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# Synthesis and characterization of advanced biobased thermoplastic nonisocyanate polyurethanes, with controlled aromatic-aliphatic architectures

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## ABSTRACT

The aim of this study was the elaboration of thermoplastic and biobased nonisocyanate polyurethanes (TNIPUs) based on different aromatic-aliphatic architectures. A rigid aromatic bis(cyclic carbonate) was synthesized from terephthalic acid, and subsequently used with various 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 and mechanical results show that the 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 content up to 76%.

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## 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 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 (respectively, HS and SS) 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 [1–3]. A two-step process, also called prepolymer technique, is frequently used for the elaboration of TPUs with controlled architectures [4,5].

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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 [6]. 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 [6–11]. Among the various synthetic pathways considered (*e.g.*, AB-type azide condensation [12], transurethane polycondensation [13,14]), aminolysis reaction is the most reported one. This synthesis involves the reaction of cyclic carbonates with amine-based compounds [15].

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 (TPA) [16,17], Bisphenol A, Bisphenol S and their derivatives [15,18,19] are the main aromatic cyclic carbonate precursors, whereas isophorone diamine [20–22], *m*-xylylenediamine and *p*-xylylenediamine [23] 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 [22], vanillin [24], cashew nut shell liquid (CNSL) [25], or limonene [26], derivatives were described in NIPU synthesis. However, only one paper reported the use of an aromatic biobased diamine, called phenalkamine, obtained from CNSL, for the elaboration of NIPU [27]. Nevertheless, other rigid diamines, mainly developed for epoxy applications as hardener, were already synthesized from isosorbide [28], vanillin [24], and limonene [29]. More recently, aromatic NIPUs were elaborated from tannin and lignin derivatives [30–32].

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 (TPA), and in substituting long-chain and short-chain diols by various diamines. TPA is presently obtained from fossil-based *p*-xylene but some renewable alternatives from *e.g.*, biobased isoprene and acrylic acid [33,34], methyl coumalate and methyl pyruvate [35] or limonene [36] 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 TPA is 2,5-furandicarboxylic acid (FDCA). FDCA was already successfully tested in PET-like bottles [37]. A dimer fatty amine (DFA) was used as a biobased chemical. DFAs or high molar mass polyetheramines could act as SS, and short chain 1,4-butanediamine (BDA) or *m*-xylylene diamine (*m*XDA) were used as chain extenders.

The aims of this study were (i) to evaluate the effects of the building blocks 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 NIPU with a strong elastomer character.

## 2. Experimental part

### 2.1. Materials

Terephthaloyl chloride (TPCI, 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<sup>®</sup> D2000, were obtained from Huntsman (Everberg, Belgium). Jeffamine<sup>®</sup> D2000 presents a high molar mass, equals to 2000 g mol<sup>-1</sup>. Dimer diamine (DDA) commercially available under the trade name Priamine<sup>™</sup> 1075 was kindly supplied by CRODA (Goole, England). DDA is a C<sub>36</sub>-biobased molecule obtained from dimer fatty acids [38]. 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<sub>g</sub>*) lower than -50 °C. At room temperature, DDA is a yellowish, slightly viscous liquid. Dichloromethane (DCM, ≥99%), dimethylformamide (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.

### 2.2. Synthesis

#### 2.2.1. Synthesis of bicyclocarbonate from terephthalic acid (TPBisCC)

The terephthalic bicyclocarbonate was synthesized following the pathway given by Fig. 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), preliminarily 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<sub>3</sub>·HCl was removed by two distilled water washing. The powder was then dried in an oven under vacuum at 60 °C during 20 h to yield 93.7 g (81%) of TPBisCC as a white powder.

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