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Transcarbamoylation in polyurethanes: underestimated exchange reactions?

Camille Bakkali-Hassani,^{a,*} Dimitri Berne^a, Vincent Ladmira^a, Sylvain Caillol^{a,*}

^a ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Abstract

While transesterification has been largely explored by chemists, only a few studies comparatively dealt with its “sluggish cousin”, transcarbamoylation. Originally suggested seventy years ago to explain the stress decay observed at high temperature in polyurethane chemical networks, transcarbamoylation -also called transurethanization or urethane exchange- is still underexploited in both organic and polymer chemistry. This is mainly related to the use of toxic reactants such as isocyanates and tin-based catalysts involved during the preparation of molecular carbamates or polyurethanes (PUs) as well as harsh conditions required to observe such exchanges in molecular transformations. Many studies have focused their interest on alternatives to the use of isocyanates, underestimating the potential of transcarbamoylation to produce, recycle or reprocess PUs (wastes). This perspective review presents the latest developments and plausible future directions to prepare sustainable PU-based materials using transcarbamoylation with a focus on covalent dynamic networks.

Keywords: transcarbamoylation; transurethanization; polyurethane; polyhydroxyurethane; covalent adaptable networks; vitrimers

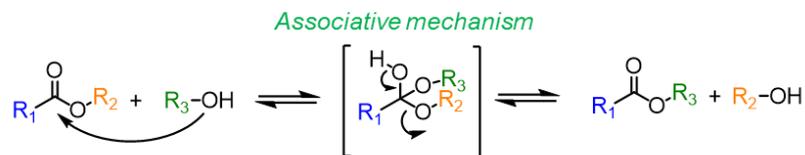
Introduction

Since their discovery back in the 1930s by Prof. Otto Bayer, polyurethanes (PUs) have been used in a wide range of applications and represent today the sixth class of commodity polymers in terms of global production.¹ PUs, initially employed as a replacement for natural rubber during the Second World War, are found nowadays in daily-life materials from coatings and adhesives to shoe soles, mattresses or insulation foam.^{2,3} PU elastomers possess high hardness for a given modulus, high abrasion and chemical resistance, excellent mechanical and elastic properties, blood and tissue compatibility, and also some other specific properties.⁴ The broad variety (aromatic, aliphatic, multifunctional) of commercially available monomer feedstock as well as the wide range of physical and chemical properties attainable make them particularly versatile materials. PUs are composed of carbamate (or urethane) linkages and are industrially prepared *via* polyaddition between a di-(or poly)isocyanate and a di-(or poly)ol. Over the past two decades, many researchers focused their interests on the replacement of isocyanate in PU formulations⁵⁻⁸ whereas recycling, reprocessing or depolymerization of existing PUs have been cast aside. Interestingly, one unique reaction is able to perform all the above mentioned process: the transcarbamoylation (TC) or urethane exchange. The first step towards polyurethane with inherent dynamic covalent exchanges was actually made more than seventy years ago by Offenbach *et al.*⁹ They found out that polyurethane elastomers obtained from polyester or polyether polyols, diisocyanate and a crosslinker (without catalyst) were able to relax stress at temperature above 90°C. They suggested that urethane exchange –among others- could be one plausible mechanism involved in the stress decay.

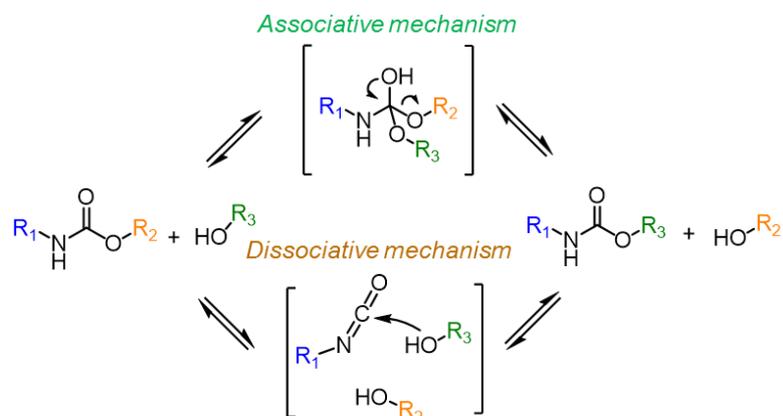
In molecular chemistry, the interchange reaction between carbamate/urethane functions and hydroxyls are named TC/transurethanization. Urethane exchange refers to the specific case where no free hydroxyl groups are involved. Both reaction are often described as “sluggish”.¹⁰ Despite strong similarities with transesterification, significant differences in reactivity emanate from the presence of a nitrogen atom borne by the carbamate moiety (Scheme 1). On the one hand, transesterification is commonly used in either academic or

industrial contexts.^{11,12} It is an equilibrated reaction that can be shifted by the distillation of the volatile formed alcohol and thus allows the synthesis of esters under very mild conditions. In addition, transesterification can be promoted using a wide range of catalysts including organic acids and bases, organometallic Lewis acid and even biocatalysts such as lipases.¹¹⁻¹³ On the other hand, and despite being catalyzed by the same type of molecules, including acids or bases but preferentially metallic or organometallic derivatives, the reduced nucleophilic character of the carbonyl of carbamate makes TC more difficult to perform than transesterification. It requires generally higher temperature (typically above 120°C) even in a catalyzed process and has been consequently less studied despite strong potential in PUs chemistry. The exchange mechanism also differs between these two reactions, transesterification is known to occur by a classical displacement mechanism *via* a tetrahedral intermediate (associative, Figure 1a) regardless of the catalyst (acidic, basic, nucleophilic or electrophilic activation) or initial stoichiometry. In contrast, the transcarbamoylation mechanism is more complex, condition-dependent and has not been rationalized yet. The reaction mechanism presented in Figure 1b shows that both dissociative and associative pathways are possible for TC in the presence of free hydroxyl groups.^{10,14} Similarly to ester interchange, associative TC in the presence of free hydroxyl proceeds through a classical displacement mechanism. Alternatively, dissociative TC in the presence of free hydroxyl can also occur *via* an elimination-addition mechanism (Figure 1b). This mechanism involves the retro-formation of isocyanate and alcohol during the first reaction step which is followed by the exchange with another alcohol. Finally, urethane/urethane exchanges can occur exclusively *via* an elimination-addition mechanism (dissociative, Figure 1c).

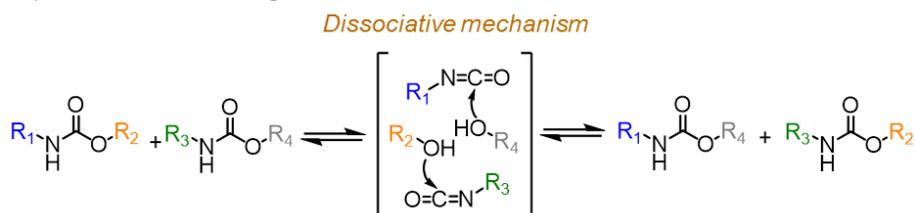
a) Transesterification



b) Transcarbamoylation



c) Urethane exchange



Scheme 1. Reaction mechanism of a) transesterification *via* an associative transition state (addition-elimination mechanism) and b) transcarbamoylation *via* both associative transition state (addition-elimination mechanism) and dissociative (elimination addition).

The difference between transesterification and TC is also evidenced in their applications in material science. In the 2010s, a unique class of materials using dynamic covalent exchange reactions within a chemically crosslinked networks have emerged.¹⁵ The so-called vitrimers are materials which combine aspects of both thermosets and thermoplastic polymers (e.g. insoluble polymers flowing like glass at high temperature with an Arrhenius dependency). These networks were originally designed with Zn(II) catalyst able to catalyze both addition (polymerization/gelation) and exchange reactions (transesterification).¹⁵ Later on, various catalysts were used to promote transesterification in vitrimers.^{16,17} These chemically crosslinked yet thermally reprocessable networks were capable of stress relaxation, self-healing, shape memory, and recyclability. Since this pioneering work, numerous exchange chemistries have been applied to prepare covalent adaptable networks.^{18–22} In PU-based

vitrimer chemistry or more generally in covalent adaptable network PU chemistry, the focus was put on incorporating other dynamic bonds into PU networks instead of exploiting the inherent dynamics of the urethane linkages.^{23,24} Transcarbamylation has nonetheless been reported in a few studies as the main exchange reaction for polyurethane or polyhydroxyurethane (PHU) networks with dynamic links. Despite its large potential to produce reprocessable and potentially recyclable P(H)U-based covalent adaptable networks (CANs), a deep comprehension of the mechanism involved and of the plausible perspectives for PU are still lacking.

To tackle these issues, the present perspective review intends to highlight the potential of TC as a multi-task tool, from the preparation of isocyanate-free PUs to the synthesis of covalent adaptable networks. After an overview of catalysts employed, potential candidates, and their related mechanism, applications of TC in material science are discussed towards more sustainable and inherently recyclable poly(hydroxy)urethane-based materials (Figure 1). A critical analysis of literature studies is provided to determine the grey areas and potential improvements to fully understand such exchange reaction from molecular level to material dynamic properties.

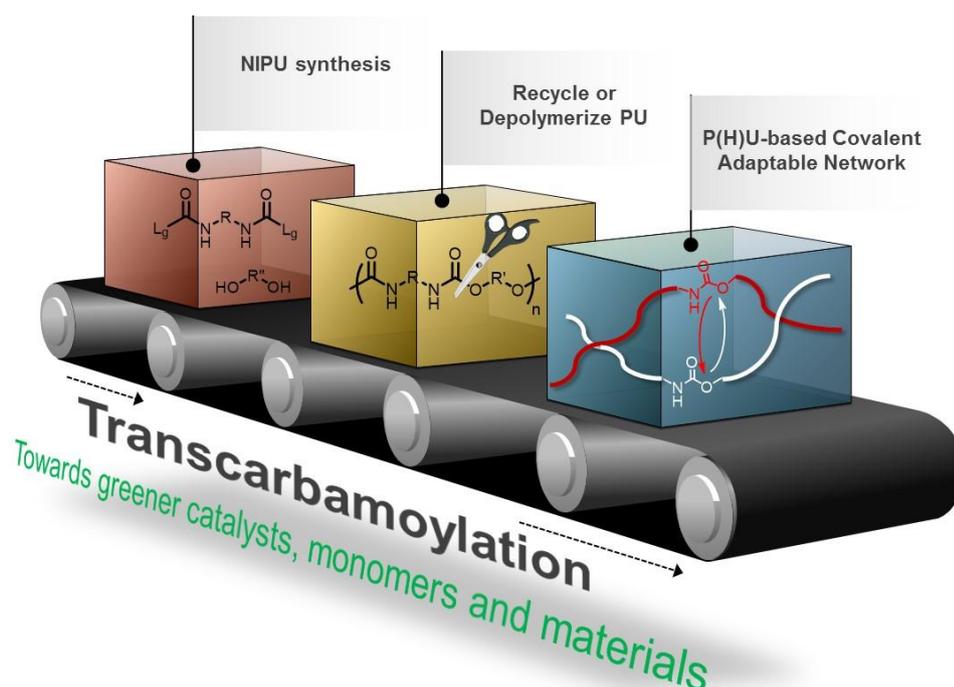
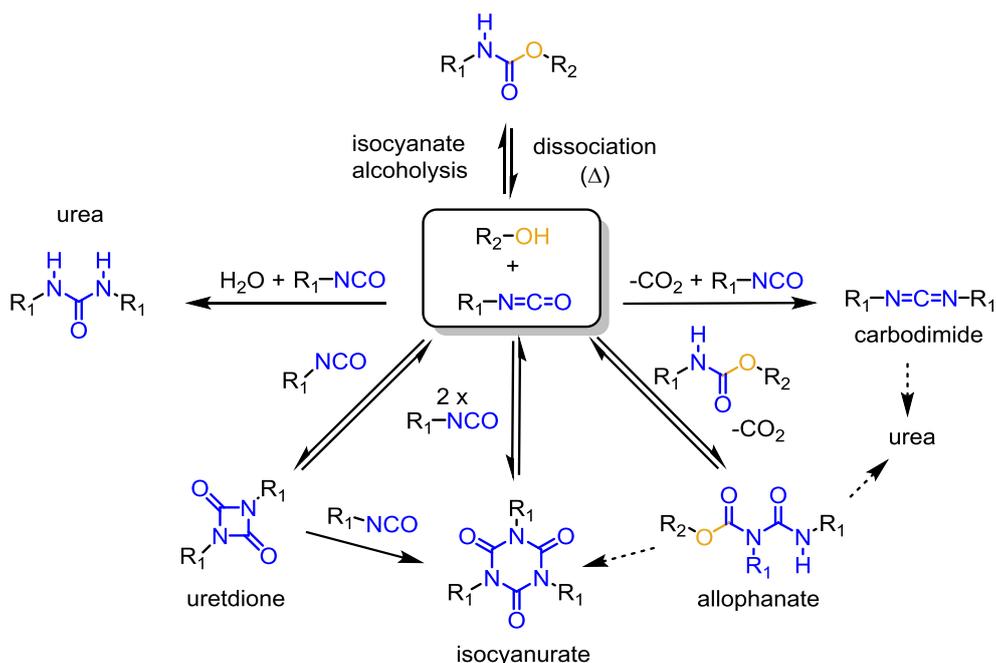


Figure 1. Overview of transcarbamoylation applications in PU chemistry

1- Generalities, Catalysts employed and related mechanisms

In this section, the different catalytic systems studied as well as the proposed mechanisms for transcarbamoylation (TC) in organic and polymer chemistry are described. As catalytic activities were measured on a large variety of substrates (aryl or alkyl urethanes, polymer networks, polymer chains or small molecules) in different conditions (temperature, solid state, bulk or solution), plausible strategies of carbamate activation and future potential catalyst candidates rather than catalyst comparisons are discussed here. An overview of the catalysts used for TC is displayed in Figure 2. Organometallic Lewis acid and bases, Brønsted acid, and organic bases have been used as catalyst for TC reactions involving different mechanisms and reaction pathways. As a general comment, efficient catalyst for transcarbamoylation often derived from catalyst used in (poly)urethane synthesis, *i.e.* reaction between an isocyanate and an alcohol. Non-catalyzed TC is commonly admitted to occur through a dissociative mechanism (elimination-addition) *via* the retro-formation of isocyanate and alcohol chemical groups. As mentioned in the introduction, non-catalyzed transcarbamoylation reactions occur at high temperature (typically above 120°C) and are accompanied by side reactions leading to the irreversible formation of isocyanurate (by trimerization of isocyanate groups) or allophanate (nucleophilic attack of the carbamate NH moiety on isocyanate group) - among others (Scheme 2).^{25,26}



Scheme 2. Expected side reactions at high temperature in isocyanate chemistry

Thermally-induced carbamate dissociation (mechanism presented in Scheme 3a) depends on different factors such as the nature of the substituent (aliphatic, aromatic, electron withdrawing groups) or solvent polarity. Reactivity follows the order *alkyl*-NH-COO-*alkyl* < *aryl*-NH-COO-*alkyl* < *alkyl*-NH-COO-*aryl* < *aryl*-NH-COO-*aryl* with dissociation temperature of around 250°C, 200°C, 180°C and 120°C respectively,²⁷ which means that component stability decreases with the conjugation of the urethane bond. Addition of electron withdrawing groups (halides, nitro, etc.) on the aryl substituent as well as the use of polar solvent were also shown to reduce the dissociation temperature. As the urethane bond is more and more depleted of its electrons, its thermal stability decreases. Efficient non-catalyzed TC using *N*-sulfonyl carbamate derivatives²⁸ or oxime-based derivatives²⁹ have been reported under mild conditions. Despite those original examples, TC performed in a catalyzed fashion, allowed to decrease the dissociation temperature, and favored the formation of the desired products. Nevertheless the tunability of the dissociation temperature by simple judicious substituent selection is an interesting feature for the preparation of materials with controlled exchange properties.³⁰

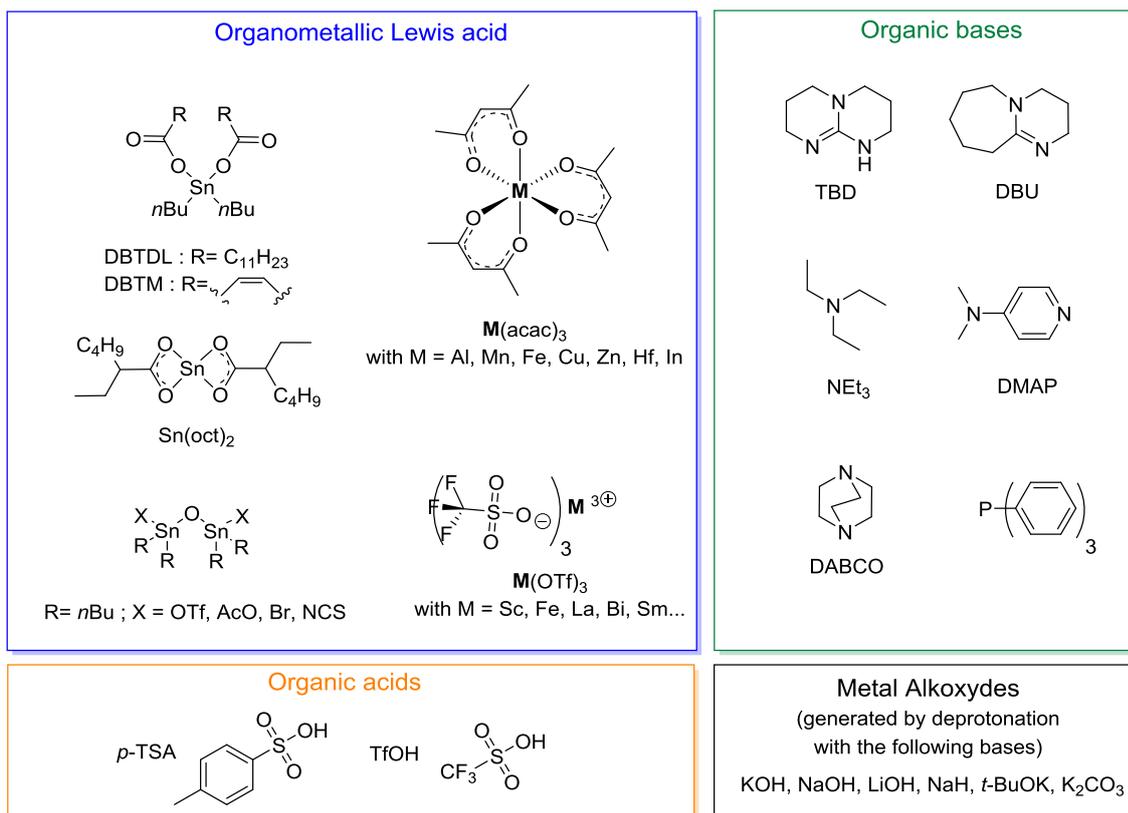


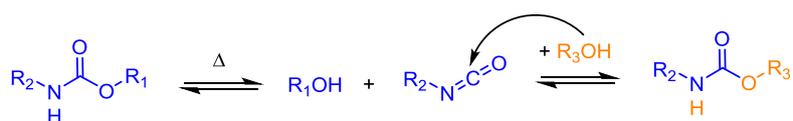
Figure 2. Range of catalysts employed for transcarbamoylation reactions

Among TC catalysts, organometallic Lewis acid and especially tin(IV)-based catalyst have been widely used in both PU synthesis and as TC agent.^{31,32} Di-alkyl di-carboxylate tin(IV) catalysts are the preferred option and have been largely employed for both molecular and macromolecular transformations. In PU chemistry, they are known to preferentially and rapidly promote isocyanate-hydroxyl reactions. Among tin(IV)-based catalysts, DBTDL (di-*n*-butyl tin(IV) di-laureate) is often considered as the standard due to its high activity even at very low concentration (down to 0.001 mol%) and stability in a wide range of temperatures (65-200°C). In comparison to the well-known mechanism for isocyanate alcoholysis (Scheme 2),³³⁻³⁵ the TC mechanism is still unclear and has been little studied to date. The proposed dissociative and associative mechanism of Lewis acid-catalyzed TC is depicted in Scheme 3b.³⁶ The Lewis acidity effect on organotin activity has been investigated by Jousaume *et al.* through the preparation of distannoxane derivatives with different electron withdrawing groups such as triflate (OTf), acetyl (AcO), bromide (Br) and thioisocyanide (NCS).¹⁰ In

organostannate-catalyzed transesterification reactions, electronegative groups are known to be displaced during the transesterification reaction and exchange occurs *via* a coordination-insertion mechanism.^{11,37} Combining molecular model reactions (ligand exchange) and ¹¹⁹Sn NMR kinetic analysis, the authors demonstrated that tin(IV)-based Lewis acids are not subjected (or only partially) to ligand displacement regardless of the ligand electronegativity. They concluded that organotin derivatives act more as Lewis acid than as alkoxide carriers (see mechanism Scheme 3b).¹⁰ Recent works have shown that TC can occur under mild conditions (at typically 70°C or above) with different alkoxides alone generated by bases and hydrides such as KOH, NaOH, LiOH, *t*-BuOK and NaH.³⁸ Semetey and co-workers investigated the depolymerization of PU wastes in MeOH using an excess of alkoxide (2 equivalents per isocyanate functions). Despite slight differences between the bases studied, dimethyl carbamate molecules were obtained in relatively high yield (45-80%) after 20h at 65°C.^{38,39}

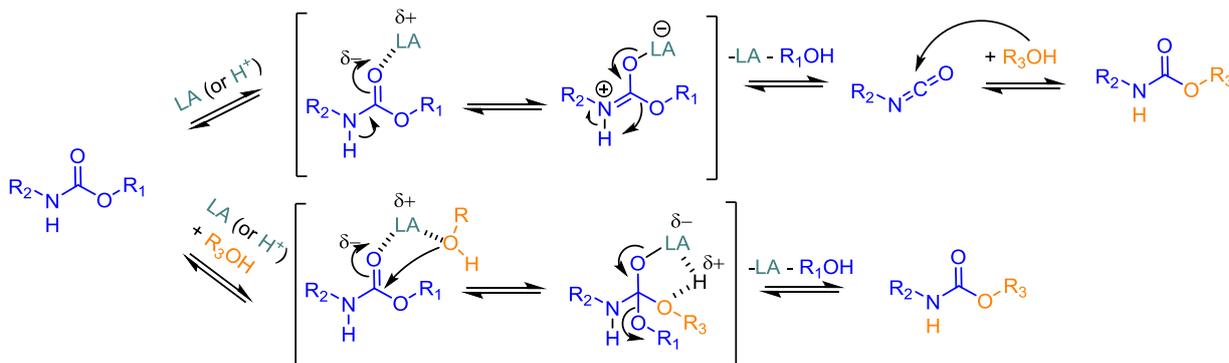
In order to replace the toxic and poorly degradable di-alkyl tin-based catalysts, (Sn-alkyl bonds is stable under hydrolytic conditions), acetylacetonate salts such as Fe(III)(acac)₃, Cu(II)(acac)₂, Cr(II)(acac)₂, Zn(II)(acac)₂, transition metal or rare earth triflate salts derivatives (M(X)(OTf)_x) have been also investigated.^{14,40,41} Predominantly used as a catalyst for urethane bonds formation, a few studies have demonstrated the potential of these catalyst to promote TC, mostly for the synthesis of PU-based covalent adaptable networks.⁴¹ Among other candidates, bismuth (III) and iron (III) derivatives stand out from the crowd. Iron is abundant, non-toxic and possesses an excellent activity which can compete with DBTDL even at really low concentration (as low as 0.001 mol% for urethane alcoholysis⁴²). Iron acetyl acetonate also demonstrated its potential to prepare vitrimer-like materials with relaxation properties once again rivaling those obtained with organotin catalysts. A similar behavior characterized bismuth derivatives considered as non-toxic and active in both organic synthesis and polymer matrices.⁴¹ Moreover, they have been reported to be also more selective than organotin catalysts towards associative TC as no volatile isocyanates were detected in model reactions (Scheme 3b).¹⁴

a) Non-catalyzed transcarbamoylation (thermal dissociation)

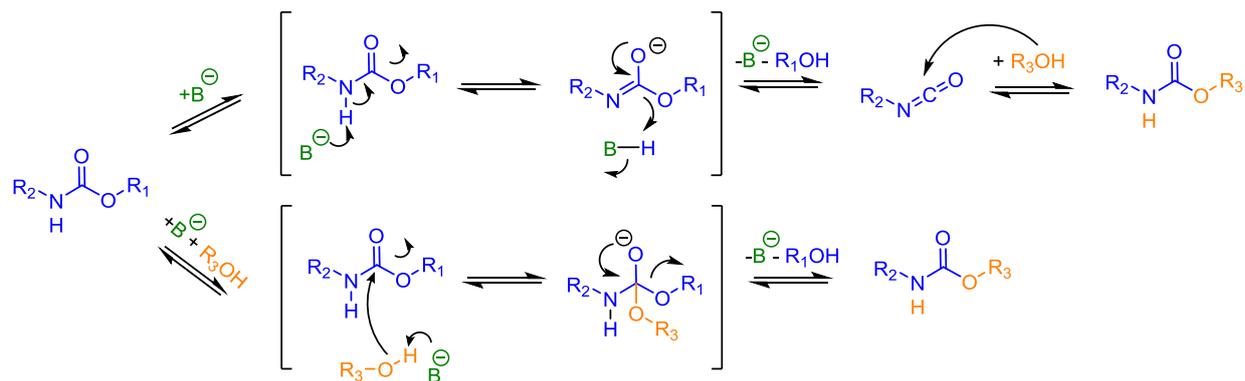


Reactivity order: ($R_1=R_2$ =aryl) > (R_1 = aryl, R_2 =alkyl) > (R_1 = alkyl, R_2 =aryl) > ($R_1=R_2$ =alkyl)

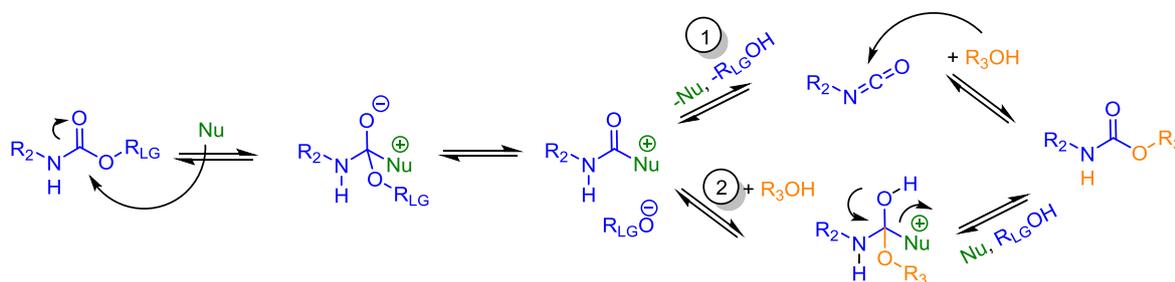
b) Acid-catalyzed transcarbamoylation (electrophilic or acidic activation)



c) Base-catalyzed transcarbamoylation (basic activation)



d) Nucleophile-catalyzed transcarbamoylation (nucleophilic activation)



Scheme 3. Proposed reaction mechanism for a) non-catalyzed (thermal dissociation), b) Lewis Acid catalyzed, c) Base-catalyzed and d) Nucleophile-catalyzed transcarbamoylation. Apart from thermal dissociation both associative and dissociative mechanism can be involved in transition states and have been displayed above. Urethane exchange follows a dissociation mechanism to generate both isocyanate and alcohol necessary for the exchange.

Tertiary amine (and phosphine)-based catalysts have been mostly used for foaming reactions as these catalysts also promote the isocyanate–water reaction. Weak tertiary amine or phosphine bases such as triphenylphosphine (PPh_3), triethylamine (NEt_3) or 1,4-diazabicyclo[2.2.2]octane (DABCO) with respective pK_a values of 2.73, 10.78 and 8.82⁴³ were found to be only poorly active for TC.³⁹ Interestingly, Subrayan *et al.* demonstrated that reactions of aliphatic isocyanates with a phenolic ester alcohol, prepared using P(Ph)_3 or DABCO catalyst instead of DBTDL, exhibited different kinetics and selectivities.⁴⁴ Highly active DBTDL favored the addition of aliphatic alcohol yielding the thermodynamically stable carbamate. In contrast, the weak bases (DABCO and P(Ph)_3) or non-catalyzed reactions favored the kinetic product produced by addition of the phenol groups. They also found that DABCO was able to promote TC in a really slow process under peculiar conditions (refluxing in acetonitrile for 2 days). The poor reactivity of these weak bases can be readily explained by the mechanism suggested in Scheme 3c and d). The first step of the base-catalyzed TC is the deprotonation of the NH of the carbamate groups ($\text{pK}_a \geq 20$ depending on substituents). Weak bases, i.e. tertiary amine and phosphine, are thus not able to promote the required proton abstraction. In the case of activated carbamate (with good leaving groups), these catalysts seem basic or nucleophilic enough to induce the TC reactions (suggested mechanism in Scheme 2d). In contrast to weak bases, strong organocatalyst bases derived from guanidine and amidine- such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, $\text{pK}_{a(\text{ACN})} = 26.02$ ⁴³) and 1,5-diazabicyclo[5.4.0]undéc-5-ène (DBU, $\text{pK}_{a(\text{ACN})} = 24.31$ ⁴³) respectively, were found to be active in TC both for PU synthesis and depolymerization reactions.^{39,45} Zhao *et al.* demonstrated on molecular model reactions that TBD and DBU were able to convert respectively 86% and 65% of the desired product at 65°C in THF for 20h when almost no conversion was recorded for triethylamine under the same conditions. The organic bases were used at 2 equivalents compared to the carbamate groups and thus cannot be considered as a true catalysts.³⁸

Interestingly, the combination of both organotin catalysts and amine bases was used for the TC of 2,4-di-*tert*-butylphenol-blocked toluene diisocyanate. Dibutyltin diacetate (DBTDA),

dibutyltin dilaurate (DBTDL), and stannous-2-ethylhexanoate ($\text{Sn}(\text{oct})_2$) were associated with tertiary amines such as tri-butyl or tri-benzyl amine or diethylcyclohexylamine (DECHA). In all cases and regardless of the combination, the association of organotin Lewis acid and tertiary amine bases was found to be more active than the mono-component catalyst.²⁵ The synergistic activation *via* both electrophilic (Lewis Acid) and nucleophilic (tertiary amine) pathways has been underemployed and appears as an elegant and promising strategy to promote TC under mild conditions. With the rapid development of organocatalysis over the past three decades, numerous powerful catalysts have been developed for more facile (mild conditions) and sustainable (greener catalysts) catalysis.^{46,47} *N*-heterocyclic carbenes (NHCs) and (thio)urea anions are strong candidates for example. Indeed, NHCs and their adducts with CO_2 or metal-based Lewis acid, have already proven their potential in PUs synthesis.⁴⁸ Their strong basicity and nucleophilic character associated with their peculiar and tunable stereo-electronic properties make them obvious candidates for TC reactions (Figure 3). In a similar manner, (thio)urea derivatives associated with strong organic bases have demonstrated an outstanding activity & selectivity in ring-opening polymerization of various heterocyclic monomers.^{49,50} The simultaneous combination of an electrophilic activation (carbonyl of the isocyanate) and nucleophilic activation (alcohol groups) often referred to as “dual activation” appears as a promising strategy to accelerate *via* a synergistic activation pathway the “sluggish” TC. As mentioned throughout this section dedicated to catalysts employed in TC, chemists have limited their approaches to efficient catalyst of urethane alcoholysis without specific design. Therefore, similarities with transesterification (both are ester interchange) should prompted chemists to investigate but also adapt highly active & selective catalysts that have been developed in the past decade. Overall, a fine control of TC exchange mechanism, *i.e.* associative or dissociative, under mild conditions will limit undesired reactions depicted in Scheme 2. To this, a rationalization of this exchange reaction mechanism has not been achieved yet at both molecular and macromolecular level.

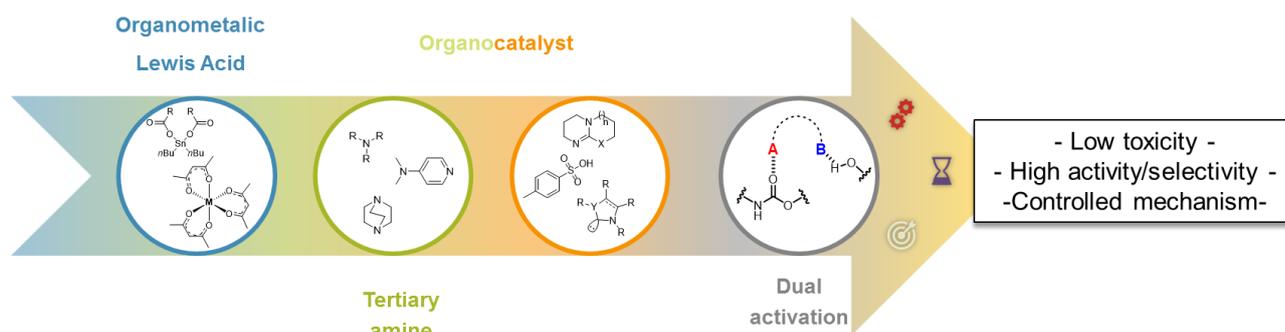


Figure 3. Catalysts employed and promising candidates towards controlled transcarbamoylation (triggered catalyst release, control associative or dissociative mechanism, no side reactions) reactions under mild conditions.

2 – Transcarbamoylation in polyurethane chemistry

In this section, applications of transcarbamoylation (TC) to sustainable and safe PU synthesis, depolymerization reactions or recycling are briefly described in order to highlight the potential, scopes and current limitations of this approach (See Figure 4). Over the past decades, many researchers have focused their interests on the synthesis of non-isocyanate polyurethanes, commonly referred to as NIPUs.^{6–8,51,52} The most studied approach was to replace the toxic isocyanate monomer by cyclic carbonates, thus yielding, by reaction with primary amine, polyhydroxyurethanes (PHUs). However, an alternative pathway used TC, *i.e.* reaction of (bi- or multi-) functional diols and (bi- or multi-) functional carbamates, as a tool to produce poly(urethane)s or polyurethane-based networks *via* the so-called blocked isocyanate strategy. The same reaction but using monofunctional short aliphatic alcohol induced the depolymerization of PU chains or chemical networks was also recently investigated. A last recent application of TC is the recycling of foams or PU thermosets into new thermoset materials *via* reactive extrusion. The preparation and characterization of covalent adaptable networks based on TC is presented in Section 3.

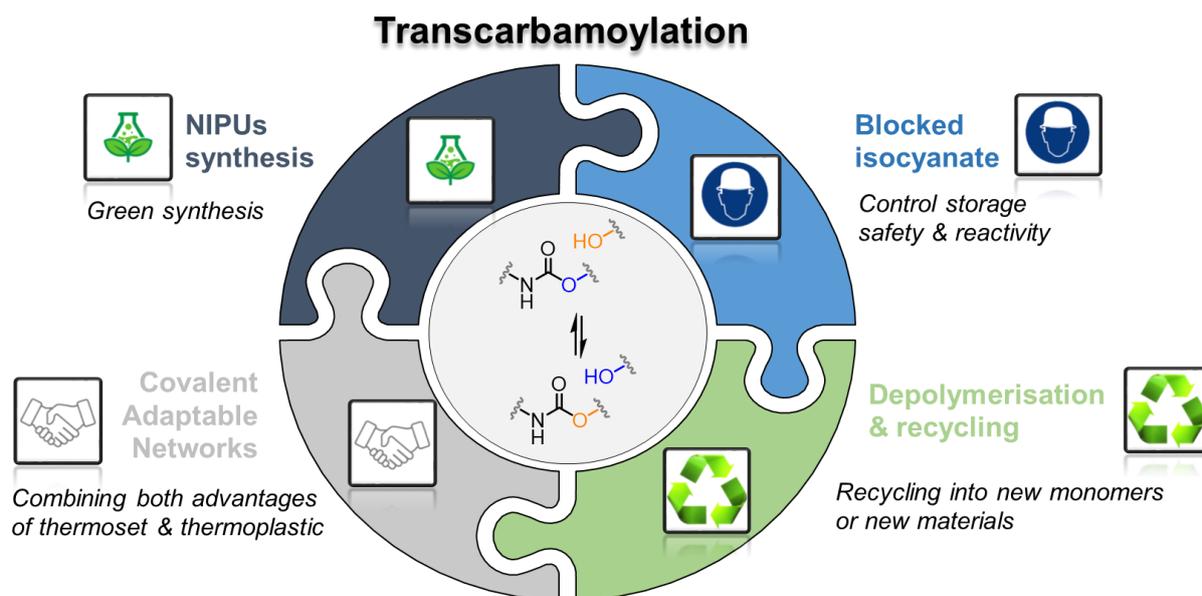
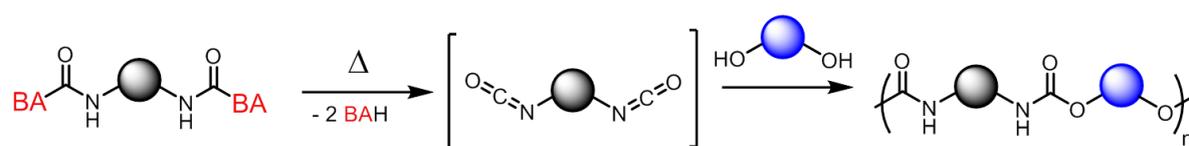


Figure 4. Application of transcarbamylation in polyurethane chemistry

2a- Blocked isocyanate

PU networks are usually obtained by mixing two components, polyisocyanates and polyols, which implies the handling of toxic isocyanates. Apart from the toxicity of reactant (and sometimes of the catalyst) the sensitivity of isocyanates towards moisture brings also major issues. The reaction between an isocyanate with water or hydroxyl-containing molecules occurs readily at room temperature even in non-catalyzed formulations and leads to the formation of a free amine and CO_2 . Hence, the prolonged storage of these compounds is unfeasible without controlled and dry atmosphere. To tackle this issue, blocked polyisocyanate/polyol formulations that do not react at room temperature were employed. This topic has been already largely reviewed.^{6,27,53} Generally the blocked isocyanate is regenerated by thermal-dissociation (e.g. at 95-200°C for *O*-alkyl carbamates)⁵³ and reacts with the polyol to give the polyurethane, thus releasing the protecting groups (Scheme 4). One of the most popular blocking agents is methylethylketoxime, which can be used at low temperature, associated with catalysts such as cobalt, tin or zinc derivatives for example. However, other blocking agents such as aliphatic alcohols have been used to reduce toxic

volatile organic compound (VOC) emissions and costs. However, the stability of *O*-alkyl carbamates necessitates higher reaction temperatures than other blocking agents such as methyl ethyl ketoxime, *N*-heterocycles (triazole, pyridine, imidazole or pyrazole) or mercaptan to liberate the isocyanate function. Typically, ethanol, butanol and isopropanol exhibit high dissociation or unblocking temperature compared to phenol and para-substituted phenol with electron withdrawing groups are easier to unblock but also highly toxic. That is the reason why more active (and latent) catalysts are needed in order to make possible the use of less reactive but less toxic blocking agents.



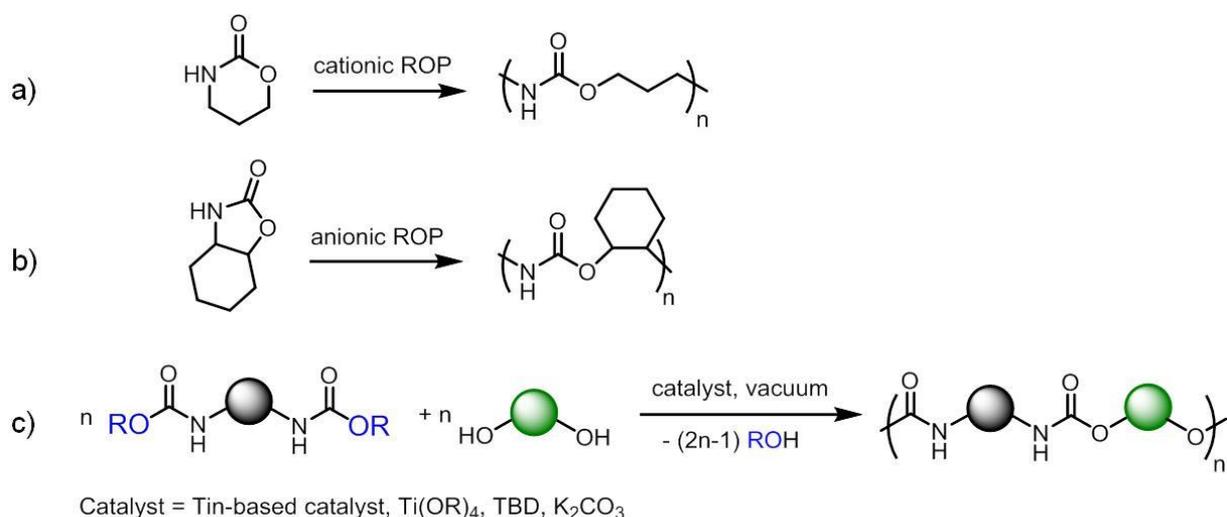
BA = aliphatic or phenolic alcohol, oximes, triazoles, pyridines, imidazoles, pyrazoles, mercaptans...

Scheme 4. Blocked isocyanate strategy for the in situ generation of isocyanate

2b-Transcarbamoylation between a biscarbamate and diol

Apart from anecdotic studies on the anionic/cationic ring-opening polymerization of cyclic carbamates by strong bases^{54,55} or electrophilic initiators⁴⁵ (methyl triflate or tosylate), a majority of investigations in TC-induced polymerization have dealt with the step-growth polycondensation of biscarbamates and polyols (Scheme 5).⁵ Due to the low reactivity of polyols/carbamate systems, polymerization is generally performed in a two-step procedure at high temperature (> 150°C). The first step consists in oligomerization under inert atmosphere followed by a second step under reduced pressure to push forward the equilibrium. Methyl and phenyl carbamates are the preferred options as methanol is easy to remove and phenol is a good leaving group. Organometallic Lewis acids such as organostannate derivatives or titane-based catalysts have been employed in such polycondensation process. Depending on the monomer and the catalyst engaged, isocyanate polyurethanes of low molar masses (a

few thousands $\text{g}\cdot\text{mol}^{-1}$) to relatively high molar masses (up to 69 000 $\text{g}\cdot\text{mol}^{-1}$) were prepared using this method. Organocatalysed polycondensation of biobased biscarbamate and polyol monomers were also reported. Biobased ricinoleic acid-derived dimethyl dicarbamates (from castor oil)⁵⁶ or limonene-based dicarbamates⁴⁵ with various diols were polymerized in bulk at 120-160 °C, using 5-10 mol% of TBD. In all cases, biobased NIPUs with limited molar masses up to 10 $\text{kg}\cdot\text{mol}^{-1}$ were obtained. The harsh conditions (high temperature and vacuum) were also reported to degrade both catalyst and monomers and specific precaution was required such as a gradual increase of temperature with sequential addition of catalyst. Interestingly, a simple inorganic salt K_2CO_3 allowed to perform the same polymerization process at 200°C using 5 mol% of K_2CO_3 yielding biobased NIPUs with higher molar mass ($M_n = 13.9 \text{ kg}\cdot\text{mol}^{-1}$). This selection of works demonstrates the current limitations of this step-growth polycondensation approach: harsh conditions (deleterious for the catalyst or monomers) and continuous removal of side products are required to obtain isocyanate PU with only relatively low molar masses.



Scheme 5. NIPU synthetic strategy *via* a) cationic ring-opening polymerization of 6-membered cyclic carbamates, b) anionic ring-opening polymerization of fused cycle 5-membered cyclic carbamates and c) step-growth polycondensation of a dicarbamate and polyol.

2c- Solvent assisted depolymerization

Pyrolysis of polymers is an interesting recycling strategy, polyurethanes can be difficult to pyrolyze into useful small molecules and release a significant amount of nitroxides. Thankfully, the carbamate groups of these polymers are susceptible to reactions with nucleophiles such as water or alcohols, allowing them to be depolymerized into compounds suitable for repolymerization. Industrially, PU wastes including both rigid and flexible or polyisocyanurate foams are depolymerized via the so-called glycolysis process.^{57,58} In this process, the cleavage of carbamates links is induced chemically by glycol-type molecules such as ethylene glycol (with ethanol amine as co-reactant), after a first step in which PUs are mechanically grinded into micrometric particles. It requires high temperature generally above 180°C (and limited to $T \leq 220^\circ\text{C}$ to avoid decarboxylation) and catalysis. All the catalysts mentioned in section I: organometallic (tin-based, bismuth derivatives, etc), inorganic salt, organocatalyst such as phosphoesters or tertiary amine were used for this purpose. The glycolysis process focuses on recycling polyols without regenerating valuable isocyanate or blocked isocyanate (under the *O*-alkyl carbamate form).^{58,59} Recently, a simple methodology was applied to depolymerize/repolymerize PUs under mild and efficient conditions using a simple base (TBD or inorganic salts) in a THF/MeOH mixture or MeOH alone as the solvent at 65°C (Figure 5).^{38,39} The production of *O*-dimethylcarbamates (blocked diisocyanates) makes this strategy attractive since this intermediate is able to react with polyols to regenerate PUs using TC releasing methanol. The reactivity of this intermediate also offers huge versatility in the outputs of this strategy since the mixture resulting from the depolymerization can be used directly to regenerate new PUs through step-growth polycondensation.

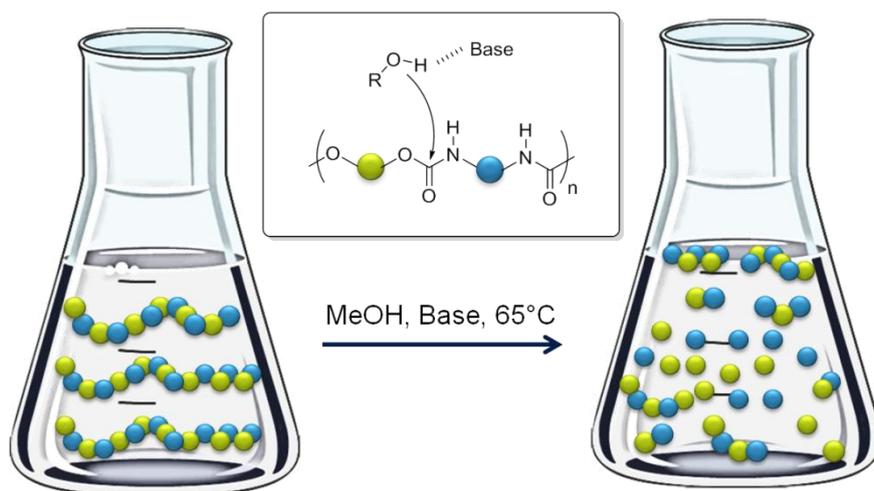


Figure 5. Solvent-assisted depolymerization of polyurethanes^{34,35}

2d- Recycling by reactive extrusion

In two recent publications, Dichtel and co-workers combined the use of Tin-catalyzed TC and industrially relevant polymer processing techniques, twin-screw extrusion (Figure 6).^{60,61} They demonstrated that PU thermosets and foams could be reprocessed into new thermosets *via* blending networks containing DBTDL, or by post-introduction of DBTDL in the foams (2.3-3.1 wt.%, 1.5 mol% to NCO groups). They initially evidenced the potential of this recycling strategy by incorporating sequentially “soft” PU networks into “hard” PU networks using co-extrusion. Mechanical properties of the blends were compared to reference networks (with the same theoretical compositions) and exhibited similar thermo-mechanical behavior (tensile test and DMA) and far more superior properties than those prepared by simple compression molding. As the large majority of PUs (around two-thirds) are PU foams, they applied the same strategy to recycle commercial PU foams. Once again, microcompounding of PU foams and Tin-catalyst exhibited a higher efficiency than solvent techniques (swelling in a catalyst solution followed by evaporation) associated with compression molding. These examples demonstrate the efficiency of combining TC agents and polymer processing techniques to recycle PUs thermosets and foams. This method could be applied to recycle and produce high-value and tunable materials from PU waste. Caillol and co-workers applied the same strategy for biobased polyurethanes foams in which DBTDL was used as catalyst

for the polymerization/crosslinking process. Biobased PU foams were then recycle into thermosets able to be reprocessed multiple times by compression molding.⁶² Those promising examples mixed the use of industrially relevant polymer processing methods and one of the today top-investigated research topics in material science: the design, preparation and analysis of covalent adaptable networks.

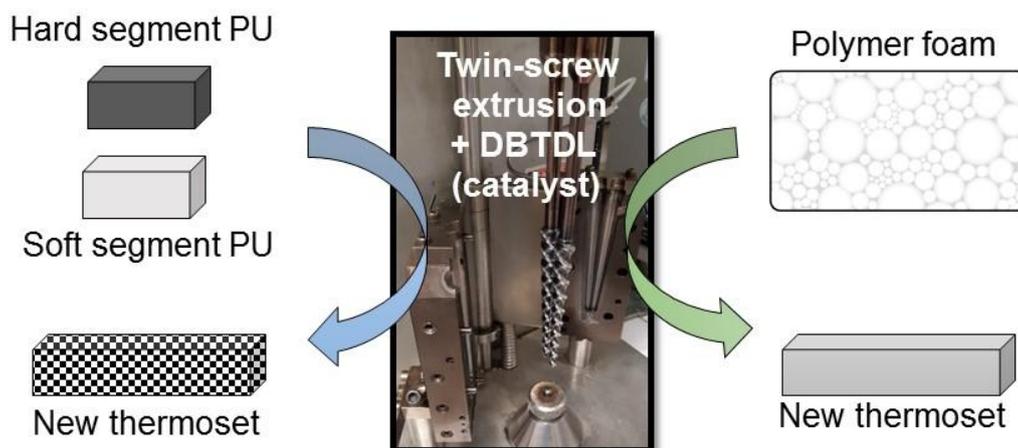


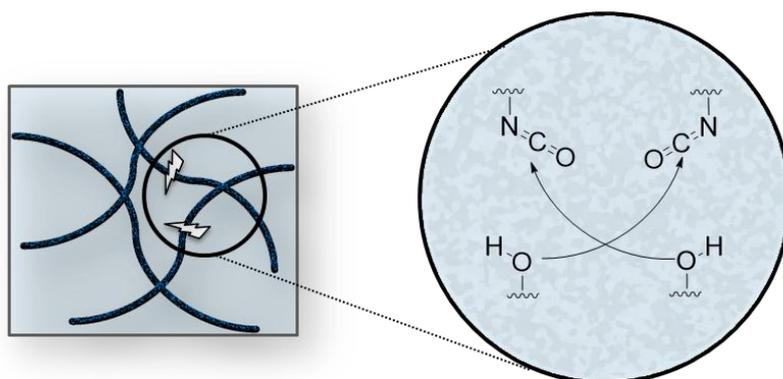
Figure 6. Recycling of PU foams and PU thermosets by catalysed (DBTDL) reactive extrusion^{53,54}

3- Covalent adaptable network based on transcarbamoylation reactions

Since seminal investigations in the 2010s, covalent adaptable networks (CANs) have been largely explored and reported in the scientific litterature.^{18,20,63,64} They are polymer networks whose cross-links undergo associative (vitrimer) or dissociative bonds exchange at elevated temperature, usually in the presence of a catalyst. This peculiar feature, *i.e.* catalytic properties beyond the polymerization process, enables the dynamic bond exchanges in chemically crosslinked networks *via* covalent exchange reactions. CANs thus combine advantages from both thermoplastics (reshaping, reprocessing and recycling) and thermoset resins (good mechanical properties, creep and solvent resistance etc...). Generally, CANs can be divided into two main categories based on the nature of the dynamic exchange, *i.e.*

dissociative or associative mechanism or in more unusual way, a combination of those two. As already mentioned throughout this publication, TC in the presence of free hydroxyl can occur *via* both mechanisms, (i) in a dissociative way via bond breaking and retro-formation of alcohol and isocyanate moieties, and (ii) in an associative way through an addition-elimination mechanism similarly to transesterification reactions (See Figure 7). In the case of urethane exchange, solely dissociative mechanism is expected. The nature of the exchange mechanism is known to have an impact, even if in practice differences are sometimes subtle, on viscosity profile at high temperature (Arrhenius-like vs. WLF model). The control of rheological properties *via* a comprehensive understanding of exchange mechanisms of CANs is a hot topic in material research.⁶⁵ In this section, CANs based on TC exchange reactions that have been described so far are reported. Some examples of carbon-carbon backbone polymers playing with TC chemistry as exchange reactions have been reported recently but a focus is given on PU or PHUs derivatives.^{66,67} Critical discussions about the mechanisms and rheological interpretations as well as comments on the remaining grey areas are provided herein.

a) Urethane exchange : dissociative CAN



b) Transcarbamylation : associative CAN

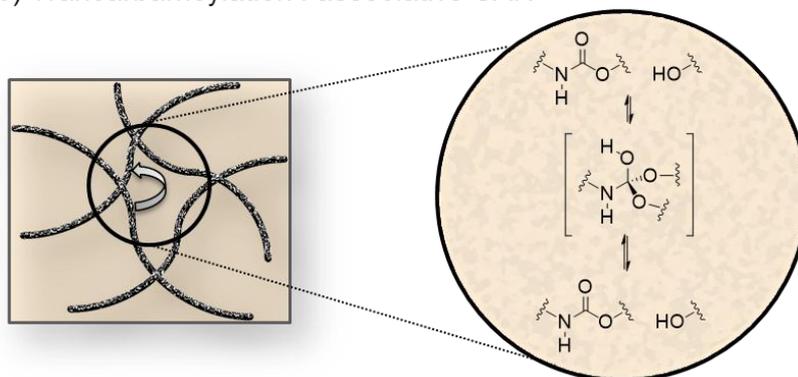
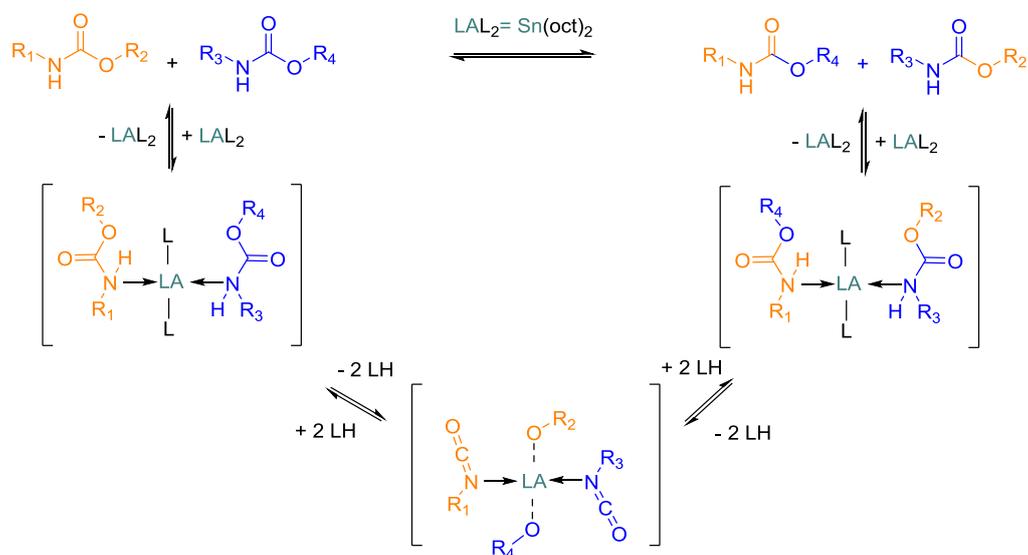


Figure 7. a) Dissociative and b) Associative CANs in polyurethanes chemistry
3.a) Transcarbamylation in PUs networks (urethane/urethane exchange)

TC *via* dissociative urethane/urethane exchanges was first introduced -among other “side reactions”- to explain the stress decay in PUs elastomer networks in the late 1950s.⁹ In 2014, Hillmyer and co-workers first described a covalent network able to fully relax stress *via* such exchanges while attempting the synthesis of poly(lactic acid)-based vitrimers.⁶⁸ The crosslink material was prepared by reacting a hydroxyl-terminated star-like PLA polyol and diisocyanate (MDI) in presence of $\text{Sn}(\text{oct})_2$, a well-known transesterification catalyst. The activation energy $E_A = 150 \pm 3 \text{ kJ.mol}^{-1}$ combined with short relaxation time (typically 50s at 140°C) were respectively higher and shorter than those expected for transesterification. In a following study,⁶⁹ they suggested that TC was the solely reaction occurring in this particular system (where two plausible relaxation mechanisms using the same catalyst were possible) by comparing them with polyether-urethane (made from star poly(ethylene oxide)) in which transesterification is impossible. The authors demonstrated that both networks relaxed stress at the same rate, the latter depending more on the crosslink density than on the backbone

nature. Both networks also dissolved at high temperature in polar organic solvent such as DMSO but not in non-polar solvent such as trichlorobenzene under the same conditions. Using molecular model reactions, they suggested that dissociative urethane exchange was the predominant exchange mechanism instead of alcohol-induced associative exchange, and proposed a coordination-insertion mechanism (Scheme 6). Model reactions confirmed that carbamate bonds are strongly favored at equilibrium at these temperatures (120 to 140°C) and isocyanates have not been detected by real time ^1H NMR spectroscopy at high temperature (due to too short life time). This behavior was also consistent with the Arrhenius dependence (vitrimer-like) of the characteristic relaxation times because the cross-links never dissociated to the degree which should cause a rapid drop in viscosity. This behavior was also previously observed on other dissociative exchange reactions in specific range of temperatures.^{70–72}



Scheme 6. Proposed reaction mechanism for a) $\text{Sn}(\text{oct})_2$ catalyzed urethane exchange in absence of free-hydroxyl groups.⁶²

These pioneering reports led to several studies for both polyether- and polyester-urethane CANs.^{41,73–76} Polyols, isocyanates and catalyst employed for the synthesis of PU-based covalent adaptable networks are displayed in Figure 8. Biobased polyols such as castor oil,⁷⁵

kraft lignin⁷⁴ or furan derivatives⁷⁶ were used to produce partially biobased dynamic covalent PU networks. Even if biosourced polyols were employed, most of the studies still use alkyl tin-based catalyst. However, regulations are about to evolve, and the use of di-alkyl organotin catalysts will be restricted, if not forbidden. The principal features as well as the synthesis conditions can be found in Table 1. PU-based CANs were prepared with a focus on material properties such as shape memory or the ability to relax internal stress. The relaxation mechanism was not investigated in detail. This data collection (Table 1) also highlighted how the comparison between systems is tedious and unfruitful due to the heterogeneity of structures (various polyols) and conditions (catalyst concentration or $[NCO]_0/[OH]_0$ initial ratio) used for the preparation of PU-based CANs. Some characteristic features can nonetheless be established from these results. Rapid stress relaxations (from tens to hundreds of seconds) at $T \geq 120^\circ\text{C}$ were commonly recorded by rheological measurement (although only normalized relaxation moduli were presented). The urethane exchange preferentially occurred following dissociative mechanisms as evidenced by model reactions on small molecules, dissolution tests or by characterization of rubber to liquid transition using dynamic mechanical analysis at high temperature (up to 275°C).

Table 1. Summary of monomers, catalysts, conditions and dynamic properties for preparation and characterisation PU-based

Isocyanate	Alcohol	Ratio $[NCO]/[OH]$	Catalyst (mol% NCO)	T°C (SR)	τ (s) (E_A in $\text{kJ}\cdot\text{mol}^{-1}$)	Exchange mechanism	ref
HDI, MDI	PEG 2k + glycerol	1	DBTDL (0.5, 1, 3%)	120-150	200-10 000 (113-130)	dissociative	77
HDI, MDI	3 arms s-PPG + hexane diol	0.9 – 1.0	DBTDL <i>p</i> -TSA TBD (2% mol)	100-140	≤ 600 (153-163)	associative & dissociative	89
MDI	PPG + triol/tetraol	0.8-1.0	DMAP	n.d.	n.d.	Dissociative	92
MDI, PMDI	4 arms s-PEG 4 arms s-PLA	0.75	Sn(oct) ₂ (2.5% mol)	130	75-2 000 (142-165)	dissociative	68, 69
MDI	4-arms-s	1.0	DBTDL	140	~ 40	dissociative	41

	polyester 4-arm s- PEG		Bi(neo) ₃ Fe(acac) ₃ (2 mol%)		(144-148)		
HDI	modified rosin	0.30 - 0.80	DBTDL	165-180	250-1 200 (112-178)	dissociative	73
MDI	PEG + tertiary amine tetraol	1.0	none	170	1 000-25 000 (<i>n.d.</i>)	<i>n.d.</i>	87
HDI	Castor oil + PEG 2k	1.0	DBTDL (1-3 wt.%)	130-150	<i>n.d.</i> (<i>n.d.</i>)	<i>n.d.</i>	75
HDI	<i>m</i> -erythritol + hexane diol + furan diol	1.0	DBTDL or Tertiary amine (1-10 mol%)	160-190	200-10 000 (~ 180)	dissociative	76
HDI	PEG 2k + kraft lignin	1.2	DBTDL (≈ 0.5 wt.%)	100-160	100-10 000	dissociative	74
IPDI HDI	PEG2k, castor oil Bisphenol derivatives	1.0	DABCO (0.5- 0.7 wt%)	40-120	40-10 000 (80-120)	dissociative	30 93, 94

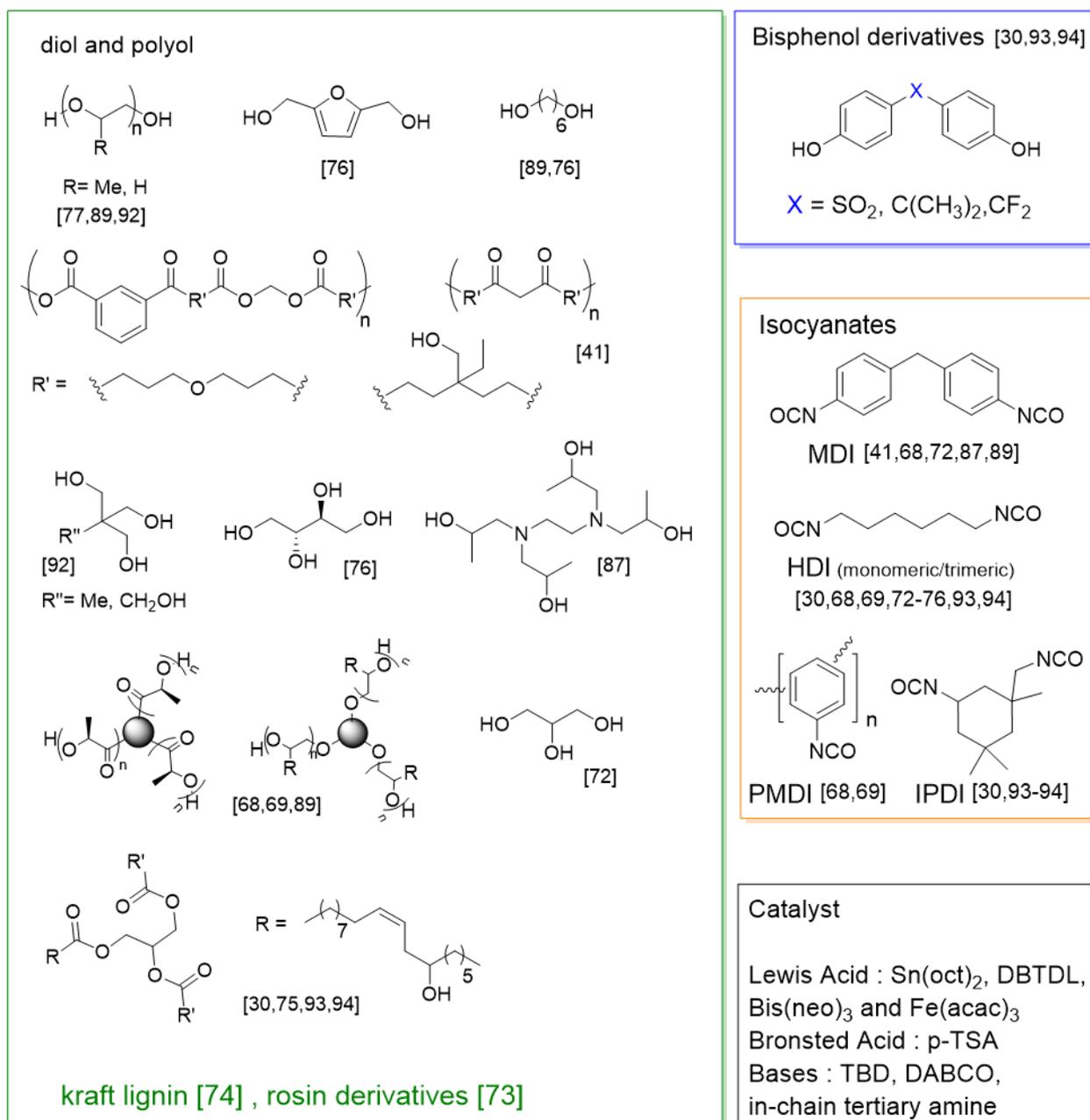


Figure 8. Chemical structure of polyol, isocyanates and catalysts employed in the preparation PU-based CANs

As already mentioned, the tin-based catalyst (DBTDL) was the preferred option in both PU synthesis and TC reactions for its high activity even at really low concentration. Looking for substitutes to replace di-alkyl organotin catalysts, Dichtel and co-workers compared the relaxation properties of polyester-urethane crosslinked networks with different Lewis acids such as iron acetylacetonate [Fe(acac)₃] or bismuth neodecylate [Bis(neo)₃] and DBTDL (the reference).⁴¹ The authors showed that the incorporation of Tin-free Lewis acid-type catalysts

into cross-linked PUs yielded materials that relax stress as fast as the networks containing DBTDL (less than 40s). This approach was found to be compatible with both polyether- and polyester-based PUs, and therefore likely to be directly applicable to commercially produced crosslinked PUs. Once again the relaxation properties seemed to be caused by the urethane exchange rather than by transesterification or a hybrid mechanism as similar activation energies and relaxation times were recorded for both polyether/ester-urethanes.^{41,68,69}

In order to avoid the risk of catalyst leaching and accelerated material ageing, neighboring group participation (NGP) and internal catalysis concepts have recently gained interest in the vitrimer community.^{78,79} The incorporation of tertiary amine,⁸⁰ hydroxyl group,⁸¹ carboxylic acid,^{82,83} sulfonic⁸⁴ or fluorinated group^{85,86} into a polymer network accelerated the exchange rate and enabled catalyst-free reprocessing of these networks. Recently, these concepts have also been implemented in a TC-based CAN using a tertiary amine containing polyol, MDI and no-exogenous catalyst.⁸⁷ PU networks containing in-chain tertiary amines of various crosslink densities and thermo-mechanical properties were thus prepared. As observed in the case of PLA-PU based CANs, stress relaxations were found to be slower for more crosslinked structures. This expected effect for dissociative network was actually the opposite of what had been described for poly(β -hydroxy ester) associative CANs. Indeed a recent study, demonstrated that stress decay was accelerated by increasing β -hydroxy esters concentration and consequently the crosslink density.⁸⁸

Sardon and co-workers proposed a mechanistic insight of PU-CAN using various polyurethane structures and catalysts (TBD, *p*-TSA and DBTDL).⁸⁹ Different networks were synthesized by changing the initial ratio ($[NCO]_0/[ROH]_0$) and the isocyanate monomer (aromatic or aliphatic). Combining molecular model reactions and stress relaxation experiments. They demonstrated that *p*-TSA and DBTDL were efficient catalysts whereas TBD did not exhibit any significant activity. In addition, they claimed that the type of catalyst strongly influences the exchange mechanism. For instance in the presence of free hydroxyl

groups, *p*-TSA was found to catalyze TC reaction exclusively in an associative fashion, while DBTDL was shown to catalyze both associative and dissociative mechanisms. This work contradicts previous studies in the field which suggested that even in the presence of large excess of alcohol, tin-catalyzed TC preferentially occurred through a dissociative mechanism. However, Sardon and co-workers drew their conclusions based on small-molecule characterizations and on normalized stress relaxation experiments which can be misleading. Indeed, difference between the behaviors of model molecules and that of materials are often observed, and a decrease of the storage moduli of the rubbery plateau is classically observed for dissociative CAN.^{90,91} Torkelson and co-workers prepared PU-CAN from diisocyanate-terminated PPG using an excess of triol/tetraol (up to 20 mol%) and DMAP as a catalyst at 80°C. Despite slightly shifted flow temperature measured by DMA (at $T \geq 230^\circ\text{C}$), all samples, *i.e.* with or without free hydroxyl, were characterized by the rubbery to liquid transition expected for dissociative exchange.⁹²

As previously mentioned in the case of blocked-isocyanate, *O*-phenyl carbamate bonds are easier to dissociate than their *O*-alkyl homolog and even more readily when the phenyl ring is substituted by electron-withdrawing substituents. Zu and coworkers judiciously applied this feature for the preparation of PU-based CANs with *O*-phenol linkages. PUs were synthesized using bisphenol derivatives with various electron density and DABCO as catalyst (0.5-0.7 wt%).^{30,93,94} The introduction of phenol-carbamate linkages allowed to finely tune the dissociation temperature depending on the bisphenol linker groups (Figure 7). For instance, bisphenol S starts to dissociate at temperatures as low as 30°C while dissociation starts at 60°C and 80°C for bisphenol AF and bisphenol A, respectively. In consequence PU-CANs based on phenolic-urethane exchange were able to relax stress at temperature as low as 40°C and to fully recover their mechanical properties multiple times (up to 4 times as measured by strain-stress tensile experiment) after a few minutes/hours at moderate temperature (80-130°C). Viscous flow activation energy E_A from 81 to 115 kJ.mol⁻¹ and fast relaxation (e.g. 40s at 80°C for bisphenol F) were also recorded for such networks. DABCO

used initially to catalyze the alcoholysis of isocyanate by less reactive phenol, was found to also participate in the dissociation process. Increasing the amount of catalyst from 0.7 to 1.5 wt.% led to divide the characteristic relaxation time by a factor 2. Interestingly, the authors also demonstrated that the characteristic relaxation time vs. cross-linking density relationship evolved linearly. Such relationship associated with the tunability induced by the phenolic substituent allows a fine control of mechanical properties and relaxation behaviors.

The vast majority of exchange reactions in PU adaptable networks, or more generally CANs, are thermally induced. In some original studies on PU-based composites, the dynamic exchange was not directly triggered by a rise in temperature. For instance, Zhang *et al.* prepared Iron oxide-polyurethane nanocomposites for magnetic solders application. In this case, the TC (catalyzed by DBTDL) was triggered by magnetic activation.⁹⁵ The magnetic field allowed the bond exchange reaction only to occur locally at the interface keeping the welded parts unaffected. PU-carbon nanotubes composites have been also prepared and TC triggered by microwave irradiation allowed repairing damages within seconds.⁹⁶ Even if the exchange reaction is triggered by magnetic or microwave stimuli, the nanoparticles or nanotubes locally generate heat under irradiation enabling the healing process *via* covalent exchange reactions.

Even if dissociative TC/urethane exchanges are commonly admitted to explain the stress decay in PU networks, a comprehensive understanding of the viscoelastic behavior and detailed mechanistic investigations have not been reported yet. In a recent publication, Montarnal and co-workers detailed the different rheological parameters and experiments required for the fine characterization of CAN properties.⁹⁷ The authors emphasized that presenting and discussing non-normalized stress relaxations, or small amplitude oscillation shear for fast exchanges, is of “utmost importance” for the comprehensive understanding of the rheological behavior of CANs. They also mentioned that the replacement of thermoplastics by CANs is restrained due to relatively low viscous flow activation energy and

consequently processing difficulties. According to the same authors, the “ideal CANs” (not reported yet) should exhibit high viscous flow $E_A \geq 200 \text{ kJ.mol}^{-1}$ with a zero-shear viscosity higher than 10^{12} Pa.s at $100 \text{ }^\circ\text{C}$ and a zero-shear viscosity lower than 10^6 Pa.s at a processing temperature of $200 \text{ }^\circ\text{C}$. The authors think that dissociative networks with controlled rheological behavior (rubbery to liquid transition) could potentially fit those requirements (See figure 9). In addition to those rheological requirements and characterizations, researchers should perform solid-state spectroscopy analysis such as Fourier transformed infrared or Raman (directly coupled or not with rheology) to monitor *in situ* the formation of chemical groups during thermal treatment.

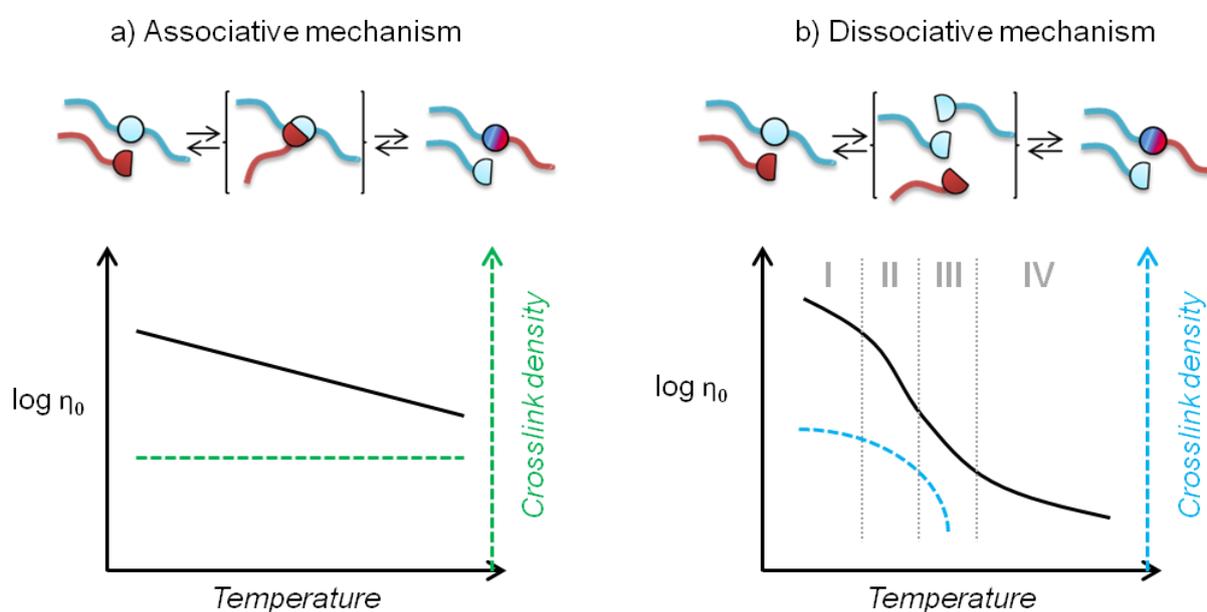


Figure 9. Expected evolutions of zero-shear viscosity $\eta_0(T)$ and cross-link density at temperatures above the glass transition for a) associative exchange and b) dissociative exchange. In the case of dissociative networks, four distinct viscoelastic regimes noted from I to IV are expected.⁹⁷

Researchers have only recently started to investigate PU-CANs using TC or urethane-exchange reactions. Numerous questions are also rising from the published studies as a deep understanding of the rheological properties or relaxation behavior of PU-CANs have not been rationalized yet. As noted by Xu and co-workers in the case of phenol carbamates,

when designing CAN-containing carbamates, chemists should not focus their attention only on the network rearrangement kinetics but also on the thermal stability and hydrolytic resistance of the polymer chains.⁹⁴ The occurrence of side reactions at high reprocessing temperature involving urethane groups (see Scheme 2) could lead to the formation of potentially non-exchangeable covalent links and has not been investigated so far for PU-based CANs. For instance, the formation of urea bonds has been shown to influence the relaxation properties. Also, most PUs are known to be comprised of alternating “soft” segments, polyol-rich domains with low glass transition temperature, and “hard” segments with carbamate-rich domains (hydrogen bonds). The incompatibility of these two segments leads to phase separation in which hydrogen bonding interactions between urethane groups in the “hard” domains lead to physical crosslinking. The effects of such phase separation as well as the distribution of the catalyst has not been investigated in the PU-CANs yet, although it is strongly suspected to have an influence on the CAN properties.^{98–101} The design of more sustainable PU-CANs materials have also been investigated through the use of biobased alcohols and greener catalysts. In contrast, only a few non-renewable and hazardous isocyanates monomers have been used. Recent studies in the field, have demonstrated that PU chemical networks containing up to 95% of biobased content can be prepared starting from commercially available biosourced and potentially less-toxic isocyanates.^{102–104}

3.b) Transcarbamoylation in PUs networks (urethane/hydroxy exchange)

Unlike conventional PU chemical networks, PHU networks synthesized *via* ring-opening of cyclic carbonate by primary amine contain as many primary/secondary alcohol groups as carbamate linkages. The presence of hydroxyl groups in the vicinity of the carbamate functions is claimed to affect not only relaxation properties but also exchange mechanisms, affording levels of reprocessability that are not achievable with conventional PU networks,

i.e. without TC catalyst. The list of cyclic carbonates and amines used for PHUs vitrimers or CANs is provided in Figure 10.

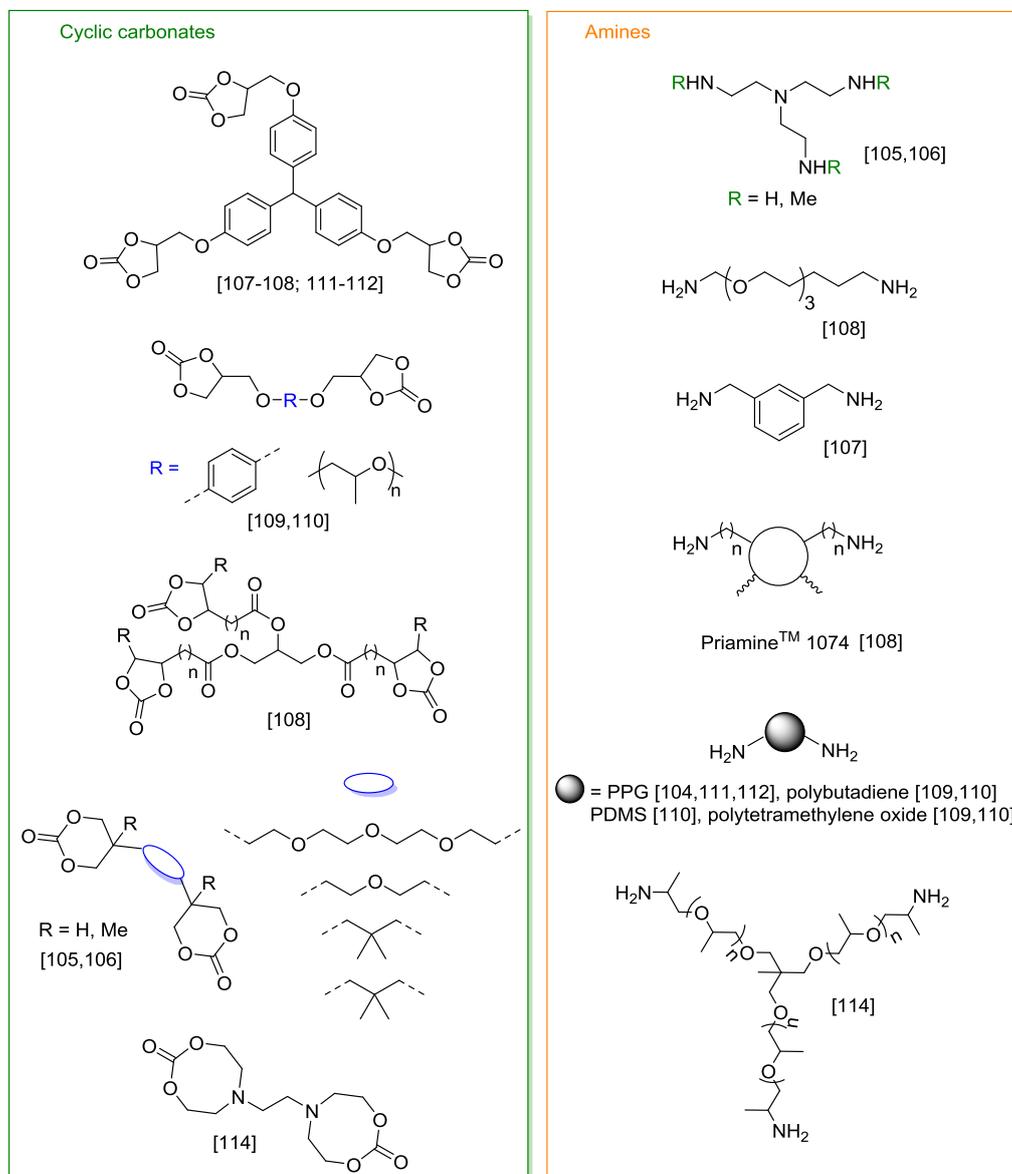


Figure 10. Cyclic carbonate and amine monomers employed for the synthesis of polyhydroxyurethanes dynamic covalent networks based on transcarbamoylation.

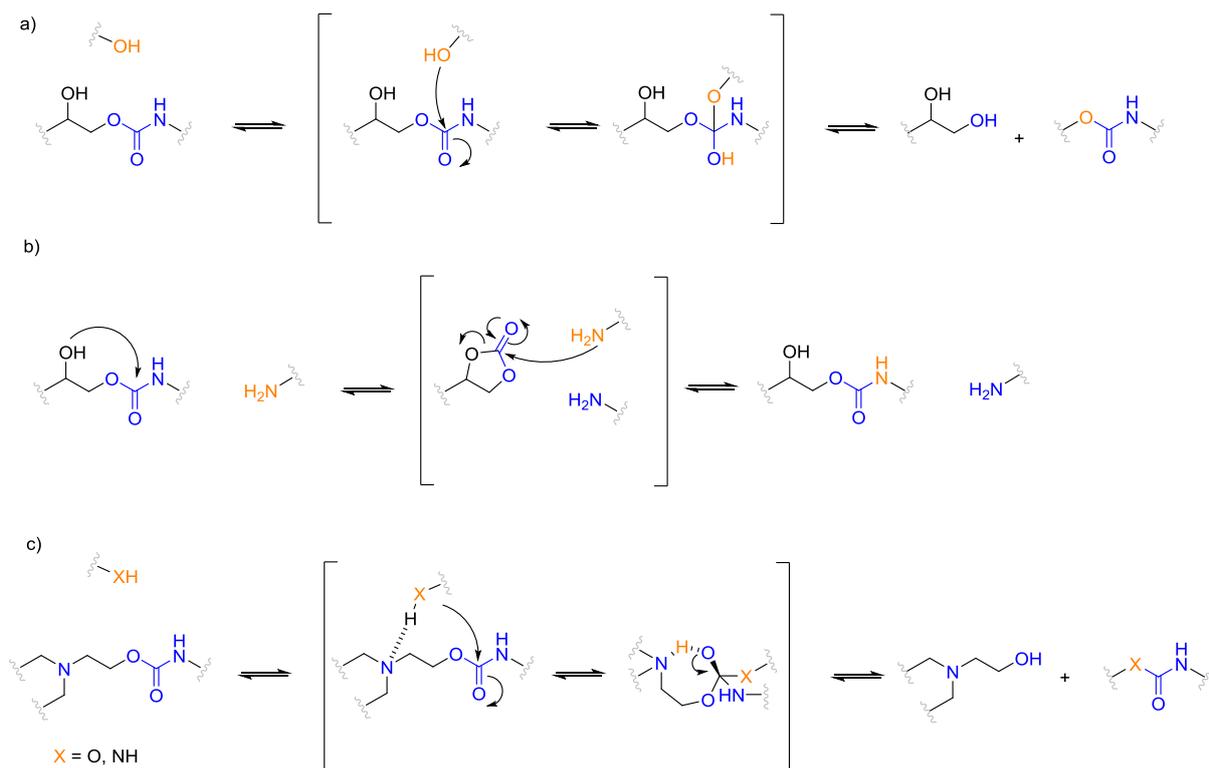
In 2015, Fortman *et al.* reported the first PHU-based CANs synthesized from bifunctional six-membered cyclic carbonates and tri-amine crosslinker. These PHU networks were claimed to rearrange at high temperature *via* associative TC exchange reactions between carbamate groups and free hydroxyl groups distributed along the backbone without any catalyst (Scheme 7a).¹⁰⁵ From the activation energy ($E_A = 110 \text{ kJ}\cdot\text{mol}^{-1}$) and thanks to the synthesis of

model material as well as DFT calculations, they suggested that TC exclusively occurred in an associative fashion. The prepared networks were also not soluble after multiple hours in diphenylacetone at high temperature (180°C) confirming an associative mechanism. Relaxation times were also logically longer (around ten times) than those of PU-CANs, as the exchange was not catalyzed even if the presence of tertiary amine in the crosslinker structure can play the role of an internal catalyst. Later on, the same group demonstrated, in a comparative study, that five-membered cyclic carbonates were poor candidates for CAN application due to the presence of a majority of less-reactive secondary alcohols.¹⁰⁶ In addition, PHU networks prepared from 5-membered cyclic carbonates were prone to both thermal decomposition (decarboxylation) and side reactions (urethane formation) at 180°C. In the same report, the authors studied the influence of crosslink density and mechanical properties on the relaxation properties. Chemically crosslinked PHUs prepared from 6-membered cyclic carbonates containing a polyether chain exhibited lower activation energy ($E_A = 98-108 \text{ kJ.mol}^{-1}$) than monomers bearing aliphatic side chains ($E_A = 134-136 \text{ kJ.mol}^{-1}$). In all cases, only partial recovery of mechanical properties was recorded by tensile test measurement. They suggested that internal or in chain-tertiary amine (coming from the tertiary-amine containing crosslinker, (triethanolamine) can undergo, under these conditions (180°C), oxidation side reactions responsible for the incomplete recovery of material properties.

Torkelson and co-workers reported that PHU networks prepared from 5-membered cyclic carbonates and a simple organocatalyst (DMAP) were able to combine within the same chemical network structure both associative (TC exchange reaction) and dissociative (reversible cyclic carbonate ring-opening/ring-closure) (Scheme 7a and b) processes.¹⁰⁷⁻¹¹² The retro-formation of 5-membered cyclic carbonates was evidenced by FTIR measurement and the side reactions previously observed by Fortman *et al.* were limited by the use of non volatile reactant.¹⁰⁹ In this particular case, *i.e.* in the presence of DMAP as catalyst, complete recovery of the initial mechanical properties was recorded by both tensile and dynamic

mechanical analysis after 1h at 140°C. In a following contribution,¹⁰⁷ the same group presented typical stress relaxation of DMAP-catalyzed PHU-based CANs (with and without nanofillers). Rapid characteristic relaxation times (within hundreds of seconds) at 140°C and activation energy ranging from 132 to 160 kJ.mol⁻¹ were recorded for such systems. Interestingly, by applying the Kohlrausch–Williams–Watts (KWW) stretched exponential decay function for fitting stress relaxation profiles, they demonstrated that DMAP-catalyzed PHU-CAN stress decay follow a single-exponential decay response. This result suggested a narrow distribution of relaxation times and was attributed to the occurrence/involvement of one main mechanism governing the exchange dynamic, *i.e.* the transcarbamoylation. In a recent publication, Evans and co-workers investigated the relaxation profile of two kinetically distinct boronic ester dynamic bonds within the same network.¹¹³ The mixed vitrimers exhibited also a single relaxation peak, which more closely follows the dynamics of their faster component. These two investigations implied that the kinetically predominant exchange reaction will govern both stress relaxation time and profile, thus masking the occurrence of more complex mechanisms.

Fully biobased PHU-CANs were prepared using the same strategy (DMAP-catalyzed reactions) and tris-(5-membered cyclic carbonates) derived from soy bean oil in combination with diamine such as Priamine 1074TM or diethylene glycol bis(3-aminopropyl) ether.¹⁰⁸ This elegant design of PHUs networks combined good reprocessability under mild conditions but also multiple potential exchange mechanisms including transesterification, transcarbamoylation and retro-cyclization. Unfortunately, no stress relaxation experiments nor activation energy were presented nor discussed.

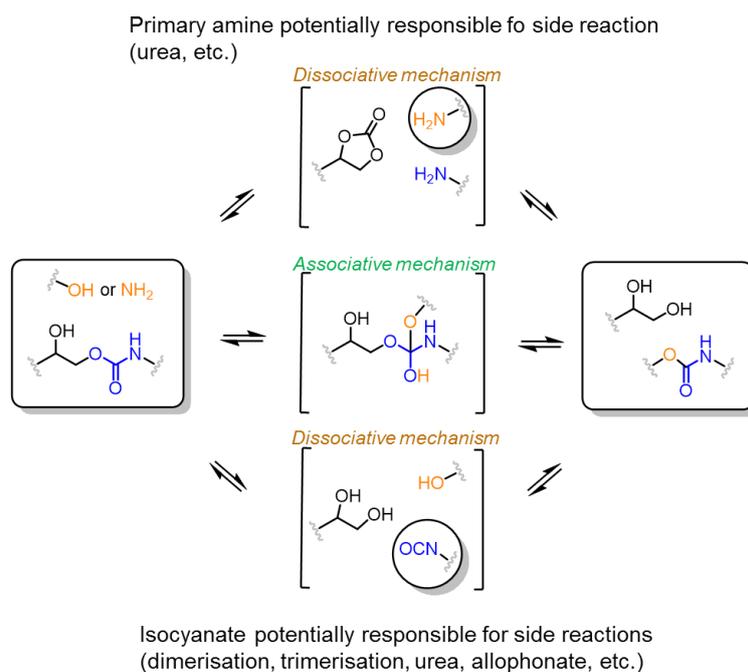


Scheme 7. Exchange reactions in PHUs via a) associative transcarbamoylation, b) reversible ring-closure/ring-opening of cyclic carbonate by amine and c) internal tertiary amine catalysis associative transcarbamoylation.

In a recent publication, Du Prez and co-workers used molecular model reactions to study the effect of tertiary amine position as internal catalyst in PHU networks.¹¹⁴ A prototype network was synthesized by reacting a stoichiometric amount of a bis 8-membered cyclic carbonate and Jeffamine® T-403 as multifunctional amine crosslinker (24h at room temperature followed by 3h at 100°C). The PHU network exhibited shorter relaxation times (100s at 150°C) and roughly identical activation energy of 118 kJ.mol⁻¹ compared to its 6-membered cyclic carbonate analogs. Model reactions demonstrated that exchanges were more effective on samples containing internal tertiary amine. The authors suggested a hydrogen-bonded intermediate transition state (Scheme 7c) to explain the increased activity of the in-chain tertiary amine. The formation of primary amine responsible for urea formation has not been rationalized in this study. However, side reactions leading to urea formation were also detected. Despite its slight impact on the reprocessing efficiency, the continuous formation of

urea chemical functions indicates a more complicated dynamic exchange pathway than a simple associative exchange.

Despite the lower reactivity of the cyclic-carbonate/amine system towards polymerization-crosslinking than monomers typically used for the synthesis of PU, polyhydroxyurethane chemistry appears as an elegant pathway to produce fully biobased (with or without catalyst) CANs based on TC or multiple exchange mechanism. Similarly to PU-CAN, a complete understanding of the reaction involved in the relaxation mechanism and structure/properties relationship is still lacking. For example, urea formation was detected in both molecular model reactions and polymer matrices. While ring-closure of hydroxyurethane explained the formation of primary amine able to induce transurethanization, urea bonds were also detected in model reactions where cyclisation is impossible. Such results are therefore questioning the associative or dissociative behavior of (complex) carbamate exchanges in PHU-CANs. As already mentioned, non-normalized stress relaxation experiments combined with creep analysis could provide crucial information for potential application as well as mechanistic insights. Moreover, the effect of the catalyst on the exchange mechanism should be further evaluated in order to gain control on the thermal behaviour of the material. Determination of factor influencing and controlling the “mechanism switch”, if there is one, from the dissociative mechanism well-established in PU-CANs to an associative exchange in PHU-CANs could also lead to a fine control of exchange properties (Scheme 8).



Scheme 8. Exchange reactions in PU catalyst reversible ring-closure/aminolysis, associative and dissociative transcarbamoylation. The formation of primary amine or isocyanate lead potentially to side reactions during the relaxation process at high temperature.

4- Perspectives and conclusions

PU are a unique class of materials and possess a wide range of applications from simple plastic shoe soles to biocompatible, self-healing or smart composites materials. Their peculiar rheological properties such as tunable elasticity/plasticity, induced by the presence of segmented structures as well as the near unlimited architectures that can be prepared, make them fascinating materials for both academic research and industrial applications. This perspective review intended to demonstrate the vast potential of transcarbamoylation/urethane-exchanges to produce more sustainable PU-based materials or design PU-covalent adaptable networks. This simple but sluggish exchange reaction finds application ranging from the synthesis of isocyanate-free polyurethanes to their depolymerization, recycling and reprocessing. The design of polyurethane-based covalent adaptable networks is also one of the major applications of transcarbamoylation. Rapid stress relaxation (tens of seconds in some cases) combined with unique mechanical/rheological properties, self-healing and processability of PU-CANs, make them

industrially relevant dynamic materials. In addition, fully biobased and potentially biodegradable PU-CANs can be prepared from novel, greener and commercially available isocyanate monomers. Nevertheless, more detailed investigations of the structure-property relationship or effect of catalyst on the exchange mechanism – among others - are needed. Breakthrough developments in polymer chemistry often arise from design and controlled process established at the molecular level. Transcarbamoylation control - *i.e.* control of mechanism (associative or dissociative), no side reactions (urea, etc.), and mild conditions - should promote the development of new highly active tin-free catalytic systems. The ideal catalytic system will thus combine high activity and selectivity, sustainability and low toxicity.

Author information

Corresponding authors

Camille Bakkali-Hassani, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
<https://orcid.org/0000-0003-3633-2675>; Email: camille.bakkali-hassani@umontpellier.fr

Sylvain Caillol, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
<https://orcid.org/0000-0003-3106-5547>; Email: sylvain.caillol@enscm.fr

Authors

Dimitri Berne, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
<https://orcid.org/0000-0003-1782-9627>

Vincent Ladmiral, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France
<https://orcid.org/0000-0002-7590-4800>

Notes

The authors declare no competing financial interest

Biographies

Camille BAKKALI-HASSANI



Camille Bakkali-Hassani studied molecular and macromolecular chemistry at the University of Bordeaux and got his Ph.D working on controlled ring-opening polymerization of heterocyclic monomers (2018). After conducting postdoctoral research at Monash University (Melbourne, Australia (2019–2020)) working on controlled continuous flow polymerisation of cyclic esters and at ESPCI (Paris, France (2020–2021)) on biocalysis & biobased strategy for self-healing material design, he is currently postdoctoral researcher at ICGM (Montpellier, France). His research focuses on-demand catalysis for covalent adaptable networks.

Dimitri BERNE



Dimitri Berne was born in 1996 in Lons-le-Saunier, France. In September 2020, he received his Master's degree in Chemistry from the National Graduate School of Chemistry of Montpellier, France (ENSCM). In 2020, he started a PhD at the Institut Charles Cherhardt Montpellier (ICGM, University of Montpellier), under the supervision of Dr Sylvain Caillol, Dr Vincent Ladmiral and Dr Eric Leclerc. His PhD work is funded by the French National Research Agency ANR (AFCAN project ANR-19-CE06-0014) and mainly focuses on the development of CANs whose exchange reactions are activated by fluorinated groups.

Vincent LADMIRAL



Vincent Ladmiral graduated from Montpellier chemistry school (France) in 1998 and received his PhD from the University of Warwick (UK) in 2006. He then worked as a postdoctoral associate at Kyoto University (Japan), at the University of Sydney (Australia), at the University of New South Wales (Australia) and at the University of Sheffield (UK). In 2012 he was recruited by CNRS as a research scientist at the Institute for Molecular Chemistry and Material Sciences in Montpellier (France). His research interests pertain to the study of the structure-property relationship in polymers and organic materials.

Sylvain CAILLOL



Sylvain Caillol is Research Director at CNRS. He was born in 1974. He graduated engineer from the National Graduate School of Chemistry of Montpellier in 1998 and then received his M. Sc. Degree in Chemistry from the University of Montpellier. He received his PhD degree in 2001 from the University of Bordeaux. Subsequently he joined *Rhodia* Company. Later, promoted Department Manager, he headed the Polymer Research Department in the Research Center of Aubervilliers. In 2007 he joined the CNRS at the Institute Charles Gerhardt of the University of Montpellier where he started a new research topic dedicated to Green Chemistry and Biobased Polymers. He is co-author of more than 200 articles, patents and book chapters. He won the Innovative Techniques for Environment Award in 2010, the Green Materials Prize in 2018 and 2019 and was nominated Pioneering Investigator by the Royal Society of Chemistry in 2019.

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