



Synthesis of isosorbide based polyurethanes: An isocyanate free method

Vincent Besse^{a,1}, Rémi Auvergne^{a,1}, Stéphane Carlotti^{c,2}, Gilles Boutevin^b, Belkacem Otazaghine^{d,3}, Sylvain Caillol^a, Jean-Pierre Pascault^e, Bernard Boutevin^{a,*,1}

^a Institut Charles Gerhardt Montpellier UMR 5253 – Equipe Ingénierie et Architectures Macromoléculaires, Ecole Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

^b Specific Polymers, Avenue de l'Europe, 34830 Clapiers, France⁴

^c Laboratoire de Chimie des Polymères Organiques UMR 5629 Université Bordeaux 1/CNRS, Ecole Nationale Supérieure de Chimie, de Biologie & de Physique, 16, Avenue Pey-Berland, 33607 Pessac Cedex, France

^d Ecole des Mines d'Alès, Centre des Matériaux de Grande Diffusion (CMGD), 6, Avenue de Clavières, 30319 Alès Cedex, France

^e University-Lyon, INSA-Lyon, Ingénierie des Matériaux Polymères, IMP, UMR5223, F-69621 Villeurbanne, France

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ABSTRACT

The synthesis of isocyanate free polyurethanes is a major concern. This paper first reports the synthesis of new biobased isosorbide dicyclocarbonates from isosorbide. Then polyhydroxyurethanes (PHUs) were synthesized by a cyclocarbonate–amine step growth polyaddition with four commercial diamines (e.g. jeffamine D-400, 1,10 diaminodecane, diethylenetriamine and isophoronediamine). These unprecedented products, obtained with high yield, were characterized by ¹H NMR, FTIR, DSC, SEC and TGA analyses. PHUs exhibited glass transition temperatures from –8 °C to 59 °C, and degradation temperatures (Td 5%) between 234 °C and 255 °C. Last but not least, the compounds produced during the degradation of these PHUs were analyzed by ATG-IR technique and showed that carbon dioxide and secondary amines are released.

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1. Introduction

Generally, linear polyurethanes (PUs) are obtained by the reaction between an oligomeric diol (low molecular weight polymer with terminal hydroxyl groups), a short diol as chain extender and a diisocyanate. To prepare cross-linked PUs, polyols or isocyanates with functionality higher than 2 can be used. However the use of diisocyanate should be avoided for several reasons. Isocyanate reactants are generally very harmful for human health, particularly for people exposed during polyurethanes synthesis and could entail adverse health effects such as asthma, dermatitis, conjunctivitis and acute poisoning [1]. Therefore the synthesis of PUs, from step growth polyaddition of dicyclocarbonates and diamines should be favored. This method is particularly interesting since no hazardous isocyanates are used. Thus, this old reaction is currently gaining a lot of attention as a substitution route for the synthesis of PUs [2–9].

Following this route, polyhydroxyurethanes (PHUs) are obtained with inter- and intramolecular hydrogen bonds, which are expected to present higher chemical and hydrolysis resistances.

We previously reported several works on the synthesis of new dicyclocarbonates by esterification of diacids such as terephthalic acid with glycerol carbonate. These works led to the synthesis of PHUs with ester bonds which exhibited poor stability towards hydrolysis [10,11]. We overcame this issue with the synthesis of dicyclocarbonates from allyl-cyclic carbonate and dithiols by thiol–ene coupling [12]. But these dicyclocarbonate were based on aliphatic structures. Yet, PUs contain generally rigid segments made of aromatic groups such as toluene diisocyanate (TDI), which is a hazardous compound. Therefore we intended to synthesize new biobased PHU with rigid segments and with ether bonds. Isosorbide is obtained from the dehydration of sorbitol, which is a product of the sugar industry and contains two cycloaliphatic rings likely to provide a good rigidity to the polymer. Its structure is also composed of two secondary hydroxyl groups.

Isosorbide is a biobased platform chemical extensively studied in literature with various industrial applications (isosorbide nitrate, diesters, lubricant and plasticizers, green solvents, etc.) [13–16]. It has to be noticed that the synthesis of the corresponding isosorbide amine and isocyanate was already reported [17–19]. Applications of isosorbide in polymers and materials are even more important and are summarized in Scheme 1. As depicted, a lot of derivatives

* Corresponding author. Tel.: +33 467144300; fax: +33 467147220.

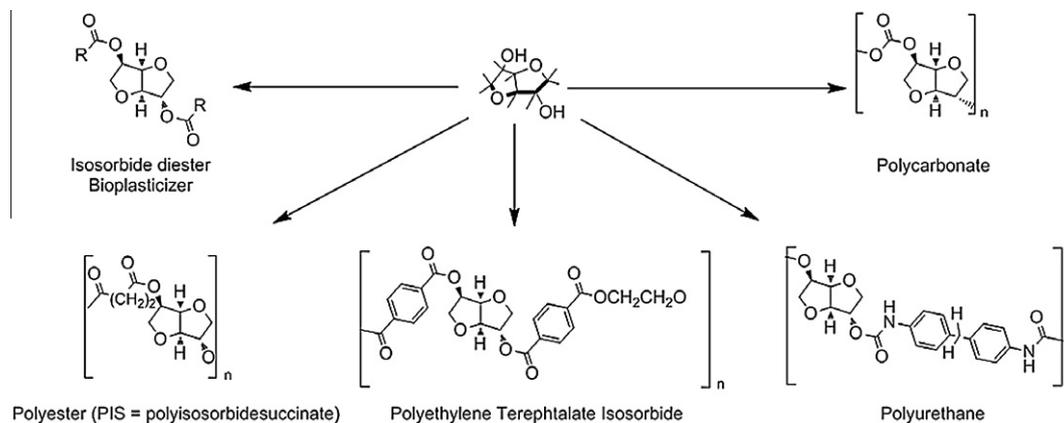
E-mail addresses: carlotti@enscbp.fr (S. Carlotti), belkacem.otazaghine@mines-ales.fr (B. Otazaghine), bernard.boutevin@enscm.fr (B. Boutevin).

¹ Tel.: +33 4677144305; fax: +33 467147220.

² Tel.: +33 540002734.

³ Tel.: +33 466785669.

⁴ <http://www.specificpolymers.fr>.



Scheme 1. Isosorbide based polymers.

could be synthesized such as polyesters [13,20] polytriazoles [21–23] and polycarbonates [24–26,33]. A recent patent reports the synthesis of polycarbonates from isosorbide. However, few works deal with PUs synthesis from isosorbide [27]. A first study was reported by Dirlikov and Schneider [28]. Then other teams reported the use of isosorbide for the synthesis of PUs with high glass transition temperature (T_g) values, from 80 to 240 °C (Table S1, Supporting information) [29–31]. These works show that isosorbide leads to rigid PUs with T_g values higher than those obtained from other diols such as butanediol, neopentyl glycol, dihydroxymethylcyclohexane) and reveals the interest of isosorbide for industrial PUs.

These results led Cognet-Georjon et al. to use isosorbide for rigid segments of PUs with longer diols such as hydroxylated polybutadiene for the soft segments [30]. Most of PUs from isosorbide are synthesized by reaction between isosorbide and methylenediphenyl-4,4'-diisocyanate (MDI) which is a carcinogenic mutagenic reprotoxic (CMR) compound [32]. This drawback reduces the interest of using isosorbide as a biobased diol and led to the synthesis of PHUs thereof. Moreover, PU materials for coatings should have a T_g around or below 0 °C which is not described in the literature.

The synthesis of PHUs from step growth polyaddition of dicyclocarbonates and diamines was extensively reported in literature, particularly by Endo [3,4,6,34,35]. Indeed, several cyclocarbonates were synthesized and some PHUs were thereof characterized [35–38]. Several methods are used to synthesize five-membered cyclic carbonates [39–44]. Most of these methods are based on epoxide or diol reactants. This is also the case of dicyclocarbonate syntheses [6,20,45–47]. Two bis and polycarbonates families were reported in the literature. The first one is constituted of carbonate esters from glycerin carbonate, the second one is constituted of carbonate ethers from glycidyl ether carbonatation [10,11]. In a recent paper, Brocas et al. [48] have reported the synthesis of cyclocarbonates using mild conditions to synthesize crosslinked polyethers (Scheme S1, Supporting information). Cyclocarbonate groups were synthesized by carbonatation of the corresponding epoxide groups using a low carbon dioxide pressure (1 bar) and a catalytic amount of lithium bromide (LiBr) at 80 °C.

Our work aims to synthesize new cyclocarbonate from isosorbide by carbonatation. The originality of this work consists not only in the synthesis of isosorbide dicyclocarbonate but also in the elaboration of original building block to synthesize low T_g PHU, designed for coating applications, whereas isosorbide was exclusively used for high T_g in literature. Moreover, we studied the thermal degradation of PHUs and the compounds resulting of degradation, which was never studied to the knowledge of the authors. To the best of our knowledge, no paper or even patent reports the synthesis of these new PHUs, synthesized according the concept of “green chemistry”.

2. Experimental section

2.1. Materials

Isosorbide, epichlorohydrin, lithium bromide and 1,10-diaminododecane were purchased from Sigma Aldrich and used as received. *N,N*-dimethylformamide (DMF) was purchased from SDS Carlo Erba (Val de Reuil, France). Before use, DMF was dried according to current methods, distilled and stored under argon atmosphere. Deuterated solvents (CDCl_3 and $\text{DMSO}-d_6$) were purchased from Eurisotop (Saint-Aubin, France).

2.2. Synthesis

2.2.1. Epoxy index determination

The epoxy index (EI) is defined by the mass of monomer containing one mole of epoxide group. This index was determined by an acid–base titration. Epoxide groups were ring-opened by an excess of hydrochloric solution and this excess was determined by titration with a sodium hydroxide solution with phenolphthalein as a color indicator.

2.2.2. Isosorbide diglycidyl ether (E1)

In a two necks round bottom flask equipped with an addition funnel, isosorbide (8.5 g, 37.6 mmol) and chloroform (50 mL) were introduced. Then, *m*-chloroperbenzoic acid (47.2 g, 273.4 mmol) solubilized in chloroform (200 mL) beforehand, was introduced in the funnel and added dropwise. The mixture was stopped after 16 h when no more double bond signals were found in ^1H NMR. The organic layer was washed three times: first with Na_2SO_3 , then Na_2CO_3 and water. Organic layers were put together and the solvent removed under reduced pressure. The crude was purified by column chromatography under silica (eluent: ethyl acetate). Evaporation of the solvent with a rotary evaporator gave the corresponding product (5 g, 14.2 mmol) as yellowish viscous oil.

Yield: 38%

^1H NMR (400.1 MHz, CDCl_3 , δ): 2.50–2.58 (m, 2H, H_{1a} & H_{2a}); 2.72–2.76 (m, 2H, H_{1b} & H_{2b}); 3.04–3.17 (m, 2H, H_{2a} & H_{11a}); 3.29–3.42 (m, 2H, H_{2b} & H_{11b}); 3.51–3.59 (m, 2H, H_{3a} & H_{10a}); 3.72–3.81 (m, 2H, H_{3b} & H_{10b}); 3.85–4.05 (m, 6H, $\text{H}_{\text{isosorbide cycle}}$); 4.46 (ddt, 1H, $^3J_{\text{HH}} = 4.4$ Hz, $^3J_{\text{HH}} = 11.6$ Hz, $^4J_{\text{HH}} = 1.2$ Hz, H_6); 4.60 (ddt, 1H, $^3J_{\text{HH}} = 4.4$ Hz, $^3J_{\text{HH}} = 8.4$ Hz, $^4J_{\text{HH}} = 1.6$ Hz, H_7).

^{13}C NMR (100.6 MHz, CDCl_3 , δ): 44.4 (C_1 & C_{12}); 50.9 (C_2 & C_{11}); 70.4 (C_5 & C_8); 73.5 (C_3 & C_{10}); 80.6 (C_4 & C_9); 86.0 (C_6 & C_7).

2.2.3. Isosorbide diglycidylether oligomers (E2 and E3)

In a round bottom flask equipped with an addition funnel and a reverse Dean Stark surmounted by a condenser, isosorbide (1 eq.)

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