios.

1.5.4.2. Effect of the average amine functionality of DNIPU samples

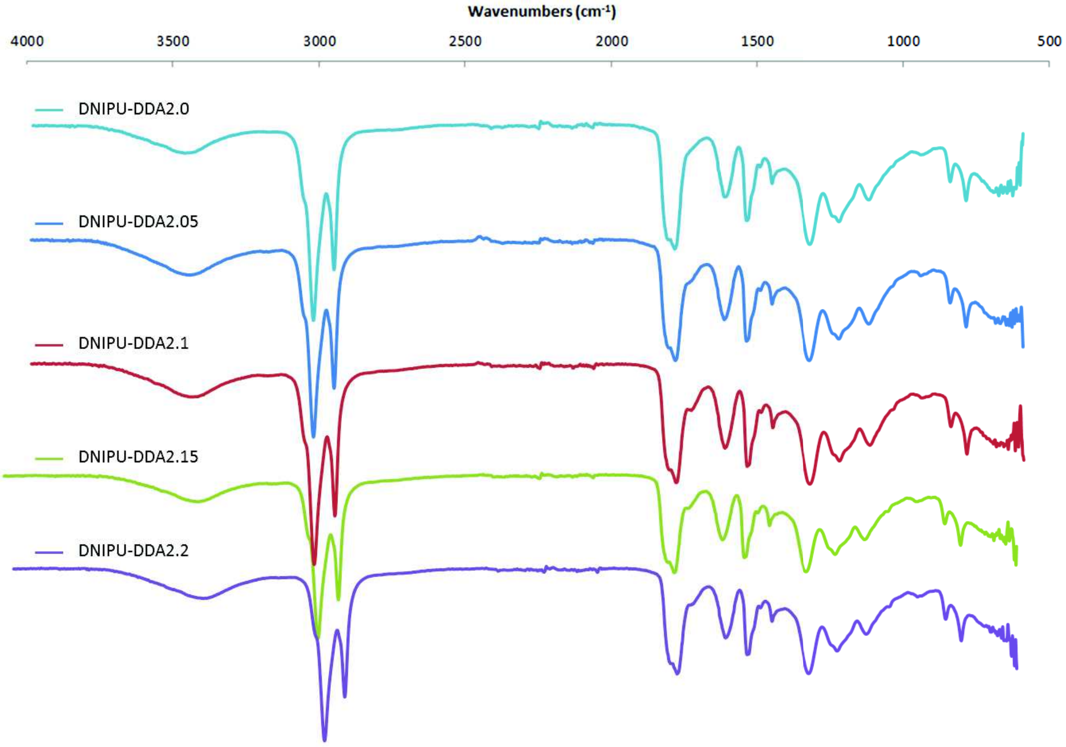

Figure 3-S7. FTIR spectra of DNIPU samples.

Table 3-S1. Characteristic degradation temperatures of the different DNIPUs.

Samples	**$T_{98\%}$ (°C)**	**$T_{50\%}$ (°C)**	**$T_{2\%}$ (°C)**	**T_{max} (°C)**
DNIPU-DDA2.0	245	437	479	452
DNIPU-DDA2.05	201	426	467	445
DNIPU-DDA2.1	240	434	488	444
DNIPU-DDA2.15	246	433	544	442
DNIPU-DDA2.2	251	436	514	444

1.5.4.3. Particular case: DNIPU-DDA2.0, study of its mechanical properties

Figure 3-S8 displays the mechanical behavior of NIPU-DDA2.0 sample under uniaxial tensile test. Three samples were tested and show a similar behavior typical of elastomeric materials. The sample picture after breaking indicates that no necking phenomenon occurred.

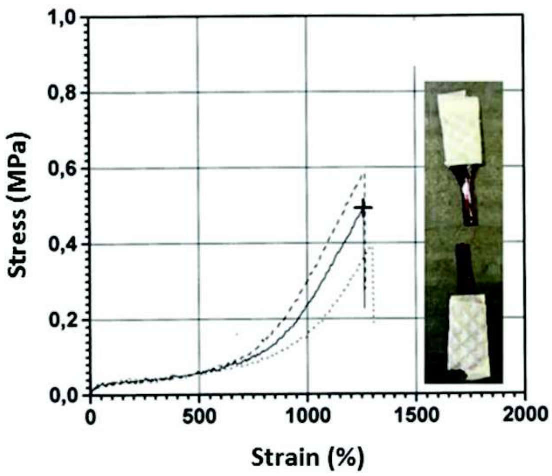

Figure 3-S8. Stress-strain curve of DNIPU-DDA2.0.

2. Conclusions et perspectives

La synthèse bibliographique présentée dans le Chapitre 1 a montré que les acides gras figurent parmi les composés issus de ressources renouvelables les plus utilisés pour la synthèse de NIPU biosourcés. Toutefois, les dimères d'acides gras n'ont que très peu été étudiés et aucun NIPU entièrement issu de cette ressource n'avait encore jamais été rapporté. Ainsi, les travaux développés dans ce Chapitre 3 sont novateurs en associant deux molécules issues de la biomasse pour l'obtention d'architectures macromoléculaires originales, 100% biosourcées et obtenues par une voie de synthèse sans solvant, sans catalyseur et ne présentant pas de résidus toxiques.

Tout comme dans le Chapitre 2, l'importance du ratio molaire entre les monomères, et la fonctionnalité moyenne de la diamine ont été mis en exergue. La comparaison de ces NIPU dimériques avec des NIPU issus de synthons linéaires a également permis de mettre en évidence l'importance de telles structures sur l'amélioration de la stabilité thermique des NIPU correspondants, ainsi que sur la structuration des matériaux finaux. En effet, de façon inhérente à leur procédé de purification, les « building blocks » dimériques ne sont pas toujours strictement bifonctionnels et il est ainsi possible de jouer sur leur pourcentage en trimères afin de former un réseau tridimensionnel contrôlé. La structure même des trimères issus d'acides gras engendre cependant de faibles densités de réticulation. Le module de conservation est nettement inférieur à ceux rencontrés dans le cas de réseaux thermodurcissables classiques. La souplesse de ces matériaux permet d'envisager des applications dans le domaine des adhésifs et mastics, ou encore dans l'étanchéité liquide pour le bâtiment.

Afin de mesurer l'intérêt et le potentiel de cette nouvelle classe de PU, une étude comparative a également été menée par rapport à des PU conventionnels présentant des structures de monomères équivalentes à celles des NIPU synthétisés. Il ressort de cette étude que les NIPU, bien que performants, présentent cependant des propriétés inférieures à celles des PU conventionnels. La principale raison de cette différence est la faible réactivité de la réaction d'aminolyse et les faibles masses molaires obtenues.

Ce travail est en totale adéquation avec le concept de chimie verte. Des produits chimiques novateurs et performants issus de ressources biosourcées disponibles commercialement ont été synthétisés. Cependant, de nombreux verrous restent à lever afin de pouvoir industrialiser massivement de tels matériaux, notamment l’amélioration de la cinétique et des masses molaires obtenues, bien que la possibilité de réticulation vienne partiellement combler ces limitations.

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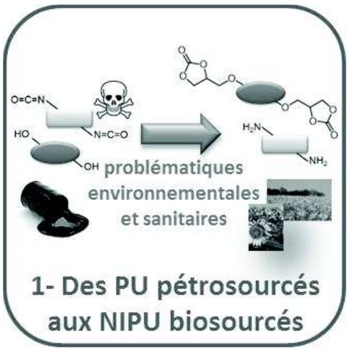
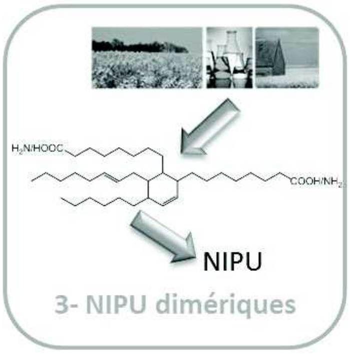
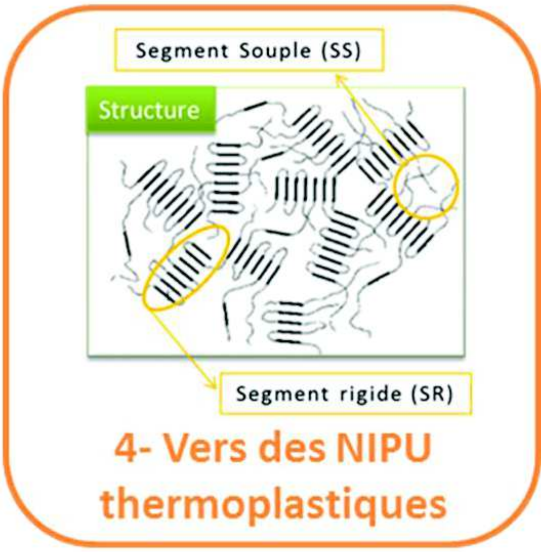
Chapitre 4

Vers des polyuréthanes sans isocyanate thermoplastiques et élastomères







Introduction

Comme cela a déjà été présenté dans le chapitre 1, les polyuréthanes thermoplastiques (TPU), sont des polymères segmentés constitués de segments souples et rigides. La démarche scientifique générale adoptée dans ce chapitre est de synthétiser des TPU sans isocyanate, appelés TNIPU, en mimant la stratégie employée pour les TPU conventionnels. Ainsi, les carbonates cycliques jouent le rôle des isocyanates et les diamines celui des polyols.

Les cyclocarbonates issus de l'acide sébacique et du dimère d'acide gras, synthétisés dans les deux précédents chapitres, étant longs et souples, de nouveaux synthons plus rigides et courts ont été envisagés dans ce chapitre afin de synthétiser des cyclocarbonates adaptés à la synthèse de TNIPU. Il s'agit de l'acide téréphtalique et d'un diacide équivalent et biosourcé : l'acide 2,5-furandicarboxylique (FDCA). Dans un premier temps, des NIPU synthétisés à partir d'un biscyclocarbonate issu de l'acide téréphtalique et de diverses diamines vont être présentés. Cette partie s'articule autour de l'étude de l'influence de la nature de la structure chimique et de la masse molaire des différents synthons, ainsi que de l'effet de leurs ratios molaires sur les propriétés finales du polymère. Ensuite, la synthèse d'un biscyclocarbonate innovant obtenu à partir de FDCA, présentant une structure similaire à l'acide téréphtalique mais issu de ressources renouvelables, sera détaillée ainsi que la possibilité d'envisager son utilisation dans la synthèse de TNIPU.

1. Des polyuréthanes sans isocyanate tricomposants pour l’obtention de matériaux thermoplastiques élastomères

La production mondiale de TPU augmente chaque année et a été estimée à 378 550 tonnes en 2010.[1] Ils sont utilisés dans de nombreux domaines d’application, tels que l’ameublement, les appareils et installations sportifs, l’automobile, le bâtiment, et le textile. Les TPU sont reconnus de par leurs grandes diversités de structures et propriétés, et de leurs usages. En effet, leurs propriétés peuvent être modulées infiniment *via* divers paramètres tels que la sélection de leurs divers synthons de base.

Bien que la majorité des recherches soient consacrées à l’élaboration de systèmes NIPU réticulés (thermodurs), certaines équipes ont travaillées sur la préparation de TNIPU. Les approches pour la synthèse de ces polymères sont celles classiquement développées pour la préparation de NIPU.[2-6] C’est la réaction de polycondensation par transuréthanisation qui a été principalement développée pour synthétiser des polyuréthanes linéaires ou thermoplastiques.[7-9] Bien que de nombreux polymères aient été synthétisés, les relations structures-propriétés ainsi que l’impact du ratio entre les divers monomères ont peu été étudiés.

Les travaux réalisés dans cette partie sont présentés sous la forme d’un article intitulé : « Synthesis and characterization of advanced thermoplastic nonisocyanate polyurethanes, based on controlled aromatic-aliphatic architectures », soumis dans *Polymer*. Cette étude présente la synthèse et la caractérisation de TNIPU issus de l’acide téréphtalique. Afin de pouvoir comprendre l’influence des structures sur les propriétés des matériaux finaux, divers paramètres ont été étudiés, notamment l’impact du ratio molaire entre les synthons de base ainsi que l’effet de la nature chimique et de la masse molaire des diamines.

Publication n°4 :

Synthesis and characterization of advanced thermoplastic nonisocyanate polyurethanes, based on controlled aromatic-aliphatic architectures

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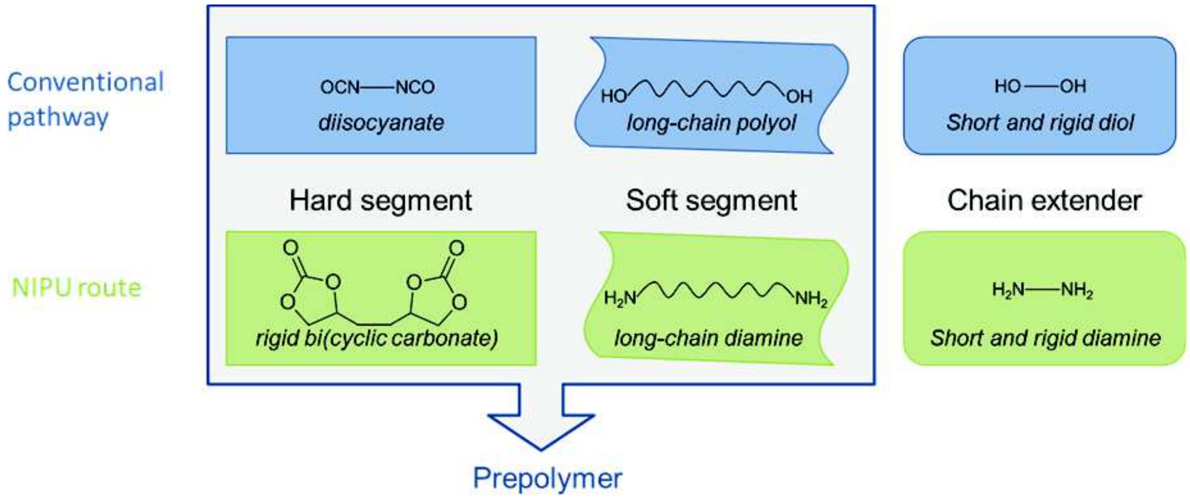
Polymer – Submitted article

Graphical abstract



Abstract

The aim of this study is the elaboration of thermoplastic nonisocyanate polyurethanes (TNIPUs) based on different aromatic-aliphatic architectures. A rigid aromatic biscyclocarbonate was synthesized from terephthalic acid, and subsequently used with aliphatic and aromatic diamines for the preparation of TNIPUs. A two-step method was investigated to design advanced macromolecular architectures. All TNIPUs and corresponding intermediates were fully characterized. The influence of various parameters such as the ratio between the constituting building blocks and the chemical structure on NIPU properties was studied. Thermal, rheological and mechanical results show that TNIPUs presenting the highest molar masses and the highest properties were synthesized from dimer diamine prepolymers. A high content of terephthalic acid and short-chain diamine increases the glass transition temperature and leads to good performances, with a balance between elongation and tensile strength properties. The final TNIPUs present biobased contents up to 76%.

Keywords

dimer diamine, glycerol carbonate, nonisocyanate polyurethane, terephthalic acid, thermoplastic polyurethane.

1.1. Introduction

Polyurethanes (PUs) are among the most common polymers in the industry since they are used in a large application range (*e.g.* foams, seals, insulation parts). The high versatility of PUs is related to the diversity of the chemical structures of the constituting building blocks, and to the various synthesis pathways used. Modulation of these parameters allows to control the chemical and physical properties of the final materials.

Among all PU structures, thermoplastic PUs, also called TPUs, exhibit attractive properties including high elongation and tensile strength, with a high elastomer character. To obtain these properties, micro/nano-segregation with hard and soft segments (HS and SS, respectively) is required. The HS, typically based on diisocyanate and a chain extender (*e.g.* a short-chain diol), brings toughness and high performance to the TPU. The SS, mainly constituted of a polyol such as a long-chain diol, brings flexibility and elastomeric behavior. A two-step process, also called prepolymer technique, is frequently used for the elaboration of TPUs with controlled architectures.[10, 11]

However, a major drawback of TPUs, and PUs in general, is related to isocyanates toxicity. Isocyanates are strong irritants for lung and skin. The most severe manifestation, caused by prolonged exposure, is professional asthma.[12] Overexposure to isocyanates can also lead to various inflammations including skin, eyes or general irritation of the respiratory system. Some isocyanates are even classified as carcinogens, *i.e.* which can cause, exacerbate or sensitize the appearance of cancer.

To solve these problems, a new range of nonisocyanate polyurethanes (NIPUs) was investigated and developed during the last few years.[2-4, 13, 14] Among the various synthetic pathways considered (*e.g.* AB-type azide condensation,[5] transurethane polycondensation[7, 15]), aminolysis reaction is the most reported one. This synthesis involves the reaction of cyclic carbonates with amine-based compounds.[16-18]

Various fossil-based chemicals were used as monomers. Most of them are aliphatic but some compounds presenting rigid cycloaliphatic or aromatic structures were also studied. Terephthalic acid (TerAc),[19, 20] Bisphenol A, Bisphenol S and their derivatives[18, 21, 22] are the main aromatic cyclic carbonate precursors, whereas isophorone diamine,[23-25] *m*-xylylenediamine and *p*-xylylenediamine[19, 26] are diamines with a cyclic or an aromatic backbone already described in NIPU syntheses *via* aminolysis. In order to develop more environmental and green materials, more and more chemicals are obtained from renewable resources. The main biobased aminolysis monomers derive from vegetable oils, with a linear structure. But recently, some biobased cyclic and aromatic amines as well as renewable cyclic carbonates were used and analyzed. For instance, cyclic carbonates from isosorbide,[25] vanillin,[27] cashew nut shell liquid (CNSL),[28] or limonene,[29] derivatives were described in NIPU synthesis. However, only one paper reports the use of an aromatic biobased diamine, called phenalkamine, obtained from CNSL, for the elaboration of NIPUs.[30] Nevertheless, other rigid diamines, mainly developed for epoxy applications as hardener, were already synthesized from isosorbide,[31] vanillin,[27] and limonene.[32] More recently, aromatic NIPUs were elaborated from tannin and lignin derivatives.[33-35]

In the present study, biobased thermoplastic NIPUs (TNIPUs) were synthesized with different macromolecular architectures, *via* a two-step process. The corresponding properties were evaluated. Our strategy was to mimic the synthesis of conventional TPUs, in replacing diisocyanate by a rigid cyclic carbonate obtained from terephthalic acid (TerAc), and in substituting long-chain and short-chain diols by various diamines. TerAc is presently obtained from fossil-based *p*-xylene but some renewable alternatives from *e.g.* biobased isoprene and acrylic acid,[36, 37] methyl coumalate and methyl pyruvate[38] or limonene[39] have been recently developed to be industrialized in a close future for *e.g.*, the production of fully biobased PET. Another efficient biobased chemical, which should be manufactured to substitute TerAc is 2,5-furandicarboxylic acid (FDCA). FDCA was already successfully tested in PET-like bottles.[40] A dimer fatty amine was used as a biobased chemical. DFAs or high molar mass polyetheramines could act as SS, and short chain 1,4-butanediamine (BDA) or aromatic *m*-xylylene diamine (*m*XDA) were used as chain extenders.

The aims of this study were (i) to evaluate the effects of the building block structures (linear, cyclic aliphatic or aromatic) and their corresponding contents on the final properties of TNIPUs with controlled macromolecular architectures, and (ii) to achieve an adequate structuration, to obtain NIPUs with a strong elastomer character.

1.2. Experimental part

1.2.1. Materials

Terephthaloyl chloride (TerCl, 99%) and 1,4-butanediamine (BDA, >98%) were purchased from Alfa Aesar (Karlsruhe, Germany). Glycerol carbonate (GC, Jeffsol GC, 93%) and polyetheramine, commercially available under the trade name Jeffamine® D2000, were obtained from Huntsman (Everberg, Belgium). Jeffamine® D2000 presents a high molar mass, equals to 2000 g.mol^{-1}. Dimer diamine (DDA) commercially available under the trade name Priamine^{TM} 1075 was kindly supplied by CRODA (Goole, England). DDA is a C_{36}-biobased molecule obtained from dimer fatty acids.[41] DDA has an average functionality of 2.0, a dimer content higher than 99%, an amine value (AV) of 204 mg KOH/g, and a glass transition temperature (T_g) lower than -50°C. At room temperature, DDA is a yellowish, slightly viscous liquid. Dichloromethane (DCM, ≥99%), diméthylformamide (DMF, ≥99%) and *m*-xylene diamine (*m*XDA, 99%) were purchased from Sigma-Aldrich, and triethylamine from Carlo Erba. Except DCM, which was purified with a drying solvent station, all chemicals were used as received without any purification step.

1.2.2. Synthesis

1.2.2.1. Synthesis of biscyclocarbonate from terephthalic acid (TerBisCC)

The terephthalic biscyclocarbonate was synthesized following the pathway given by Figure 4-1. Glycerol carbonate (150 g, 1.26 mol) was dissolved in freshly distilled dichloromethane (500 mL) and mixed with triethylamine (95.8 g, 0.95 mol), under a light stream of inert gas to prevent reactions with air humidity. The flask was cooled in ice water bath. Terephthaloyl chloride (64.1 g, 0.32 mol), preliminary dissolved in dichloromethane (500 mL), was added dropwise to the stirred reaction mixture. After an overnight reaction, the reaction mixture was filtrated and a white powder containing the cyclic carbonate product was recovered. Excess of glycerol carbonate and triethylamine hydrochloride $NEt_3\cdot HCl$ was removed by two distilled water washing. The powder was then dried in an oven under vacuum at 60°C during 20 hours to yield 93.7 g (81%) of TerBisCC as a white powder.

The structure of TerBisCC was determined by ^{1}H- (Figure 4-2) and ^{13}C-NMR spectrum (Figure 4-S1 in the ESI†). In FTIR spectra (Figure 4-S2 in the ESI†), the characteristic peaks of the ester and cyclocarbonate functions are 1720 (-COO-) and 1778 cm^{-1} (-OCOO-), respectively.

^{1}H-NMR (400 MHz, DMSO-d$_6$, δ, ppm, Figure 4-2): 4.45-4.56; 4.60-4.69 (4H; 4H, m; m, -OCOO-C*H*$_2$-CH-C*H*$_2$-), 5.17-5.24 (2H, m, -OCOO-CH$_2$-C*H*-CH$_2$-), 8.10 (4H, s, -C*H*=).

^{13}C-NMR (100 MHz, DMSO-d$_6$, δ, ppm, Figure 4-S1 in the ESI†): 64.7 (-OCOO-CH$_2$-CH-*C*H$_2$-), 66.1 (-OCOO-*C*H$_2$-CH-*C*H$_2$-), 74.2 (-OCOO-CH$_2$-*C*H-CH$_2$-), 129.6 (-*C*H=), 133.3 (-*C*H=), 154.7 (-O*C*OO- from the cyclocarbonate ring) and 164.5 (Ø-*C*OO-CH$_2$-).

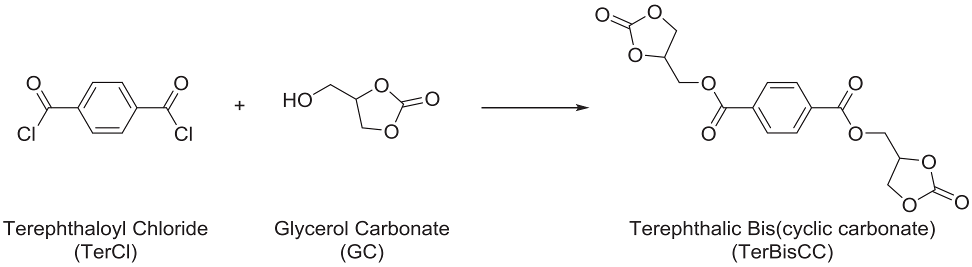


Figure 4-1. Esterification of TerCl to yield TerBisCC.

1.2.2.2. Prepolymer synthesis

Prepolymer is obtained from the reaction between TerBisCC and a long-chain diamine (DDA or Jeffamine®), referred to as Dia1. Various monomer structures and corresponding ratios were investigated. Table 4-1 presents a summary of all formulations with their designations and main reactant contents. Typical prepolymer synthesis is carried out as follows: in a 100 mL reactor equipped with a mechanical stirrer, TerBisCC is preliminary dissolved in DMF (100 mL). The appropriate amount (Table 4-1) of Dia1 (DDA or Jeffamine®) is then added to the TerBisCC. The reaction took place under inert gas flow at a temperature of 75°C. After 24 hours for DDA or 12 days for Jeffamine®, a titration is realized to confirm that all the diamines have reacted (Titration protocol and Figure 4-S3 in the ESI†). The resulting prepolymers are called P_{DDA} or P_{Jeff} depending on the Dia1 used, DDA and Jeffamine®, respectively. Furthermore, a TerBisCC:Dia1 molar ratio was also assigned to each prepolymer, according to the amount of TerBisCC and DDA, or Jeffamine®, used.

1.2.2.3. TNIPU synthesis

All the TNIPUs were prepared to reach a stoichiometric molar ratio between TerBisCC and the total diamines, *i.e.* Dia1 and Dia2 (Table 4-1). The appropriate amount of Dia2 (BDA or *m*XDA) was added to the prepolymer and the mixture was stirred at 75°C during 24 hours for TNIPU-P$_{\text{DDA}}$ or 7 days for TNIPUs-P$_{\text{Jeff}}$, respectively. After, the polymer is precipitated and washed in distilled water under stirring. Finally, the polymer is dried in an oven at 75°C, under vacuum for 3 days. The TNIPU was obtained as a colourless or slightly yellow product, correlated to the diamine used. In order to perform rheological and mechanical tests, the TNIPU samples were processed into films by compression molding between two plates at around 120°C.

Table 4-1. Designations and formulations of the different TNIPU samples.

Sample	**Prepolymer (TerBisCC: Dia1)**	**Chain extender (Dia2)**	**Ter BisCC: Dia1 molar ratio**	**Ter BisCC**[a]	**Dia1**[a]	**Dia2**[a]	**Biobased content**[b] **(%)**
TNIPU-P$_{\text{DDA}}$/BDA-1.33:1	P$_{\text{DDA}}$ (TerBisCC: DDA)	BDA	1.33:1	16 (43.7)	18.04 (32.8)	0.71 (8.1)	76.3
TNIPU-P$_{\text{DDA}}$/BDA-2:1			2:1		12.05 (21.9)	1.93 (21.9)	65.4
TNIPU-P$_{\text{DDA}}$/BDA-3:1			3:1		8.03 (14.6)	2.57 (29.1)	56.0
TNIPU-P$_{\text{DDA}}$/*m*XDA-1.33:1		*m*XDA	1.33:1		18.04 (32.8)	1.10 (8.1)	74.9
TNIPU-P$_{\text{DDA}}$/*m*XDA-2:1			2:1		12.05 (21.9)	2.98 (21.9)	61.5
TNIPU-P$_{\text{DDA}}$/*m*XDA-3:1			3:1		8.03 (14.6)	3.96 (29.1)	50.9
TNIPU-P$_{\text{Jeff}}$/BDA-2:1	P$_{\text{Jeff}}$ (TerBisCC: Jeffamine®)	BDA	2:1		43.80 (21.9)	1.93 (21.9)	4.5
TNIPU-P$_{\text{Jeff}}$/BDA-3:1			3:1		29.20 (14.6)	2.57 (29.1)	6.0
TNIPU-P$_{\text{Jeff}}$/*m*XDA-2:1		*m*XDA	2:1		43.80 (21.9)	2.98 (21.9)	4.4
TNIPU-P$_{\text{Jeff}}$/*m*XDA-3:1			3:1		29.20 (14.6)	3.96 (29.1)	5.7

[a] Initial composition (in g) of the different synthesized NIPUs. The molar masses (in mmol) are given between brackets. [b] Calculation based on ^{13}C.

1.2.3. Measurements

Infrared spectrometry was achieved with a Fourier transformed infrared spectrometer Nicolet 380 (*Thermo Electron Corporation*) working in Reflection Mode and equipped with an ATR diamond module (FTIR-ATR). The FTIR-ATR spectra were collected at a resolution of 4 cm^{-1} and with 64 scans per run.

^1H- and ^{13}C-NMR spectra were recorded on a *Bruker* Ascend^{TM} 400 spectrometer at 300 or 100 MHz, respectively. Chloroform-d_6 was used as a solvent.

Thermal degradation was studied by thermogravimetric analyses (TGA). Measurements were conducted under air or inert gas (flow rate = 25 $mL.min^{-1}$) using a Hi-Res TGA Q5000 apparatus from *TA Instruments*. The samples (3–5 mg placed in an aluminium pan) were heated up to 600°C at 10°$C.min^{-1}$. The characteristic degradation temperatures are the temperatures at the maximum of the derivative thermogram (DTG) curve (T_{max}) and at which the sample weight equals 98%, 50% and 2% of the initial one ($T_{98\%}$, $T_{50\%}$ and $T_{2\%}$).

The main characteristic temperatures were determined by differential scanning calorimetry (DSC Q200, *TA Instruments*) under nitrogen flow. The samples (2–5 mg) were heated until 175°C with a heating rate of 10°$C.min^{-1}$ (first heating scan), then cooled to −80°C at 5°$C.min^{-1}$ and finally re-heated to 175°C at a heating rate of 10°$C.min^{-1}$ (second heating scan). T_g was determined at midpoint of the change in slop of the baseline, from the second heating scan in order to erase the previous thermal history of the samples during the first scan.

The number-average molar mass (M_n), the mass-average molar mass (M_w) and the dispersity (Đ) of the resulting samples were determined by Size Exclusion Chromatography (SEC), using Malvern Instrument apparatus (Viscotek RImax) for TerBisCC and prepolymers, and Polymer Laboratories apparatus (PL50 serie) for TNIPU samples. Malvern Instrument device was equipped with a guard column 10 mm (8 µm) and three 300 mm columns (50, 150 and 500 Å). Polymer Laboratories device was equipped with a guard column (5 µm) and a 300 mm PLgel mixed-C column (5 µm). Refractive index (RI) detector was used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 $mL.min^{-1}$. The apparatus was calibrated with linear polystyrene standard from 162 to 20,000 $g.mol^{-1}$ for Malvern Instrument apparatus and from 1310 to 1,650,000 $g.mol^{-1}$ for Agilent.

Dynamic mechanical thermal analyses (DMTA) were performed on samples with dimensions around 23 x 4 x 1 mm, with RSA-II apparatus from TA Instruments equipped with a liquid-nitrogen cooling system. Experiments were recorded on films with traction mode at maximum strain from 0.001 to 1% and a frequency of 1 Hz. The samples were heated from -10 to 60°C at a heating rate of 2°C.min^{-1}.

Uniaxial tensile tests were achieved using a Zwick Roell machine (Z010 serie). The experiments were performed on tensile specimens (size: 25 x 4 x 1 mm) at room temperature, using a crosshead speed of 100 mm.min^{-1} and a load cell of 5 kN sensitivity. After adjusting the parameters, experiments were carried out at least 3 times for each sample. Young's modulus (E), tensile strength at break (σ_{max}) and elongation at break (ε_{max}) were determined.

1.3. Results and discussion

1.3.1. Synthesis and characterization of TerBisCC

The esterification reaction of TerCl with GC leads to TerBisCC formation. TerBisCC was characterized by FTIR and NMR analyses. The TerBisCC FTIR spectrum shows the profile of an ester function characteristic peak at 1720 cm^{-1} attesting the esterification reaction (Figure 4-S2 in the ESI†). Furthermore, the peak at 1778 cm^{-1} confirms the presence of carbonate groups.

The esterification reaction is confirmed by NMR analysis results presented in Figure 4-2. The absence of residual peak in the NMR spectrum indicates the TerBisCC high purity.

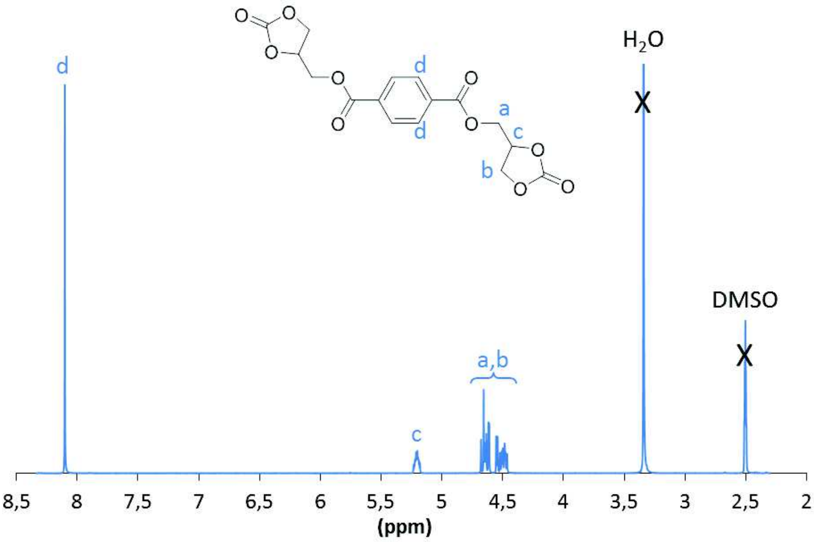


Figure 4-2. ^{1}H-NMR analysis of TerBisCC.

1.3.2. Synthesis and characterization of prepolymers

The TNIPUs were prepared *via* a two-step protocol including a prepolymer synthesis in order to enhance the control of the final architectures (Figure 4-3). The first step is the synthesis of cyclic carbonate-terminated prepolymers.

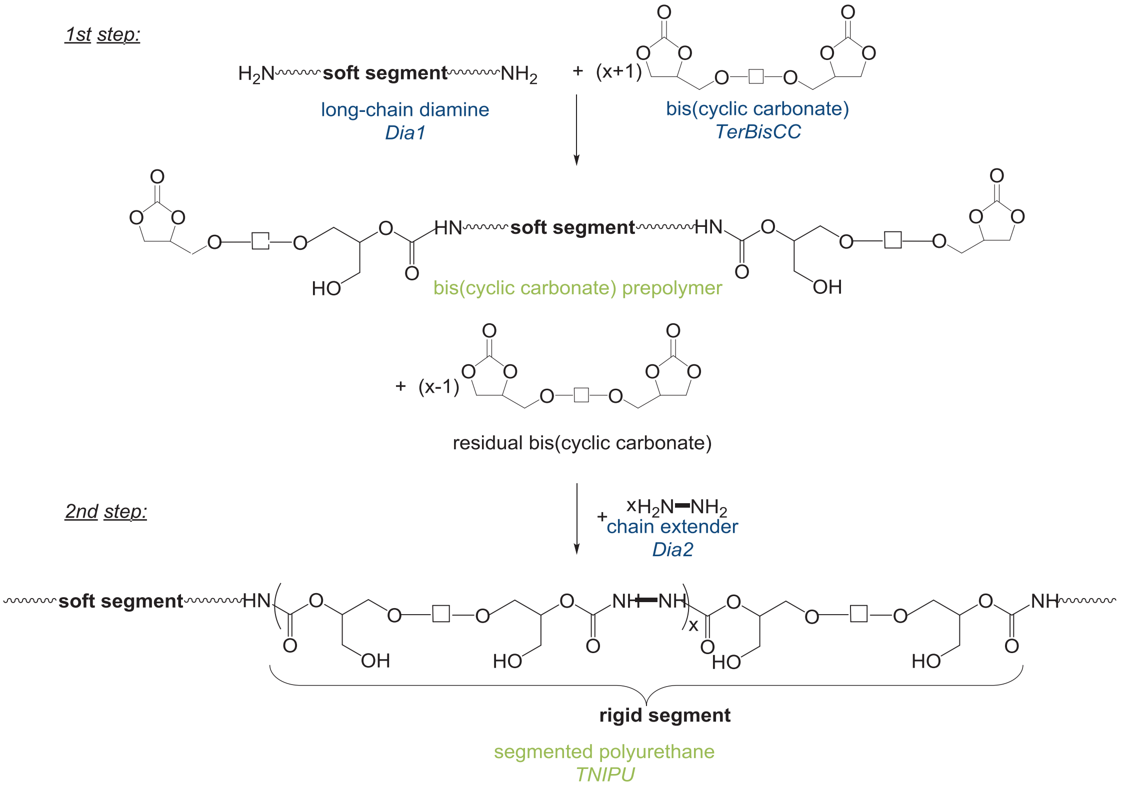


Figure 4-3. Synthetic pathway to TNIPUs.

For the first step, a study was performed to evaluate the reaction kinetics. The reaction time for each prepolymer synthesis was determined from kinetics measurements (Amine titration protocol in the ESI†). The prepolymer synthesis lasts from one to several days, according to the diamine used. Diamines with higher molar masses increase the reaction time. However, the reaction times could be optimized with an appropriate DMF concentration. A preliminary study has shown that a lower concentration promotes the reaction kinetics. Further investigations are in progress to determine the accurate concentration rate.

SEC analyses were performed on prepolymers. Both residual TerBisCC and chain lengthening were evaluated and the influence of the diamine such as the molar ratio were determined. Figure 4-4 presents the chromatographic profiles of the two prepolymer types, P_{DDA} and P_{Jeff}, at 2:1 (TerBisCC to Dia1 ratio), respectively. The molar masses of P_{Jeff} are higher than P_{DDA}, due to the higher molar mass of Jeffamine® compared to DDA. The residual TerBisCC contents were determined from the SEC results and a previous TerBisCC calibration curve (Figure 4-S3 in the ESI†), and were taken into consideration to complete the reaction by adding an appropriate amount of chain extender.

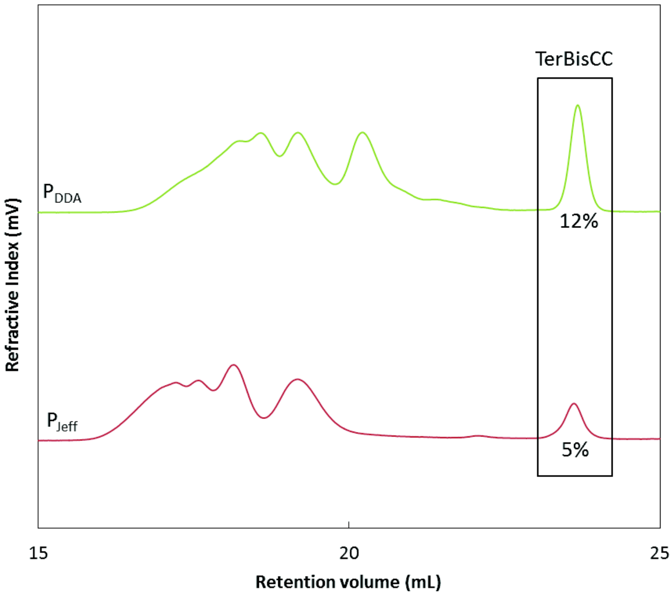


Figure 4-4. Chromatographic profile elution for P_{DDA} and P_{Jeff} prepolymers (2:1 TerBisCC:Diamine ratio).

The influence of the TerBisCC:Dia1 ratio on the prepolymer molar mass and structure was investigated on P_{DDA} (Figure 4-5). The chromatographic profiles indicate that various prepolymer chain lengths were obtained. This result shows that even a prepolymer method for the TNIPU synthesis does not enable to perfectly control the final polymer architecture. However, a general trend is observed. As expected, Đ shifts towards higher values and the residual TerBisCC is lower when the TerBisCC:Dia1 ratio decreases.

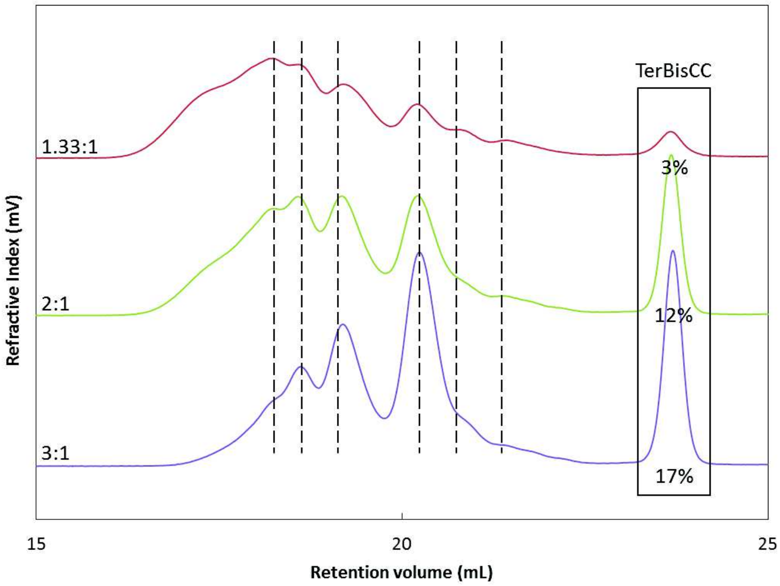


Figure 4-5. Chromatographic profile elution as a function of TerBisCC:Dia1 ratios for P_{DDA}.

1.3.3. Properties of NIPUs based on TerBisCC

TNIPUs were obtained after reaction between prepolymers and a chain extender, BDA or *m*XDA (Figure 4-3, 2nd step). All syntheses, listed in Table 4-1, were performed at a stoichiometric ratio (TerBisCC:total diamines = 1), to favour the formation of high molar mass chains. The urethane formation was confirmed by FTIR analysis (Figure 4-S4 in the ESI†). FTIR spectra of TNIPUs show distinctive absorption bands of the urethane group at 3200-3600 cm^{-1}, 1700 cm^{-1} (merged with the ester absorption peak), 1535 cm^{-1} and 1245 cm^{-1}, respectively. The absorption band at 3200-3600 cm^{-1} is also assigned to the hydroxyl group resulting from the cyclic carbonate opening. Hydroxyl and urethane groups are shown for all samples, which confirm the expected structure of TNIPUs, also known as polyhydroxyurethanes. The peak at 1790 cm^{-1} is assigned to the carbonyl function of the residual TerBisCC. As the reaction was performed at a stoichiometric ratio, the unreacted TerBisCC is due to secondary reactions such as the ester aminolysis.[26, 42] The slight shoulder around 1650 cm^{-1} confirms the resulting amide formation.[26]

1.3.3.1. Influence of the diamine structures

Several diamines were used to synthesize different TNIPU architectures. The corresponding prepolymers were synthesized from dimeric DDA and Jeffamine® polyetheramine. They present an average molar mass around 550 and 2,000 $g.mol^{-1}$, respectively. TNIPUs were finally elaborated by reaction between prepolymer and aliphatic short-chain BDA or aromatic *m*XDA. The effect of their average molar masses as well as their chemical natures on the properties of the corresponding TNIPUs will be discussed below.

Influence of the prepolymer diamine, Dia1

Table 4-2 presents the average molar masses and dispersity of the synthesized TNIPUs, determined by SEC. For a defined molar ratio and despite the highest molar mass of Jeffamine®, there is no significant difference between both TNIPUs (TNIPUs-P_{Jeff} and TNIPUs-P_{DDA}). The low average molar masses of TNIPUs-P_{Jeff} could be due to a lower reactivity. Indeed, it was demonstrated that long-chain building blocks are less reactive than shorter.[43] The low T_g values around -50°C (Table 4-2) and the sticky aspect of these samples confirm the incomplete reaction. Compared to DDA, Jeffamine® chemical structure is closer to polyols used in conventional PUs.[11] However, due to this lack of reactivity, only TNIPUs based on P_{DDA} prepolymers will be below, further studied.

Table 4-2. SEC results and thermal properties of TNIPU samples.

Sample	**SEC**			**DSC**	**DMTA**
	M_n (g.mol^{-1})	M_w (g.mol^{-1})	Đ	T_g (°C)	$T_\alpha{}^a$ (°C)
TNIPU-P_{DDA}/BDA-1.33:1	10,050	26,800	2.7	22	12
TNIPU-P_{DDA}/BDA-2:1	7,200	22,550	3.1	25	27
TNIPU-P_{DDA}/BDA-3:1	8,000	17,350	2.2	n/a	n/a
TNIPU-P_{DDA}/*m*XDA-1.33:1	6,250	15,000	2.4	9	9
TNIPU-P_{DDA}/*m*XDA-2:1	6,050	17,350	2.8	14	22
TNIPU-P_{DDA}/*m*XDA-3:1	5,100	10,400	2.0	31	28
TNIPU-P_{Jeff}/BDA-2:1	9,850	20,700	2.1	-50	n/a
TNIPU-P_{Jeff}/BDA-3:1	10,750	23,150	2.1	-52	n/a
TNIPU-P_{Jeff}/*m*XDA-2:1	11,850	21,600	1.8	-50	n/a
TNIPU-P_{Jeff}/*m*XDA-3:1	4,550	9,050	2.0	n/a	n/a

[a] Determined at the maximum of tan δ.

Influence of the diamine chain extender, Dia2

Reactivity of the chain extender is also a key parameter in TNIPU synthesis. In spite of the BDA low molar mass (88 g.mol^{-1}), compared to *m*XDA (136 g.mol^{-1}), TNIPUs:BDA ratios present the highest average molar masses (Table 4-2). These results are in correlation with previous results indicating that short-chain aliphatic amines are more reactive towards cyclic carbonates, compared to aromatic ones.[43]

To evaluate the effect of the chain extender diamine on mechanical properties of the TNIPUs, uniaxial tensile tests were performed (Figure 4-6). The global evolution of the stress-strain curves of TNIPUs is comparable to those of conventional thermoplastic polymers, with a yield point formation.[44] First, they presents an elastic region, then the samples undergo a mechanical instability, necking takes place and subsequent plastic deformation finally occurs until to the rupture point, associated to an ultimate elongation at high values in all the cases. Compared to TNIPUs/*m*XDA samples, TNIPUs synthesized with BDA as a chain extender show higher ultimate tensile strengths and lower elongations at break, whatever the molar ratio used. The *m*XDA chain extender brings a certain rigidity linked to the corresponding aromatic structure. The highest molar masses of TNIPUs obtained with BDA chain extender seem to have a great influence on the corresponding properties. TNIPUs synthesized with BDA chain extender are the most promising architectures with good balance between stiffness and elongation, equivalent to conventional TPUs.[45, 46] To obtain materials with high performances, it is thus essential not only to have soft and hard segments but also to have a high monomers reactivity, reached *e.g.* by using short aliphatic chain extender.

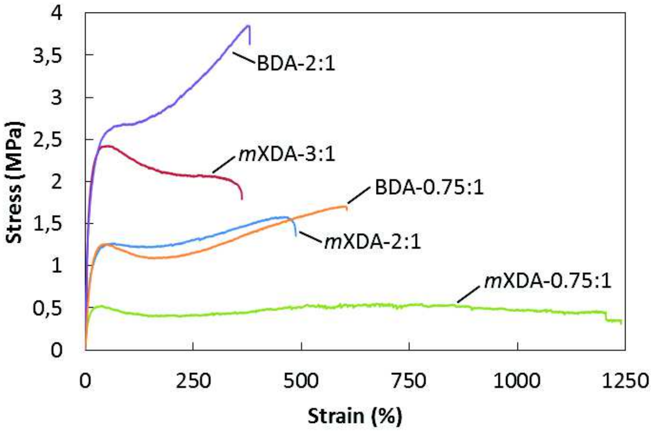


Figure 4-6. Stress-strain curves of synthesized TNIPUs based on P_{DDA} prepolymer.

1.3.3.2. Effect of the ratio between the constituting monomers

The TerBisCC:Diamines molar ratio strongly impacts the structure and the properties of the corresponding TNIPUs. The values and the evolutions of the average molar masses of TNIPU samples provide information on the effect of the monomers ratio on TNIPU structures. From Table 4-2, it is observed that number- and mass-average molar masses decrease when increasing the Dia2 content, *i.e.* when HS parts formed with TerBisCC increase. This evolution could be attributed to a higher short-chain diamine content. The highest M_n and M_w

values were found for TNIPU-P_{DDA}/BDA-1.33:1. This sample exhibits the lowest TerBisCC:Dia1 ratio and the most reactive building blocks, which promote a chain growth. These results are in good correlation with publications on equivalent conventional TPUs.[11, 47-49]

T_g of TNIPUs determined by DSC were presented in Table 4-2. Except for TNIPU-P_{DDA}/BDA-3:1 (T_g is not representative of a final polymer material due to a too low molar mass), these data show that T_g increases with the molar ratio, as expected since more rigid building blocks were incorporated. The increasing of Dia2 content brings a specific stiffness to the materials. No melting temperature was observed in the explored domain.

Additional dynamic mechanical thermal analyses (DMTA) were carried out to go deeper into the details since DMTA provides information on viscoelastic properties, which can be related to microdomains formation and phases separation. Figure 4-7 exhibits the temperature dependence of the storage modulus (E'). In the temperature range explored, enhanced storage moduli are observed when increasing the molar ratio, suggesting a higher stiffness of these materials. Even if slight inflexions are observed, no clear plateau on E' modulus curves are detected and the moduli decrease continuously with temperature, indicating that no significant structural reinforcement due to a stable hard domain formation occurs. The absence of clear phase separation in TNIPUs could be due (i) to the low reactivity of the aminolysis reaction and the corresponding low molar masses, (ii) to the "hard" segments, which are less rigid than their equivalents from the conventional PU synthesis, as well as the soft diamine, which is shorter than the classical polyols, and (iii) to the highest number of hydrogen bonding due to urethane and ester linkages but also hydroxyl bonds, in HS and SS, inhibiting the formation of microdomains. Figure 4-8 displays the dependence of the loss factor (tan δ) on temperature for TNIPU-P_{DDA}/*m*XDA samples. As expected, the T_α relaxation temperature, associated to the maximum of tan δ, increases with the molar ratio. These results confirm the previous observations obtained from DSC. Same trends are observed for TNIPU-P_{DDA}/BDA samples.

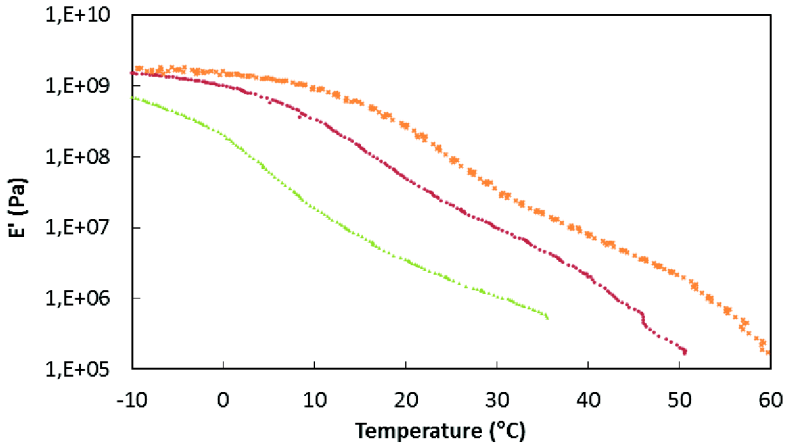


Figure 4-7. DMTA curves of TNIPU-P_{DDA}/*m*XDA samples.
Influence of the molar ratio between TerBisCC and diamines on the storage modulus (E').
The corresponding ratios are 1.33:1 (▲), 2:1 (●), and 3:1 (x).

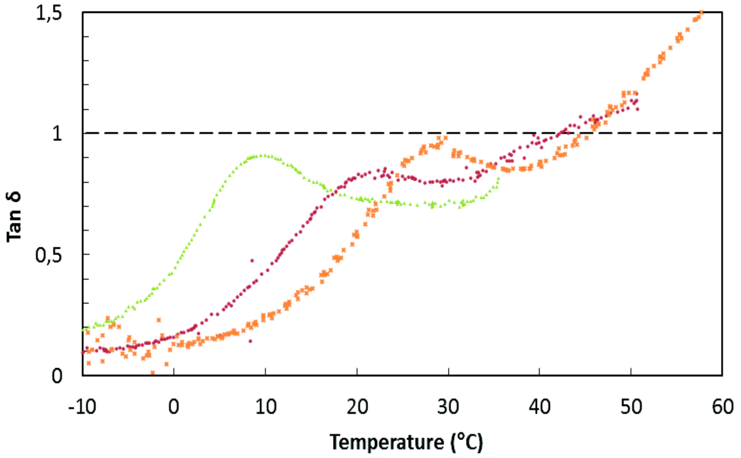


Figure 4-8. DMTA curves of TNIPU-P_{DDA}/*m*XDA samples.
Influence of the molar ratio between TerBisCC and diamines on the loss factor (tan δ).
The corresponding ratios are 1.33:1 (▲), 2:1 (●), and 3:1 (x).

Stress-strain curves at room temperature are presented in Figure 4-6, and the main mechanical properties are summarized in Table 4-3. Results show that the increase in molar ratio, *i.e.* in hard building block content, lead to lower elongation at break and higher tensile strength. Such a trend was expected due to lower chain lengths. TNIPU-P_{DDA}/BDA-3:1 sample was brittle. This behavior could be attributed to the fragility provided by the high content of rigid building blocks.

Table 4-3. Mechanical results from uniaxial tensile tests of the TNIPU-P_{DDA} samples.

Sample	**Elongation at break, ε_{max} (%)**	**Ultimate tensile strength, σ_{max} (MPa)**	**Young modulus, E (MPa)**
TNIPU-P_{DDA}/BDA-1.33:1	600 ± 100	1.5 ± 0.2	8 ± 2
TNIPU-P_{DDA}/BDA-2:1	390 ± 20	3.6 ± 0.3	25 ± 4
TNIPU-P_{DDA}/BDA-3:1		*brittle*	
TNIPU-P_{DDA}/*m*XDA-1.33:1	> 700	< 0.7	n/a
TNIPU-P_{DDA}/*m*XDA-2:1	470 ± 40	1.9 ± 0.4	10 ± 4
TNIPU-P_{DDA}/*m*XDA-3:1	330 ± 40	2.5 ± 0.2	20 ± 4

1.3.3.3. TNIPUs thermal sensitivity

Thermogravimetric analyses were achieved on TNIPU samples under air and inert gas. Whereas samples remain stable up to 250°C under inert gas, their thermal degradations start at around 200°C under air. This gap is due to additional oxidative degradation mechanisms, with air. Usually, PUs thermal decomposition is a multi-step process including the decomposition of urethane bonds and the decomposition of carbonated chains.[50] All TNIPU samples present a quite similar process with three main degradation steps. These results are similar to those of previous studies on NIPUs.[51] However, conventional TPUs have higher thermal resistances.[45, 52]

Figure 4-9 illustrates the influence of the diamine structure on TNIPU thermal degradation properties. The thermal decomposition of TNIPUs obtained from P_{Jeff} prepolymer starts before the ones of TNIPUs, obtained from P_{DDA}. This early decomposition can be explained by the shorter chain lengths, as previously discussed, from P_{Jeff}. However, the variation of the chain extender does not seem to affect the thermal degradation of the samples. As well, monomers molar ratio does not have a significant effect on the TNIPU thermal decomposition (Figure 4-10). Additionally, these results show that in the temperature range explored by DSC and DMTA, no degradation occurs.

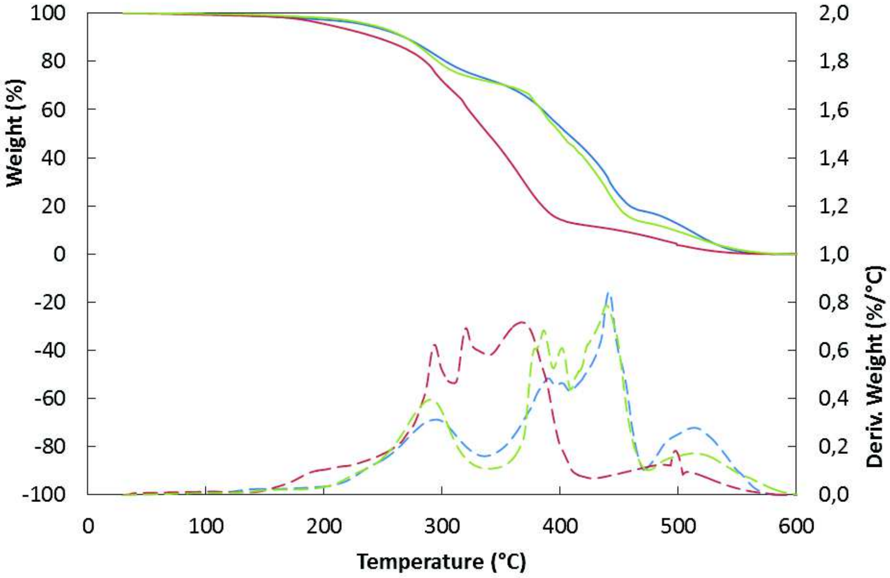


Figure 4-9. TGA (solid line) and DTG (dotted line) curves of TNIPU samples under air. Influence of the diamines.
TNIPU-P_{DDA}/BDA-2:1 (in green), TNIPU-P_{DDA}/*m*XDA-2:1 (in blue), and TNIPU-P_{Jeff}/*m*XDA-2:1 (in red) samples.

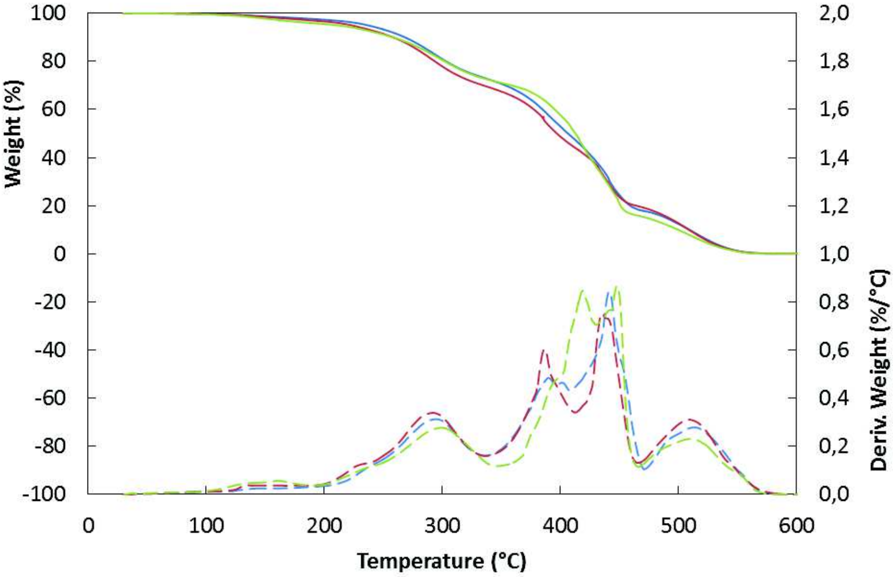


Figure 4-10. TGA (solid line) and DTG (dotted line) curves of TNIPU samples under air. Influence of the molar ratio.
TNIPU-P_{DDA}/BDA-1.33:1 (in green), TNIPU-P_{DDA}/BDA-2:1 (in blue), and TNIPU-P_{DDA}/BDA-3:1 (in red) samples.

1.4. Conclusions

Thermoplastic nonisocyante polyurethanes (TNIPUs) with aliphatic-aromatic architectures were successfully synthesized by aminolysis reaction. In a first step, biscyclocarbonate was prepared from terephthalic acid. This aromatic molecule plays the role of a rigid building block. This building block was used to react in a two-step method with a soft aliphatic diamine (DDA or Jeffamine®) to form a prepolymer, which reacts with a rigid chain extender based on an aliphatic or aromatic diamine (BDA or *m*XDA, respectively). TNIPUs presenting various macromolecular architectures were designed. All synthesized intermediates and final materials were fully characterized. The effects of the building block structure as well as the influence of the molar ratio between the constituting monomers were investigated. The prepolymer study reveals that the prepolymer chain lengths were greatly influenced by both the chemical structure of the soft diamine, and the monomers ratio. TNIPUs obtained from Jeffamine® prepolymer show lowest properties compared to BDA ones, due to the lowest reactivity of the corresponding building block and the ensuing low average molar masses of the TNIPU samples. From this study, it can also be concluded that molar ratio between the monomers strongly impact thermal, rheological and mechanical properties of the obtained TNIPUs. Particularly, TNIPUs built from soft diamine at high contents present long soft chains liable to the high elongation at break and low tensile strength. Instead, increasing the rigid building block content enhance the ultimate tensile strength and reduce the elongation at break, which remains nevertheless significant. No phase separation was clearly shown. However, original TNIPUs presenting new architectures with high biobased contents (up to 76%) and high performances were developed. Regarding these results, a wide range of durable applications can be envisaged such as in building, automotive materials and seals.

Acknowledgements

The authors thank the Alsace Region, the urban community of Strasbourg (CUS), SOPRÉMA and PSA Peugeot Citroën for their financial supports. Croda and Huntsman are also acknowledged for having kindly provided raw materials. The authors would like to acknowledge Prof. Jean-Pierre Pascault (IMP-INSA Lyon, France) and Dr. Sébastien Gallet (ICPEES Strasbourg, France) for helpful discussions.

1.5. Supporting information

1.5.1. TerBisCC characterization

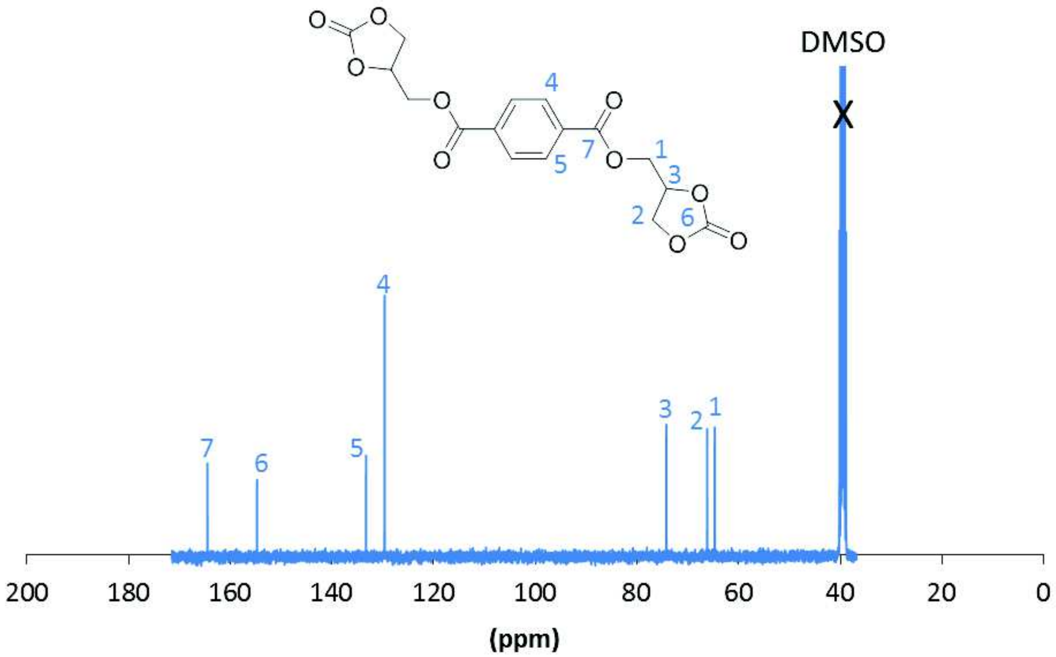


Figure 4-S1. ^{13}C-NMR analysis of TerBisCC.

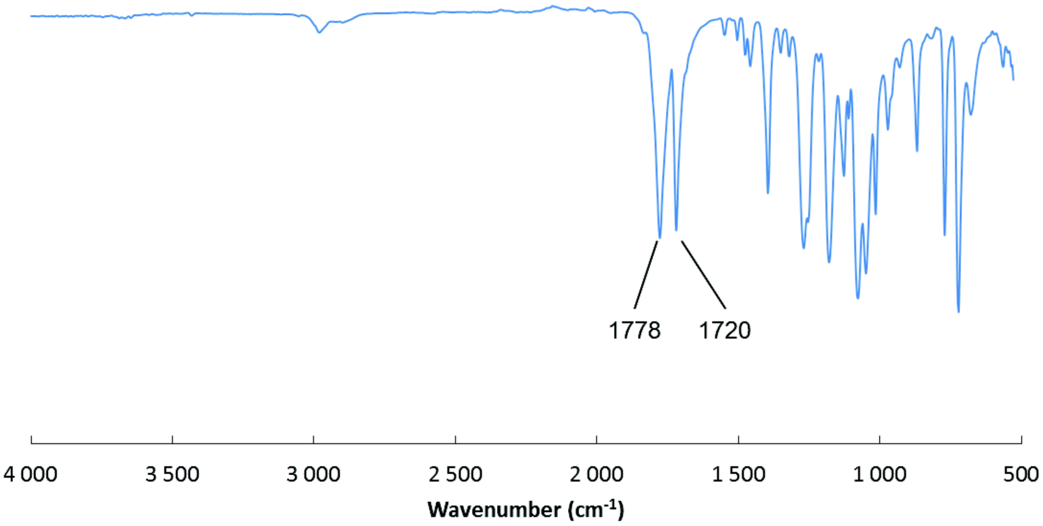


Figure 4-S2. FTIR spectrum of TerBisCC.

1.5.2. Amine titration

Amine end group content in the reaction medium during TNIPU synthesis was determined by using the following method, adapted from a previous titration protocol.[44] A TNIPU sample was removed from the reaction medium and placed in an isopropanol:toluene mixture (volume ratio = 1:1). Bromocresol green solution was added and used as a color indicator. Amine end group concentration was then determined by titration with freshly standardized HCl solution at 0.01 mol.L^{-1}. For each titration experiment, at least three replicates were collected and three titrations were carried out for determining the reproductibility.

1.5.3. TerBisCC calibration

A calibration was realized to determine the residual TerBisCC in the prepolymers. Various samples at different concentrations were prepared and analyzed in order to determine the relation between the TerBisCC peak area and its concentration in the sample. The calibration curve and its equation are presented in Figure 4-S3.

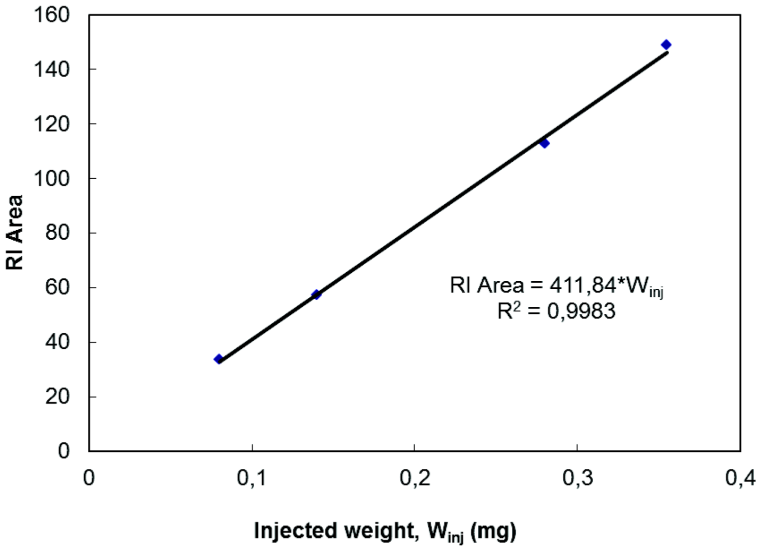


Figure 4-S3. TerBisCC calibration curve.

1.5.4. FTIR analysis of TNIPUs

Figure 4-S4 presents the FTIR spectrum of TNIPU-P$_{DDA}$/*m*XDA-2:1. However, same characteristic peaks were observed for all TNIPU samples.

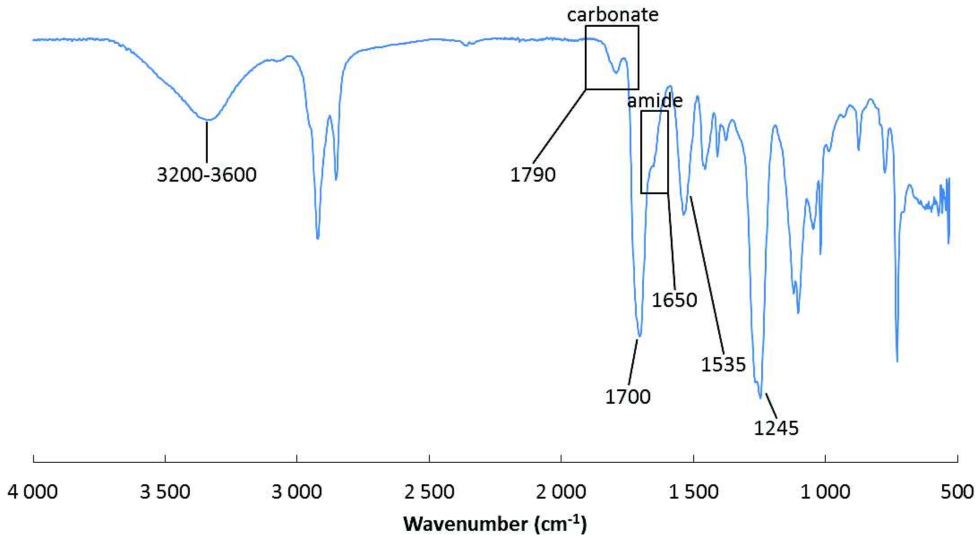


Figure 4-S4. FTIR spectrum of TNIPU-P$_{DDA}$/*m*XDA-2:1.

2. L’acide 2,5-furandicarboxylique (FDCA), un synthon aromatique biosourcé attrayant

Aujourd'hui, en raison d’une prise de conscience environnementale croissante, de plus en plus de synthons obtenus à partir de ressources renouvelables sont utilisés dans la synthèse de polymères. Ce sont principalement des composés aliphatiques ou cycloaliphatiques, conduisant à des polymères biosourcés souples et flexibles. Afin d’obtenir des polymères de hautes performances disposant de bonnes propriétés thermiques ainsi qu’un excellent comportement mécanique, des molécules biosourcées rigides ont été développées ou sont en cours de développement.[53] Par conséquent, il devrait être prochainement possible d'atteindre des propriétés similaires voire supérieures à celles de leurs équivalents fossiles, en les remplaçant par ces nouveaux polymères biosourcés.

Dans cette optique, le FDCA a été choisi comme ressource renouvelable pour la synthèse de biscyclocarbonate. Le FDCA présente un énorme marché potentiel, en particulier dû à son utilisation en tant que substituant de l’acide téréphtalique pour la synthèse d’équivalent du polyéthylène téréphtalate. Il a d’ailleurs été identifié en 2004 par le département américain de l’énergie (DoE) comme l’un des 12 synthons chimiques biosourcés les plus prometteurs pour le futur. De plus, lors de la synthèse de cylcocarbonate, il est associé à une autre molécule biosourcée : le carbonate de glycérol. Outre son origine renouvelable, le carbonate de glycérol présente une large réactivité et est largement disponible à de faibles coûts.

Les travaux réalisés autour du FDCA sont présentés sous la forme d’une communication intitulée : « Cyclic carbonate from 2,5-furandicarboxylic acid, a promising rigid building block for biobased nonisocyanate polyurethane synthesis », soumise dans *Green Chemistry*. Dans un premier temps, la synthèse du biscyclocarbonate est présentée, suivie de la préparation d’un polyuréthane sans isocyanate issu de ce nouveau synthon à fort potentiel.

Publication n°5 :

Cyclic carbonate from 2,5-furandicarboxylic acid, a promising rigid building block for biobased nonisocyanate polyurethane synthesis

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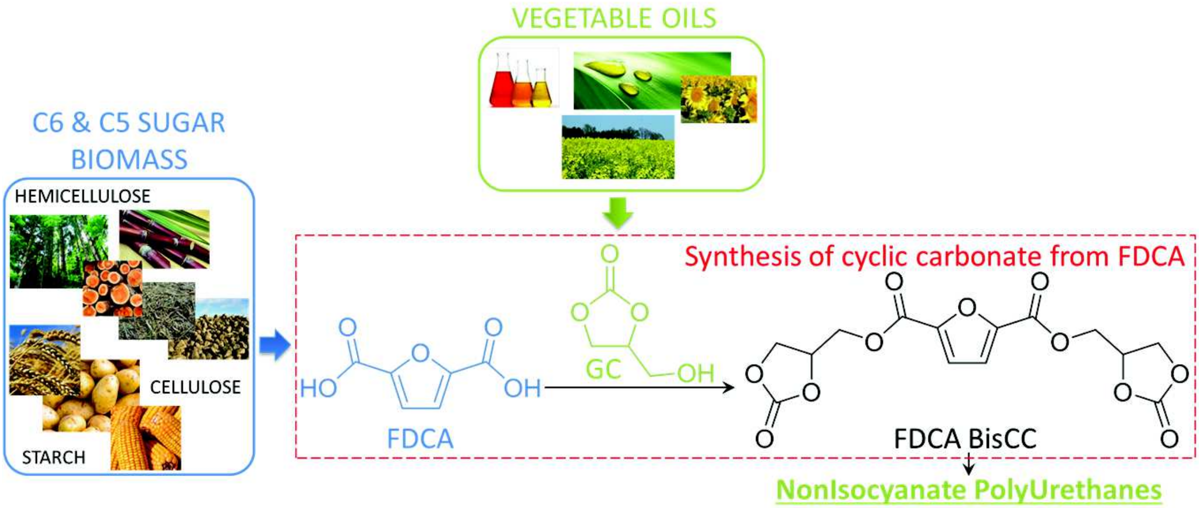
Green Chemistry – Submitted letter

Graphical abstract



Abstract

Furan-based cyclic carbonate was synthesized *via* Steglich esterification of 2,5-furandicarboxylic acid (FDCA) with glycerol carbonate using N,N'-dicyclohexylcarbodiimide and 4-dimethylaminopyridine coupling agents. The subsequent reaction with 1,8-diaminooctane to achieve the synthesis of a biobased nonisocyanate polyurethane without any solvent and catalyst systems, is described and developed for the first time.

Keywords

2,5-furandicarboxylic acid, cyclic carbonates, glycerol carbonate, nonisocyanate polyurethanes, renewable resources

2.1. Introduction

2,5-furandicarboxylic acid (FDCA) is a promising and biobased aromatic molecule. In 2004, this building block was identified by the US Department of Energy (US DoE) as one of the top value added chemicals from sugar-based biomass.[54] FDCA can be synthesized in a large scale from sugars or other non-edible carbohydrate feedstocks.[55] This diacid is mainly obtained from the oxidation of both alcohol and aldehyde groups of 5-hydroxymethylfurfural (HMF) with various catalysts, solvents and air conditions.[56] Other chemical pathways to FDCA include the dehydration of hexose derivatives and catalytic conversion of various furanic compounds.[57] FDCA can be involved in different synthesis to produce polyesters, polyamides, polyurethanes, thermoset resins, plasticizers and several other chemical products,[40, 58, 59] in replacement of various petrochemicals for a wide range of applications.[40, 53] Nevertheless, up to now, FDCA has not been produced on big scale, mainly due to the critical HMF process step (low yield and non-selective conversion obtained).[60-62] However, recently a biocatalytic process was developed by a Dutch company, namely Advantium (called YXY technology), to enable the production of FDCA under relatively mild conditions.[63] Using this new technology, larger productions at competitive prices will thus emerge. In this way, FDCA is destined to a brilliant future with a huge potential market as a renewable substitute of terephtalic acid (TerAc) to produce polyethylene furanoate (PEF), a polyester with a high potential to replace polyethylene terephthalate (PET) in a next future. It has also been foreseen as a potential and versatile chemical platform.[64]

Glycerol carbonate (GC) is another promising molecule from renewable resources due to its low price, its large availability, and its wide reactivity suggesting numerous developments and applications. GC is obtained from glycerol, a main component of triglycerides from vegetable oils or animal fats, but also a byproduct from the valorization of fatty acids for the oleochemistry or biodiesel production. As a platform to numerous high-value chemicals and materials, GC was also classified in the top twelve of value added chemicals from biomass by the US DoE.[64] Numerous synthesis routes of GC from glycerol have been developed, including carbonation and transcarbonation reactions.[65]

Due to their high potential, FDCA and GC were thus both used in this study to synthesize a novel aromatic rigid biscyclocarbonate from renewable resources. Biobased cyclic carbonates were already reported in the literature and were obtained from an intermediate epoxy molecule.[25, 27-29, 66] The biomass used for their synthesis is mainly vegetable oils,[66] but also

Cashew Nut Shell Liquid (CNSL),[28] isosorbide,[25] limonene[29] or vanillin.[27] In this paper, we report for the first time the synthesis of a biscyclocarbonate based on FDCA and glycerol, obtained from the valorization of two different biomass.

Cyclic carbonates are relevant for numerous industrial applications including monomers, polymers, surfactants, plasticizers, crosslinking and curing agents and solvents.[67] Among them, a generation of new polyurethanes, called nonisocyanate polyurethanes (NIPUs) is increasingly developed since they are nontoxic and environmental friendly. Various routes to NIPUs were reported,[2-4] including the aminolysis. This synthesis involves the reaction of cyclic carbonates with amines compounds.[16, 18] In addition to urethane bonds, these NIPUs also present hydroxyl groups due to the cyclic carbonate ring opening.[68] Unlike conventional polyurethanes, almost always based on rigid segments composed of aromatic structures, current NIPUs present softer and more flexible architectures made of aliphatic or cycloaliphatic molecules. In this context, the FDCA-based cyclic carbonate obtained in our study was further used as a rigid precursor for NIPU synthesis, with the corresponding beneficial properties. Compared with other biobased monomers, the aromatic structure of FDCA enables to enhance the material micro-organization.

2.2. Experimental section

2.2.1. Materials

FDCA **1** (97%), tetrahydrofuran (THF, >99.9%) and dimethylformamide (DMF, ≥99%) were purchased from Sigma-Aldrich. Glycerol carbonate **2** (Jeffsol GC, 93%) was kindly supplied by Huntsman (Everberg, Belgium). N,N’-diisopropylcarbodiimide (DCI, 99%) and 4-(dimethylamino)pyridine (DMAP, 99%) were obtained from Alfa Aesar (Karlsruhe, Germany). 1,8-diaminooctane (DA8) was provided by Sigma-Aldrich. Except THF, which was distilled over sodium, all chemicals were used as received without any purification.

2.2.2. General characterization techniques

Infrared spectroscopy was achieved with a Fourier transformed infrared spectrometer Nicolet 380 (*Thermo Electron Corporation*) working in Reflection Mode and equipped with an ATR diamond module (FTIR-ATR). The FTIR-ATR spectra were collected at a resolution of 4 cm^{-1} and with 64 scans per run.

^{1}H- and ^{13}C-NMR spectra were recorded on a *Bruker* Ascend^{TM} 400 spectrometer at 400 MHz and 100 MHz respectively. Dimethylsulfoxide-d_6 was used as a solvent.

Elemental analysis (C, H) was performed by using a ThermoFisher Scientific "Flash 200" analyzer (Absolute analysis accuracy: 0.3%).

The number average molar mass (M_n), and the dispersity (Đ) of the NIPU samples were determined by Size Exclusion Chromatography (SEC), using Malvern Instrument apparatus (Viscotek RImax). This device was equipped with a guard column 10 mm (8 µm) and three 300 mm columns (50, 150 and 500 Å). Refractive index (RI) detector was used. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 mL.min^{-1}. The apparatus was calibrated with linear polystyrene standard from 162 to 20,000 g.mol^{-1}.

2.2.3. Synthesis

2.2.3.1. Synthesis of biscyclocarbonate from 2,5-furandicarboxylic acid (FDCA BisCC, 3)

The esterification synthesis was carried out in a three-necked 100 mL round-bottomed flask. FDCA **1** (5.00 g, 32.0 mmol), DMAP (0.39 g, 3.2 mmol) and GC **2** (11.35 g, 96.1 mmol) were successively introduced in the flask, and mixed under argon flow with 150 mL of freshly dried THF. DCI (12.13 g, 96.1 mmol) was then added slowly to the stirred reaction mixture, cooled in an ice water bath. The reaction was then conducted overnight at room temperature under agitation and a continuous nitrogen stream. The raw product, as a white powder, was recovered from filtration, and the DCI urea by-product **4** was taken out with the organic phase. The remaining urea traces were removed with an additional THF stripping. The powder was then washed with a 5 wt% HCl solution and water, to eliminate DCI, the excess of DMAP, and GC **2**. The solution was finally dried in a vacuum oven to yield 2.51 g (22%) of FDCA BisCC **3** as a white powder. The esterification reaction and the biscyclocarbonate chemical structure were confirmed by IR, NMR and elemental analyses.

^{1}H-NMR (400 MHz, DMSO-d_6, δ, ppm, Figure 4-S5 in the ESI†): 4.41 (2H, dd, J = 6.1, 8.5 Hz, -OCOO-CH_2-CH-CH_2-O-), 4.54 (2H, dd, J = 5.0, 12.6 Hz, -OCOO-CH_2-CH-CH_2-O-), 4.59-4.66 (4H, m, -OCOO-CH_2-CH-CH_2-O-), 5.13-5.20 (2H, m, -OCOO-CH_2-CH-CH_2-O-), 7.44 (2H, s, -OCO-C=CH-).

^{13}C-NMR (100 MHz, DMSO-d$_6$, δ, ppm, Figure 4-S6 in the ESI†): 64.9 (-OCOO-*C*H$_2$-CH-CH$_2$-O-), 66.5 (-OCOO-CH$_2$-CH-*C*H$_2$-O-), 74.6 (-OCOO-CH$_2$-*C*H-CH$_2$-O-), 120.2 (-OCO-C=*C*H-), 146.3 (-OCO-*C*=CH-), 155.1 (-O*C*OO-CH$_2$-CH-CH$_2$-O-), 157.2 (-O*C*O-C=CH-).

FTIR-ATR (cm^{-1}, Figure 4-S7 in the ESI†): 1741 (-COO-) and 1778 (-OCOO-).

Elemental analysis: Calculated for $C_{14}H_{12}O_{11}$: C, 47.20; H, 3.40. Found: C, 47.20; H, 3.38.

2.2.3.2. NIPU synthesis

In a 50 mL round-bottomed flask, FDCA BisCC **3** (0.09 g, 0.26 mmol) and diaminooctane (0.04 g, 0.26 mmol) were added. The reaction took place in DMF (10 mL), at a temperature of 75°C, and under inert gas flow to avoid the amine carbonation during the synthesis. After ninety-six hours under stirring, the reaction mixture was evaporated under reduced pressure and a viscous product was obtained.

FTIR-ATR (cm^{-1}, Figure 4-12) 1650 (=CO stretching, amide, s), 1536 (-NH bending, m), 1725 (-C=O stretching of urethane, s, broad), 1725 (-C=O stretching of ester, s, broad), and 3300 (-NH and –OH stretching, respectively m and s, broad).

2.3. Results and discussion

The first part of this work deals with the synthesis of a biscyclocarbonate using FDCA **1**. To the best of our knowledge, no work on this chemical product has already been reported. Various chemical pathways can be involved for the synthesis of cyclic carbonates.[69] The main routes are (i) reactions between epoxides and carbon dioxide,[70] or (ii) an esterification between a carboxylic acid or a derivative, and GC.[71] This last approach was carried out to minimize the number of reaction steps. Several strategies for this coupling reaction can be envisaged such as:

(i) an esterification between FDCA and GC. This first route leads to a long reaction time due to a low selectivity and reaction kinetics.

(ii) an esterification between FDCA chloride derivative and GC. In order to improve the reaction time and obtain a complete reaction, the synthesis of FDCA biscyclocarbonate could be realized *via* FDCA chloride, a derivative already synthesized by Gomes *et al*.[72] However, FDCA chloride is difficult to handle due to its lower stability and so its high reactivity, especially with water molecules.

(iii) the Steglich esterification. This path was selected as the most efficient method without any side reaction. The Steglich esterification is usually performed using N,N'-dicyclohexylcarbodiimide (DCC) as coupling reagent and 4-(dimethylamino)pyridine (DMAP) as a catalyst.[73] In addition to the ester, N,N'-dicyclohexylurea (DHU) is also formed as a by-product of the organic synthesis. DCC was the first carbodiimide developed and is often used as a cheap coupling reagent. As a second approach and due to the difficulty to withdraw all DCC urea by-product, the synthesis of FDCA biscyclocarbonate **3** described in Figure 4-11 was performed using another carbodiimide called N,N'-diisopropylcarbodiimide (DCI). N,N'-diisopropylurea (DCI urea, **4**) is soluble in organic solvents and can easily be removed from the FDCA cyclic carbonate product **3** by filtration followed by an additional washing with THF.

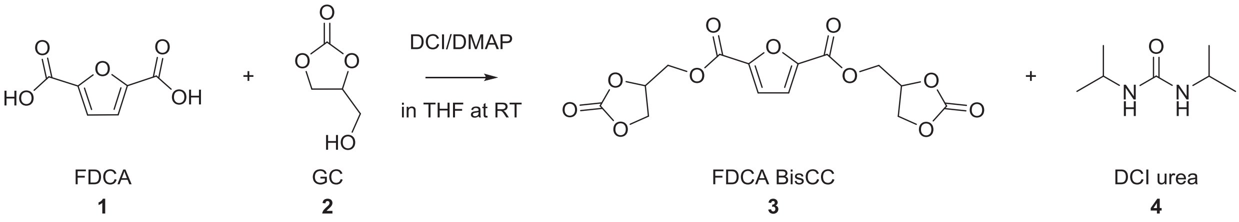


Figure 4-11. FDCA BisCC synthesis.

Steglich esterification usually achieves a good yield (40-98%) after a few hours under mild conditions.[73] FDCA **1** is a very stable compound and a longer reaction time is required for its conversion into cyclic carbonate. Unfortunately, even with long reaction times, the yield of biscyclocarbonate **3** still remains low (about 20%). To enhance the reaction kinetics and yield, additional optimizations are currently under progress.

In order to show the high potential of this new biobased cyclic carbonate, a NIPU synthesis based on FDCA cyclic carbonate **3** was successfully performed by reaction with 1,8-diaminooctane. The formation of the urethane bonds was confirmed by IR spectroscopy (Figure 4-12).

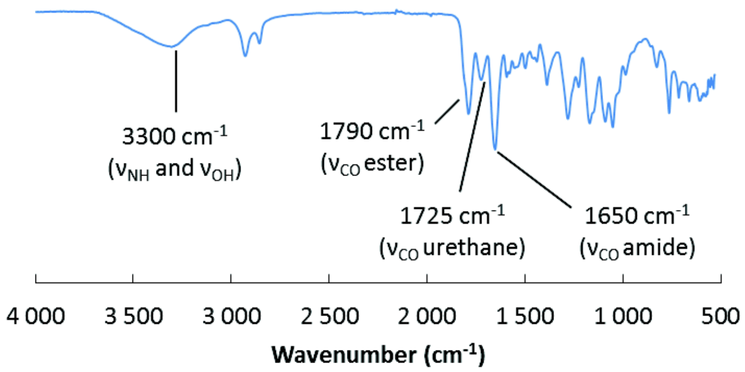


Figure 4-12. FTIR spectrum of FDCA NIPU.

The broad peak at 3300 cm^{-1} is characteristic of hydroxyl vibrations, specific to the NIPU synthesis from aminolysis.[51] Indeed, in addition to the urethane bond formed after reaction of the amines with cyclic carbonates, primary and secondary hydroxyl groups are obtained from the carbonate ring opening.[19, 68] These NIPUs are also called polyhydroxyurethanes (PHUs). The peak at 1650 cm^{-1} is assigned to the amide group resulting from the aminolysis of ester groups and leading to some chain cleavages. Although not desired, this side reaction is frequently encountered in NIPU synthesis particularly when an excess of amine is used.[26, 42]

Compared with conventional polyurethanes obtained *via* the classic isocyanate-alcohol route, the weight-average molar mass (M_w = 3230 g.mol^{-1}) of the NIPU based on FDCA present a quite low value, whereas its dispersity value (Đ = 1.26) is classical.[49, 74] This low molar mass is due to the limited reactivity of cyclic carbonates towards diamines, as well as the existence of the secondary reactions forming amide groups, already mentioned in this article. However, the M_w value is equivalent to other NIPU systems.[4, 23, 51]

The thermal gravimetric analysis of FDCA NIPU displays a high thermal resistance with a thermal stability up to 250°C (Figure 4-S8 in the ESI†). Furthermore, differential scanning calorimetry result shows a glass transition temperature (T_g) around 75°C for NIPU sample (Figure 4-S9 in the ESI†). This value is higher than T_g typically obtained for NIPUs, which are commonly in a range between -20 to 59°C. The lowest values correspond to NIPUs with linear monomers, whereas the highest ones were found for cyclic monomers, such as isosorbide cyclic carbonate or isophoronediamine.[4] The FDCA rigid building block decreases the chains mobility and thus promotes a high T_g.

2.4. Conclusion

This article discussed an innovative method for preparing a novel biscyclocarbonate from 2,5-furandicarboxylic acid (FDCA), a promising biobased building block. Cyclic carbonates show a wide range of applications including solvents, plasticizers and other organic compounds. In this paper, we focused on the elaboration of a new generation of health- and environmental-friendly polyurethanes, elaborated from two different types of biomass. This work is an opportunity to tune biobased macromolecular architectures of nonisocyanate polyurethanes with rigid building blocks based on FDCA. Corresponding polyhydroxyurethanes present some enhanced properties compared with equivalent NIPUs based on vegetable oils, such as high thermal stability and glass transition temperature.

Acknowledgements

The authors thank the Alsace region, the urban community of Strasbourg, SOPRÉMA and PSA Peugeot Citroën for their financial supports. Huntsman is also acknowledged for having kindly provided glycerol carbonate.

2.5. Supporting information

2.5.1. Chemical characterization of FDCA BisCC

The following Figures 4-S5 and 4-S6 confirm the NMR structure of FDCA BisCC, and Figure 4-S7 shows its FTIR characteristic peaks.

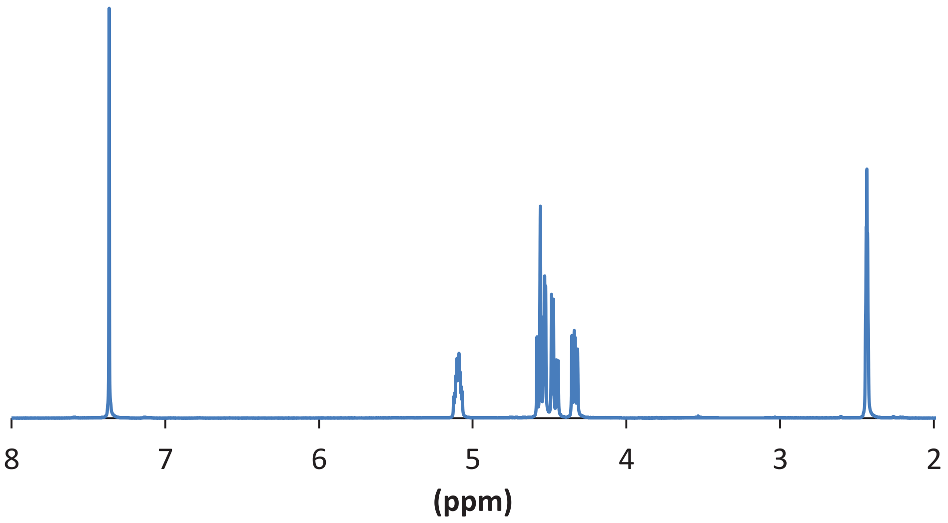


Figure 4-S5. ^{1}H-NMR of FDCA BisCC (**3**).

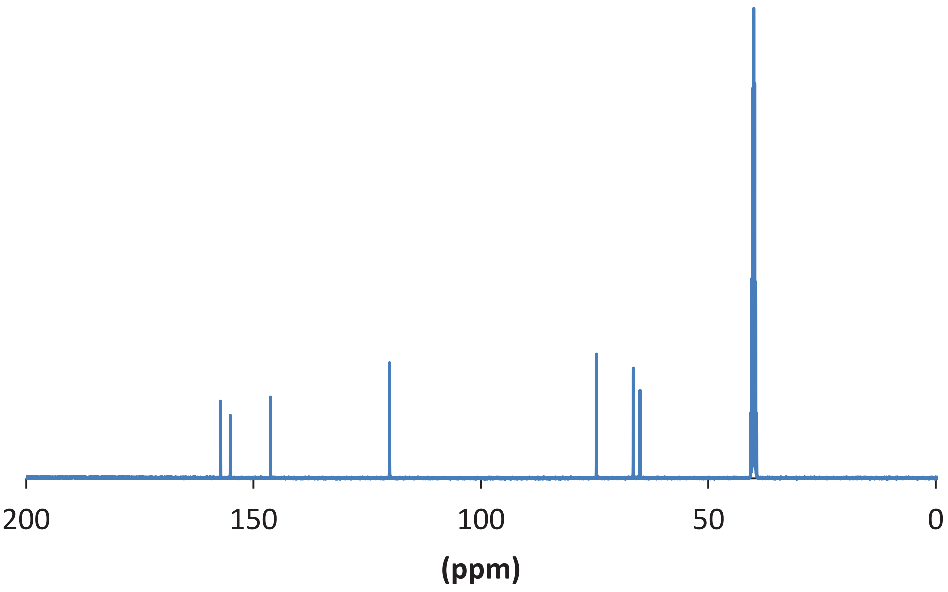


Figure 4-S6. ^{13}C-NMR of FDCA BisCC (**3**).

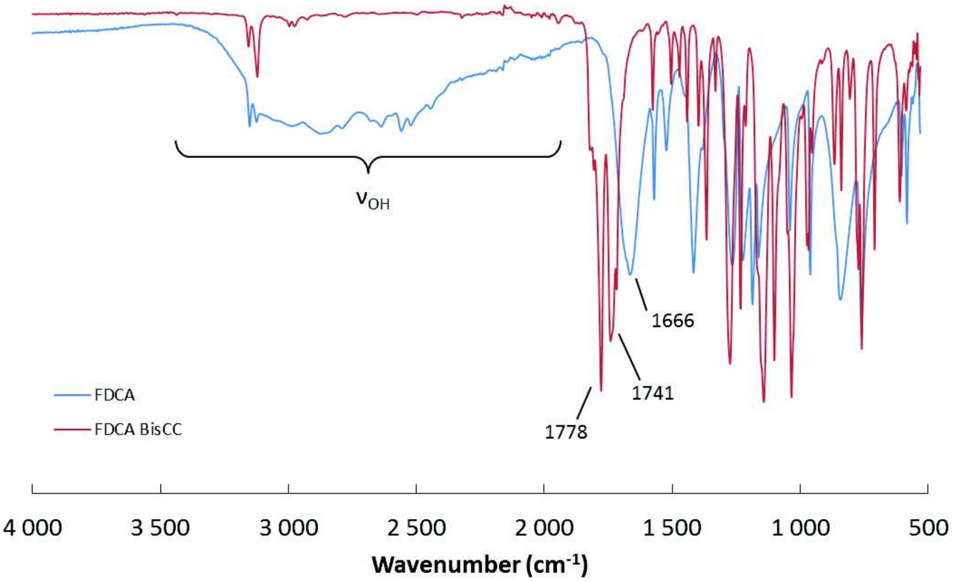


Figure 4-S7. FDCA (**1**) and FDCA BisCC (**3**) FTIR spectra.

2.5.2. Thermal characterization of FDCA NIPU

Figure 4-S8 displays the thermal degradation of NIPU based on FDCA building block. The TGA curve shows a DMF weight loss of about 20% in the temperature range of 75 to 200°C. At 700°C, the NIPU residual weight under nitrogen is about 5%. Figure 4-S9 reports a zoom in the glass transition temperature region.

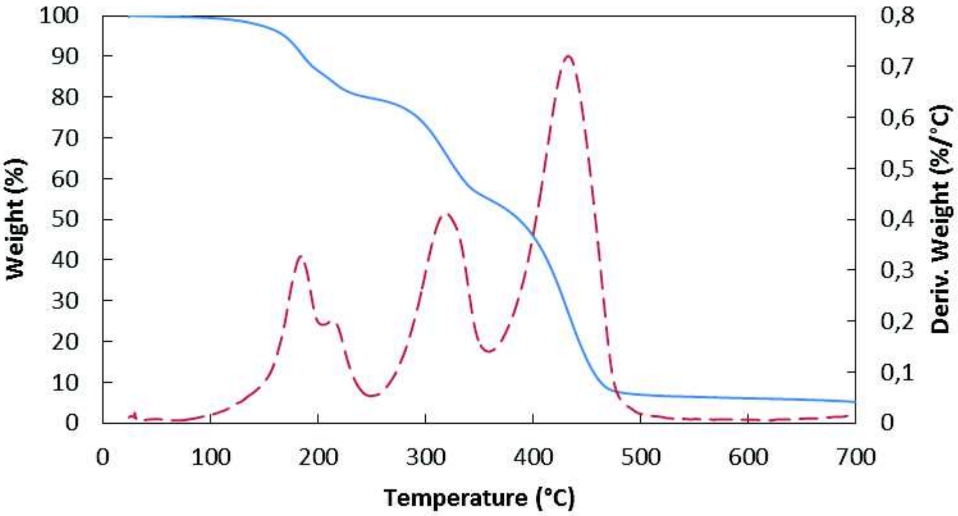


Figure 4-S8. TGA (solid line) and DTG (dotted line) curves of NIPU based on FDCA under nitrogen.

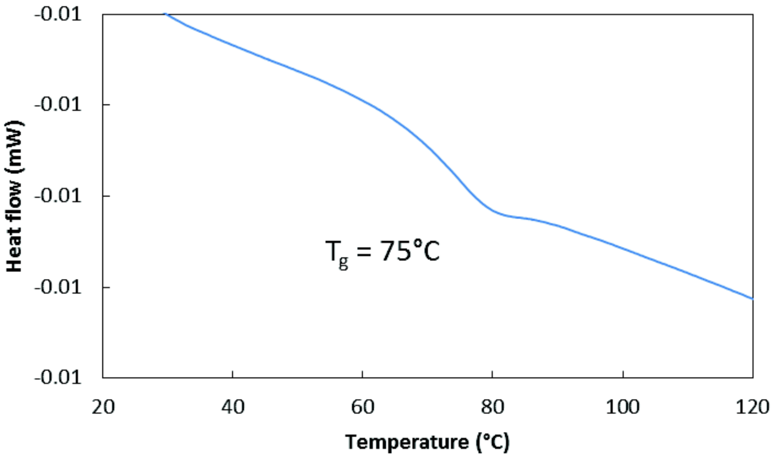


Figure 4-S9. DSC curve of FDCA NIPU.

3. Conclusions et perspectives

Au terme de ce chapitre, différents TNIPU possédant des propriétés intéressantes ont été synthétisés par réaction d'aminolyse. Tout comme pour les PU conventionnels, cette étude a montré le fort impact des structures et du ratio molaire entre les monomères sur les propriétés des TNIPU obtenus. En particulier, les synthons aromatiques apportent de la rigidité aux matériaux et s'avèrent essentiels pour des applications nécessitant de la résistance thermique et de bonnes propriétés mécaniques. Cependant, les molécules aliphatiques, plus couramment rencontrées dans la littérature, restent essentielles dans la formulation des TNIPU afin de maintenir une certaine flexibilité des matériaux, notamment recherchée dans des applications telles que les joints ou les membranes d'étanchéité. En plus du choix des synthons appropriés, c'est en ajustant ce ratio entre les différents monomères qu'il est possible d'atteindre les propriétés recherchées pour une grande variété d'application.

En revanche, il ne faut pas négliger la présence des fonctions hydroxyles inhérente à la synthèse de TNIPU *via* la réaction d'aminolyse. Les TNIPU ne sont pas strictement des TPU mais des polyhydroxyuréthanes thermoplastiques. En particulier, la présence des fonctions hydroxyles peut gêner l'organisation du matériau et la cristallisation des segments rigides, empêchant alors une bonne séparation de phase nécessaire à l'obtention de matériaux thermoplastiques élastomères. Par ailleurs, tout comme pour les NIPU réticulés étudiés dans les précédents chapitres, la faible réactivité des cyclocarbonates envers les diamines reste un frein au développement de TNIPU élastomères en empêchant l'utilisation de diamines souples de hautes masses molaires et en entraînant la formation de chaînes de longueurs relativement modérées pouvant ainsi également entraver la microségrégation de phase.

Cette étude a également montré qu'il était possible d'intégrer des monomères issus de ressources renouvelables au sein des matériaux. Les TNIPU synthétisés possèdent un contenu biosourcé pouvant aller jusqu'à 76%. De plus, cette valeur peut être accrue en remplaçant par exemple l'acide téréphtalique pétrosourcé par son équivalent biosourcé ou encore par le FDCA. En effet, le FDCA présente encore une disponibilité limitée mais a d'ores et déjà été identifié, notamment par le département américain de l'énergie, comme une molécule plateforme biosourcée prometteuse et destinée à un brillant avenir dans le domaine des matériaux polymères. En effet, les alternatives biosourcées des molécules aromatiques sont peu nombreuses, très recherchées et en constant développement ces dernières années. La dernière partie de ce chapitre consacrée au FDCA a notamment permis de montrer son potentiel dans la synthèse de TNIPU.

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Conclusion générale & perspectives

Ce travail de thèse multidisciplinaire, associant la synthèse, la physico-chimie et la caractérisation de matériaux polymères avait pour objectif l'élaboration et l'étude de nouveaux matériaux polyuréthanes synthétisés sans isocyanate et intégrant des synthons biosourcés, afin de développer des matériaux innovants et performants pour l'industrie de l'automobile et du bâtiment, notamment à travers l'étanchéité de bâtiments (exemple : toit-terrasses). De nouvelles voies permettant l'élaboration de PU plus respectueux de la santé et de l'environnement ont ainsi été étudiées. La démarche scientifique de ce travail doctoral s'est donc axée autour du développement de nouvelles architectures (macro)moléculaires pour l'élaboration de polymères fonctionnels.

L'étude bibliographique présentée dans le **Chapitre 1** dresse tout d'abord un état de l'art de la synthèse actuelle des PU, ainsi que des différentes morphologies et propriétés obtenues. Cette première partie a permis de mettre en exergue les divers atouts des PU (réactivité de la réaction, multiplicité des structures et des applications…). De plus, les limites de ces polymères, avec notamment la toxicité des isocyanates, ont été abordées. En effet, l'impact négatif des isocyanates sur la santé conduit aujourd'hui industriels et laboratoires académiques à développer de nouvelles approches, telles que la synthèse de PU sans isocyanate (NIPU). Un intérêt particulier a été porté sur les molécules biosourcées afin de produire des PU avec un impact environnemental plus favorable. Cet état de l'art a permis l'identification et la sélection de synthons et d'une voie de synthèse de NIPU, l'aminolyse, qui ont ensuite été développés et approfondis lors de ce travail de recherche.

Les **Chapitres 2 à 4** montrent les différentes stratégies mises en place dans la synthèse de NIPU biosourcés fonctionnels. Plusieurs architectures de NIPU ont ainsi été élaborées et étudiés. Pour cela, divers monomères ont été synthétisés. Différents paramètres réactionnels ont été expérimentés afin de permettre le contrôle des relations « structure-propriétés ». Ces études ont conduit à l'élaboration de différents matériaux NIPU originaux et biosourcés: thermodurcissables ou thermoplastiques (Figure C-1). Les divers polymères obtenus ont été caractérisés par des analyses chimiques, thermiques, rhéologiques et mécaniques.

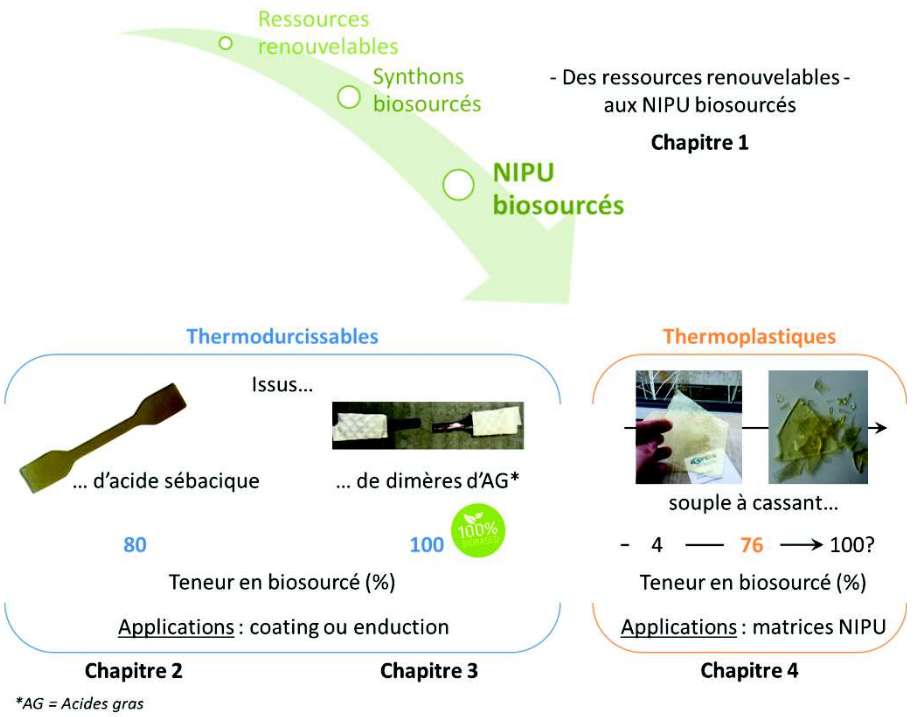

Figure C-1. Schéma récapitulatif des différents matériaux NIPU obtenus.

Le **Chapitre 2** porte sur la synthèse de NIPU et l'étude de divers paramètres réactionnels afin de comprendre la chimie mise en place et d'obtenir des matériaux avec des propriétés intéressantes tournés vers l'application. Ainsi, une voie sans solvant, sans catalyseur, et intégrant des synthons biosourcés a pu être identifiée et validée. Cependant, après optimisation, les masses molaires des NIPU obtenus restent relativement faibles par rapport aux PU conventionnels. La possibilité de réticulation développée dans ce chapitre a permis d'apporter une solution en vue d'éventuelles applications industrielles, notamment pour le coating ou l'enduction. En outre, les NIPU de faibles masses molaires pourraient être envisagés comme plastifiants dans des systèmes d'étanchéité liquide par exemple.

Le **Chapitre 3** présente la synthèse d'un matériau NIPU entièrement biosourcé, ce qui d'après l'analyse de la bibliographie n'avait encore jamais été rapporté. Dans cette étude, les dimères d'acides gras qui ont fait l'objet de nombreuses études antérieures au sein de l'équipe, sont plus particulièrement développés comme source de deux synthons différents. En plus de leur origine renouvelable et de leurs architectures très particulières, ces molécules sont intéressantes car disponibles commercialement. Ce chapitre a également permis de souligner l'effet des architectures chimiques des monomères sur les propriétés des matériaux finaux. En particulier, il a été démontré que la stabilité thermique ainsi que les très basses T_g des NIPU synthétisés sont dus à la présence des structures dimériques. Les performances des matériaux

NIPU thermodurcissables obtenus dans les **Chapitres 2 et 3** ont également pu être comparées à celles d'un PU conventionnel de structure comparable. Bien que les NIPU synthétisés présentent des performances techniques intéressantes ainsi que de fortes teneurs en biosourcé, leurs propriétés restent néanmoins inférieures à celles des PU conventionnels.

Le développement de NIPU thermoplastiques (TNIPU) à caractère élastomère a été abordé dans le **Chapitre 4**. L'intérêt de ces matériaux est associé à leur thermofusabilité permettant une mise en œuvre facile. Afin de pouvoir obtenir ces architectures macromoléculaires, un nouveau synthon plus rigide, issu de l'acide téréphtalique, a été synthétisé. L'étude a pu montrer le fort impact des structures et du ratio molaire entre les monomères correspondants sur les propriétés des TNIPU obtenus. La compréhension de l'organisation macromoléculaire a mis en évidence l'effet des monomères rigides et réactifs sur la structuration des TNIPU, caractérisé notamment par des températures de transition vitreuse ainsi que des propriétés mécaniques différentes. Cependant, aucun des matériaux synthétisés n'a pu totalement remplir les attentes des cahiers des charges des partenaires industriels de l'étude. En effet, aucune séparation de phase, propre aux thermoplastiques élastomères (TPE), n'a pu être clairement observée. Ceci pourrait être lié aux masses relativement faibles des polymères obtenus ainsi qu'à l'existence de fonctions hydroxyles dans les NIPU, non présentes dans leurs analogues conventionnels. Ce travail a néanmoins permis (i) de développer des matériaux innovants avec de nouvelles architectures macromoléculaires, et (ii) d'établir des relations spécifiques « structures-propriétés » conférant au matériau final des propriétés intéressantes, associées à une teneur en biosourcé importante (pouvant aller jusqu'à 76%). Cette teneur pouvant de plus être accrue, comme l'a montré la dernière partie de ce chapitre avec la synthèse d'un cyclocarbonate aromatique et biosourcé, pouvant également être intégré dans l'architecture de NIPU.

Cette thèse rédigée sous format d'articles a permis de soumettre 4 publications scientifiques et un article de synthèse bibliographique (review) dans des journaux à comité de lecture et ainsi de valoriser ce travail doctoral. Parmi ces derniers, une publication a d'ores et déjà été acceptée et publiée dans la revue *RSC Adv.*, 2014, 4, 54018-54025. Les 4 autres articles sont actuellement en phase de soumission dans différents journaux scientifiques de référence.

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Ce travail effectué dans l'Institut au sein de l'équipe BioTeam était le premier localement réalisé sur cette thématique de PU sans isocyanate. Il a permis d'élargir les compétences de l'équipe dans ce domaine particulier de recherche, très actif dans le monde actuellement. En effet, cette thématique de recherche est aujourd'hui considérée comme étant un sujet majeur d'actualité (« hot topic »), dans le domaine des polymères. L'approche scientifique novatrice développée par rapport aux travaux de recherches précédents, associée à la mise au point de nouvelles voies de synthèses réactionnelles a participé au développement d'une nouvelle expertise au sein de l'équipe.

Les résultats très encourageants obtenus lors de ces études n'ont tout de même pas permis à ce jour d'atteindre totalement les objectifs de formulation d'une membrane d'étanchéité ou encore de pièces pour l'automobile, décrits dans des cahiers de charge industriels. Cependant, ce travail doctoral a permis de synthétiser et de caractériser des PU innovants, plus respectueux de l'environnement et de la santé. Ce travail a aussi permis de mettre en exergue très clairement les différentes limites de cette nouvelle classe de PU et des voies de synthèse correspondantes abordées.

En effet, les PU conventionnels sont synthétisés très rapidement grâce à des isocyanates extrêmement réactifs, mais toxiques. En revanche, les NIPU présentent une faible toxicité mais leurs cinétiques de synthèse sont plus lentes, avec des masses molaires correspondantes limitées dues aux plus faibles réactivités des composés chimiques mis en présence. Il leur est donc plus difficile de répondre à l'ensemble des attentes industrielles. Malgré un potentiel de recherche au niveau mondial énorme, aucune réponse n'a pu encore être apportée à ce jour.

Outre la recherche d'une quatrième voie de synthèse performante qui ne serait pas l'aminolyse, un travail important reste à mener, notamment concernant la valorisation des fonctions hydroxyles présentes dans les structures NIPU. En effet, ces groupes réactifs peuvent être la base de réactions de post-réticulation, renforçant alors les performances des NIPU obtenus. On peut par exemple penser à de la chimie supramoléculaire pour donner aux matériaux des propriétés innovantes d'autoréparation et/ou d'auto-adhésion, très recherchées dans les domaines de l'automobile et de l'étanchéité tout particulièrement.

De manière plus générale, pour développer des produits entièrement fonctionnels dans l'industrie de l'automobile ou du bâtiment, la formulation complète de ces matériaux devra être réalisée afin de répondre entièrement au cahier des charges en terme de vieillissement, de tenue aux rayons UV ou encore de prise en eau. Dans le cas des membranes d'étanchéité par exemple, l'introduction de charges minérales ou de fibres pourrait apporter des fonctionnalités complémentaires aux matrices NIPU (processabilité, résistance, …). Pour ce faire, un travail sur l'affinité fibres/matrice ou charges/matrice serait notamment nécessaire afin d'atteindre les propriétés mécaniques et physico-chimiques souhaitées pour l'application visée. En complément de ces renforts mécaniques, d'autres additifs tels que des antioxydants et des anti-UV devront être incorporés afin d'assurer la garantie d'utilisation décennale pour des applications de très longue durée.

De plus, certains NIPU élaborés dans le cadre de ce travail doctoral permettent d'envisager une utilisation dans d'autres domaines d'applications, notamment les adhésifs et mastics. Il serait alors intéressant de poursuivre le développement de ces matériaux *via* des formulations adéquates et en mettant également en place un approche de scale-up pour notamment la synthèse des synthons de base.

Enfin, une étude d'Analyse de Cycle de Vie (ACV) des différents produits sera indispensable pour valider l'intérêt de ces matériaux d'un point de vue environnemental. Une estimation partielle de l'ACV devra être établie à chaque étape du projet d'industrialisation et pourra servir de support lorsque des choix techniques devront être faits.

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Synthèse et caractérisation de nouveaux matériaux polyuréthanes respectueux de l'environnement et de la santé

Résumé

De nouveaux polyuréthanes ont été synthétisés sans isocyanate et en intégrant des synthons biosourcés afin de développer des matériaux innovants et performants pour des applications dans le domaine de l'industrie automobile et du bâtiment. À l'issue d'un état de l'art, divers synthons et différentes stratégies ont été retenus afin d'obtenir de nouvelles architectures (macro)moléculaires et conférer aux matériaux finaux les propriétés physico-chimiques recherchées. Dans un premier temps, la réaction entre un biscyclocarbonate issu d'une molécule modèle, l'acide sébacique, et des diamines dimériques ainsi que plusieurs paramètres réactionnels ont été étudiés. Cette première étude a permis de montrer l'intérêt du ratio entre les monomères ainsi que l'influence de la fonctionnalité des diamines sur les propriétés chimiques, thermiques, rhéologiques et mécaniques des matériaux polyuréthanes sans isocyanate. Cette approche a permis dans un second temps de synthétiser des matériaux pouvant être entièrement biosourcés et de comparer leurs propriétés à celles des polyuréthanes conventionnels. Les performances de certains des matériaux thermodurcissables obtenus ont confirmé l'intérêt de cette stratégie pour les applications visées. Enfin, une troisième approche a été consacrée à la synthèse de polyuréthanes sans isocyanate thermoplastiques via la synthèse de prépolymères. Les différentes études ont montré l'importance de la structure des divers synthons sur l'organisation macromoléculaire, et ainsi sur les propriétés des matériaux finaux.

Mots-clés : cyclocarbonate, diamine dimérique, polyuréthane sans isocyanate, relations structure-propriétés, ressources renouvelables.

Abstract

Novative and performant polyurethane materials without isocyanate were synthesized using biobased molecules for applications in automotive and building industries. After a state of the art, different building blocks were selected and various strategies were established to develop new (macro)molecular architectures. First, reactions between a biscyclocarbonate from a model structure and dimer diamines were studied as well as the impact of various reaction parameters. Secondly, this approach was adapted to fully biobased materials. The properties of these nonisocyanate polyurethanes were compared with those of conventional ones. The influence of the monomer structures on the final materials was also demonstrated. The performance of some thermoset materials have confirmed the importance of the chosen strategies for the desired applications. Finally, a third approach was dedicated to the synthesis of thermoplastic nonisocyanate polyurethanes *via* a prepolymer synthesis. The various studies have revealed the specific impact of the building block structure on the macromolecular organization, and thus on the properties of the final materials.

Keywords: cyclic carbonate, dimer diamine, nonisocyanate polyurethane, renewable resources, structure-properties relationship.