Elaboration and characterization of new bio-based and sustainable aromatic polyurethane and polyurea materials

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Polyurethanes are among the most important polymer materials. Thanks to their versatile properties, they can be used in various application fields such as medical devices, footwear, automotive, shipbuilding and many others. PUs are commonly prepared by the reaction of diisocyanate with di- or multi-functional polyols. Nowadays, the polyols are easily prepared from biomass feedstock and are often biodegradable and biocompatible.[1-4] However, the diisocyanate agents are petroleum-based and are prepared from amines and extremely toxic phosgene.[4] Currently, the development of sustainable, alternative and environmentally friendly routes to polyurethane synthesis, using non-isocyanate methods and/or employing monomers from renewable resources, is of great interest.

Three main approaches have been described in the literature for the preparation of Non Isocyanate Polyurethanes (NIPUs): (i) The first approach is the reaction of diamines with five-membered bicyclocarbonates leading to poly(hydroxylurethane)s.[4-6] The cyclocarbonate groups are commonly obtained by the reaction of CO2 with oxirane groups,[7-10] like those of bis-epoxidized methyl oleate and methyl undecenoate, in presence of tetrabutylammonium bromide as a catalyst.[9-10] (ii) The second approach is the self-polycondensation upon heating of AB-type fatty monomers bearing hydroxyl and acyl azide functionalities, with and without a catalyst. This reaction involves in situ formation of isocyanate groups via Curtius rearrangement.[11-13] However, the acyl azide groups were mainly obtained from the reaction of harmful sodium azide with carboxylic acids. On the other hand, sodium azide can be substituted by hydrazine, which reacts with ester groups affording diacyl hydrazide, which can give acyl azide by reaction with sodium nitrite in presence of HCl and acetic acid.[14] (iii) The third approach is the promising transurethanization consisting in the reaction between dicarbamates and diols, in presence of a catalyst such as titanium catalysts[15] or 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD).[16] Three chemical pathways were used to prepare dicarbamates from renewable resources. The methyl carbamate groups can be obtained by reacting the previously mentioned acyl azide groups with methanol.[11] They can also be prepared by a catalytic variant of the Lossen rearrangement, performed on carboxylic acid groups, using dimethyl carbonate (DMC) as activating agent, in the presence of methanol and catalytic amounts of tertiary amine reagents.[16]

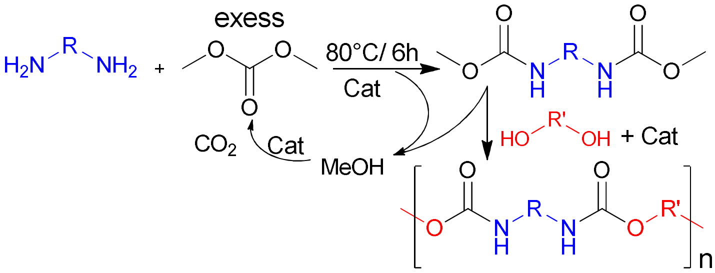

Figure 1. Green process for synthesizing NIPUs by the transurethanization polycondensation between BMC and diols.

During the last decade, our laboratory has been extensively working on a new process involving the preparation of a set of aliphatic and cyclo-aliphatic bis(methyl)carbamate (BMC) molecules through the reaction of a diamine with an excess of dimethylcarbonate (DMC), in presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst. [17-28] It is noteworthy that DMC can be recycled several times. Most importantly, it can be prepared from CO_2 and methanol.[29] Finally, using this approach, combined with the transurethane polycondensation reaction between bis(methyl)carbamates (BMC) and diols, in presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) or K_2CO_3 as catalyst, several aliphatic and cyclo-aliphatic NIPUs with various properties have been prepared (Figure 1).

In this work, we aim to prepare sustainable aromatic polyurethane and polyurea materials from lignin derivatives. The first part of this work will focus on the preparation and full characterization of a set of new aromatic molecules with specific functional groups. This part will be carried out at the CARMEN institute (UMR CNRS 6014). The second part will be carried out at the PBS laboratory (UMR CNRS 6270) and will focus on the use of the new biosourced aromatic molecules to prepare new PolyUrethane Non-Isocyanate (NIPU) and PolyUrea (NIPUrea) materials via the transurethanization approach. The thermal and mechanical properties of the resulting materials will be fully characterized.

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