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To cite this version:

Vincent Besse, Rémi Auvergne, Stéphane Carlotti, Gilles Boutevin, Belkacem Otazaghine, et al.. Synthesis of isosorbide based polyurethanes: An isocyanate free method. Reactive and Functional Polymers, 2013, 73, pp.588-594. 10.1016/j.reactfunctpolym.2013.01.002 . hal-00785178

HAL Id: hal-00785178

https://hal.science/hal-00785178

Submitted on 24 May 2022

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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, France[4]
[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

A B S T R A C T

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 ^{1}H 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.

Keywords:
Polyhydroxyurethane
Isosorbide
Renewable resources
Thermal stability
Carbonate

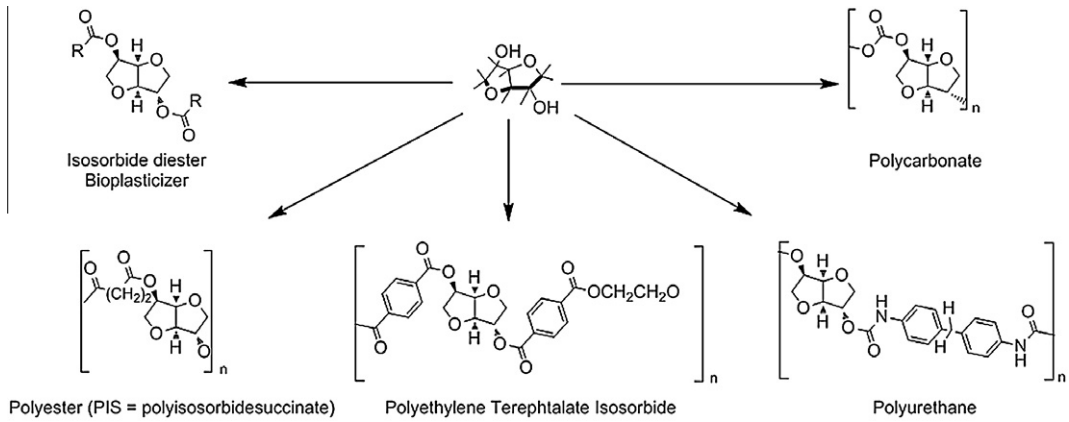
1. Introduction

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).



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-diaminodecane 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 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 ^{1}H 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%

^{1}H 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, $H_{isosorbide\ cycle}$); 4.46 (ddt, 1H, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 11.6 Hz, $^4J_{HH}$ = 1.2 Hz, H_6); 4.60 (ddt, 1H, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 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.)

and epichlorohydrin (10 eq.) were introduced. A sodium hydroxide solution (2.3 eq.) in water (50/50:wt/wt) was prepared and placed in the addition funnel. The mixture was heated at 115 °C under argon atmosphere. The sodium hydroxide solution was added dropwise. The reaction was stopped when no longer water was collected in the Dean Stark apparatus, after approximately 6 h. The mixture was then allowed to stay at room temperature and epichlorohydrin was added to precipitate NaCl. After filtration, the epichlorohydrin was removed by evaporation under reduced pressure to give the desired product as yellowish viscous oil.

Yield: 98% (epoxide/isosorbide = 1.24). Dosage: 216 g/eq. epoxide rating: 4.63 meq/g (monomer).

2.2.4. Carbonatation reaction: general procedure for DC1–DC3

An epoxidized isosorbide (10.0 mmol of epoxide groups) and LiBr (0.5 mmol, 5% mol) were dissolved in dimethylformamide (DMF, 45 mL). The solution was introduced into a reactor and the atmosphere was replaced with CO_2 (P = 6 bars). The solution was then allowed to stand at 80 °C with continuous stirring during 12 h. DMF was removed by distillation (60 °C, P = 0.01 bar). The pure product was obtained quantitatively as yellowish highly viscous oil.

FTIR (ν, cm^{-1}) = 1780 (CO), 2860 and 2890 (C—C).

2.2.5. Polyhydroxyurethane (PHU1–PHU6) syntheses: general procedure

Step growth polyaddition of dicyclocarbonates (**DC1–2**) (1 eq.) was realized with diamines (1 eq.) and a catalyst (in a course of patent registration) under stirring in distilled DMF (2 mL) and argon atmosphere during 12 h at room temperature [49]. At the end of reaction, the formed polymers are still soluble. **PHU1–6** polymers, soluble in DMF, were precipitated in water (these PHUs are not soluble in it). After drying by filtration then centrifugation, **PHU1–6** were quantitatively obtained. Both synthesized PHUs were characterized by ^{1}H NMR spectrometry, FTIR analysis and SEC in DMF. Only ^{1}H NMR spectra of the corresponding polyhydroxyurethane **PHU2** is reported.

FTIR (ν, cm^{-1}) = 1534 and 3082 (NH); 1694 (CO); 3328 (NH).

2.3. Analytical techniques

All Nuclear magnetic resonance (^{1}H NMR) measurements were recorded on a Brucker AC-400 MHz spectrometer at room temperature in deuterated chloroform ($CDCl_3$) or dimethylsulfoxyde (DMSO). The chemical shifts were reported in parts per million relative to tetramethylsilane.

IR spectra were recorded with a Nicolet 210 FT-IR spectrometer.

Differential scanning calorimetry (DSC) analyses were performed under inert atmosphere with a calorimeter DSC 200F3 from Netzsch calibrated with indium standard. The polymer was weighted in an aluminum pan and consecutively placed in the measurement heating cell. An empty pan was used as reference. All the samples were heated under inert atmosphere from −120 to 100 °C at a heating rate of 20 °C/min. Three runs were recorded and the glass transition temperature (T_g) values were measured during the second run and confirmed by a third run. T_gs were calculated at the inflexion point of the heat capacity jump.

Thermogravimetric analyses (TGAs) were performed using a TGA Q50 W/MFC apparatus of TA Instruments under air and nitrogen flow (25 ml/min) from room temperature to 500 °C at a heating rate of 5 °C/min^{-1}. The analysis consisted in registering the weight loss of the sample as a function of temperature.

Size exclusion chromatography (SEC) was performed on a Varian ProStar Model 210 equipped with an RI refractive index detector. Two PLgel 5 μm MIXED-C 600 mm were used at 70 °C with a 0.8 mL min^{-1} flow rate of DMF, calibrated using PMMA standards.

3. Results and discussion

Firstly, isosorbide was converted into epoxidized oligoisosorbide and then into cyclocarbonate oligoisosorbide by a carbonatation reaction. Then the corresponding PHUs were synthesized by reaction with synthesized dicyclocarbonates and diamines. Their spectral and physical characterizations as well as the formation of the polymer network were investigated. The last part of the article is dedicated to the degradation study of PHUs by performing ATG-IR analyses in order to analyze the released products.

3.1. Synthesis of isosorbide diglycidylether oligomers (E1–3)

This part focuses on the synthesis of diglycidylether from three different isosorbide reactants with various lengths. Epoxidized isosorbide **E1** was synthesized by allylation of isosorbide followed by its epoxydation using *m*-chloroperbenzoic acid. Isosorbide oligomers **E2** and **E3** were obtained by reaction of epichlorohydrin with isosorbide at room temperature. Monomers **E2** and **E3** are different by the length of the spacer between the two epoxide functions; this aspect will be discussed below (Scheme 2).

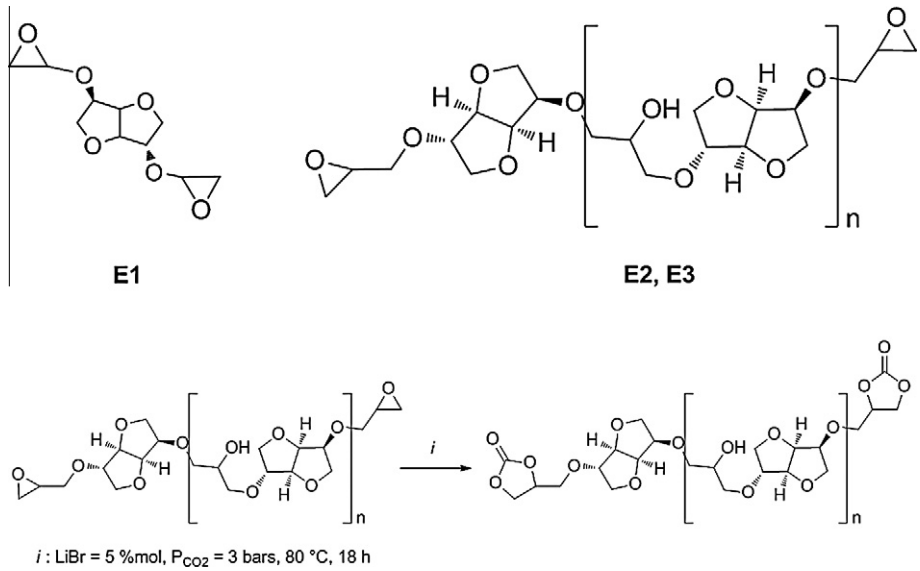
Two epoxidized oligoisosorbides **E2** and **E3** were obtained with an epoxy index respectively of 4.13 meq/g and 2.9 meq/g (Fig. 1). The ratio R of epoxy cycle to isosorbide cycle is given by the ratio between the integration of the epoxide protons (H_{1a-b} and H_2) and the isosorbide protons (H^*) following the method described by Chrysanthos et al. [50]. Both ratio R obtained by NMR spectroscopy and titration are in agreement either for epoxidized oligoisosorbide **E2** and oligoisosorbide **E3** (Table 1). Chrysanthos et al. [50] mentioned other linear and branched oligomers. Branched oligomers can be explained by a competition during the reaction with epichlorohydrin, between the secondary hydroxyl groups of isosorbide and the secondary hydroxyl groups formed after a first reaction of isosorbide diglycidyl ether with isosorbide. It means that some oligomers can have more than two glycidyl groups.

3.2. Synthesis of dicyclocarbonates DC1–3

The dicyclocarbonates **DC1**–**3** were synthesized by carbonatation of isosorbide diglycidyl ether oligomers **E1**–**3**. This reaction was carried out owing to Brocas et al. [48] conditions during 18 h. Total conversion was confirmed by the total disappearance of the protons of the epoxide moiety between 2.56 and 2.82 ppm and also by the appearance of signals corresponding to the carbonate protons between 4.20 and 4.88 ppm (Fig. 1).

3.3. Polyurethanes synthesis (PHU1-6)

Then, step growth polyadditions of **DC1**–**2** with commercial diamines were carried out in presence of a catalyst (in a course of patent registration) and yielded **PHU1–6** PHUs at room temperature (Table 2). The various diamine backbones are expected to provide a large range of mechanical properties to the PHUs. This part is focused on the development of polymers for coatings so that one of the absolutely desirable milestones is a T_g below 0 °C. According to the theory, a more flexible carbon chain should provide a lower T_g. The reaction between a cyclocarbonate and a diamine leads to two regioisomers depending on the carbonate position attacked by the amine. Isomers such as primary/primary alcohol, primary/secondary alcohol and secondary/secondary alcohol were obtained [51]. We firstly report the results obtained with oligomers **DC2** and **DC3** when polymerized with DA10. The analyses show the high reactivity of the reactants, the mechanical properties of the PHUs but also the effect of the oligomer length on these properties. These two PHUs (**PHU2**–**3**) were characterized by ^{1}H NMR, FTIR and SEC analyses.



Scheme 2. Idealized structure of glycidylisosorbide oligomers and synthesis of isosorbidedicyclocarbonates by carbonatation.

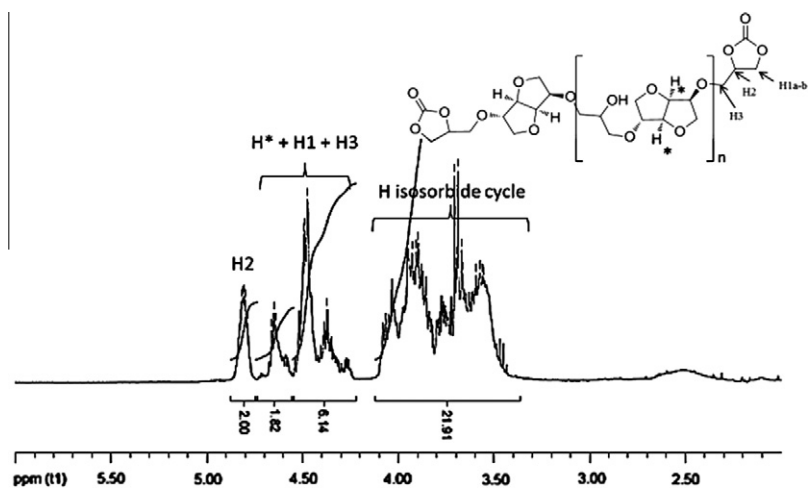


Fig. 1. ^{1}H NMR spectrum of carbonated oligoisosorbide **DC2**.

Table 1
Determination of *R* using ^{1}H NMR.

	E2	E3
Protons	*I* (Integration value)	*I* (Integration value)
H1a + H1b	1.00 + 1.02	1.00 + 0.88
H2	1.03	0.96
H* (isosorbide cycle)	0.84 + 0.85	1.12 + 1.16
Ratio *R*	1.20	0.83
Ratio *R* (titration)	1.24	0.88
n	0.66	1.32
Molar mass (g mol^{-1})	392	524

Table 2
Table of composition of **PHU1-6.**

Isosorbide	Amines	PHUs
DC1	DA10	**PHU1**
DC2	DA10	**PHU2**
	IPDA	**PHU4**
	DETA	**PHU5**
	JEFF400	**PHU6**
DC3	DA10	**PHU3**

^{1}H NMR spectrum of synthesized **PHU2** is confirmed by the formation of carbamate group with signal of proton H—NCOO at 7.10 ppm [52] and alcohol at 4.40 ppm (Fig. 2).

FTIR spectrum confirms the formation of **PHU2** with the three characteristic bands of carbamate function: N—H bond stretching vibration, hydrogen bonded C=O stretching and N—H bond deformation are respectively observed at 3082 cm^{-1}, 1694 cm^{-1} and 1534 cm^{-1}. The large absorption of the hydroxyl group OH at 3328 cm^{-1} also appeared. Moreover, the absence of the absorption band of the carbonyl of the carbonate group at 1785 cm^{-1} reveals a total conversion of initial carbonated isosorbide (Fig. S1, Supporting information).

Size exclusion chromatography (SEC) analyses have been performed on **PHU2** and **PHU3**. Molecular weights were found to be quite low, M_n (7800 and 8600 g/mol for **PHU2** and **PHU3** respectively) and PDI were quite high (2.6 and 6.3 for **PHU2** and **PHU3** respectively) (Fig. S2 and Table S2, Supporting information).

The properties of these synthesized polyurethanes are similar to those found for isosorbide based polyurethanes described by Cognet-Georjon et al. [15] especially concerning the low value obtained for M_n. The high value of PDI and low molecular weight is certainly due the presence of initial branched oligomers which are insoluble

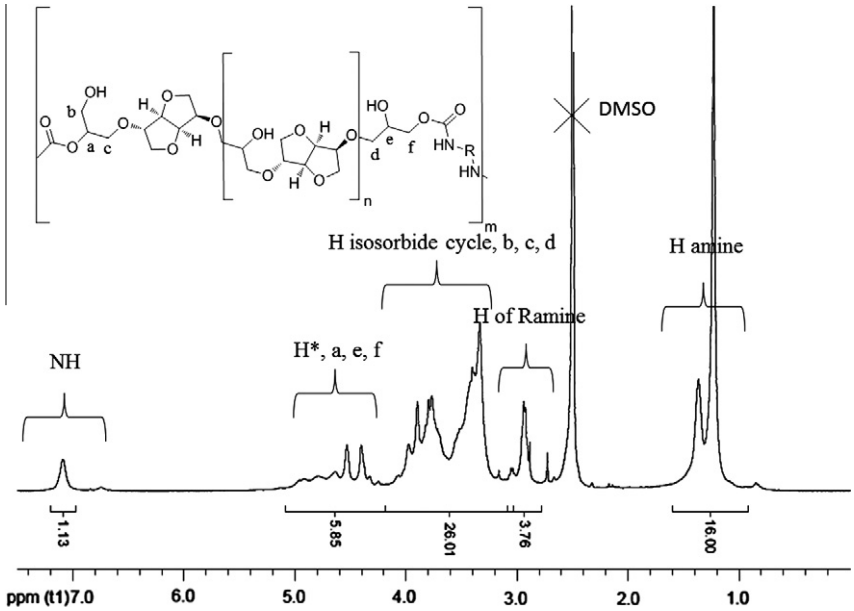


Fig. 2. ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of **PHU2**.

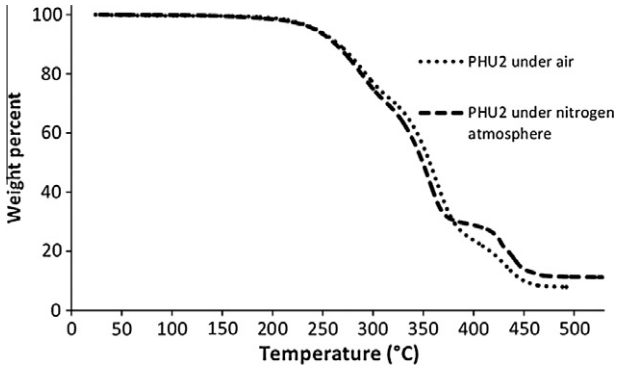
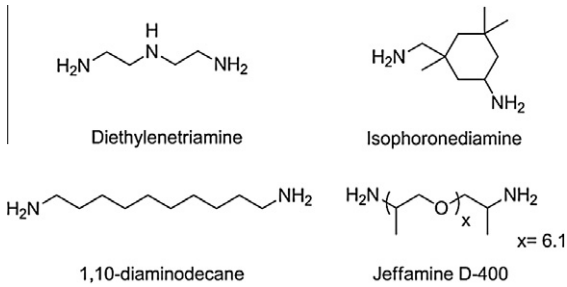


Fig. 3. TGA spectrum of **PHU2** under air and nitrogen atmosphere.



Scheme 3. Structures of amines used in this study.

in DMF and can interact intensively with the GPC column. Both **PHU2** and **PHU3** are amorphous as determined by DSC analysis (Fig. S3, Supporting information). They exhibit similar T_g values of 15 and 19 °C respectively. Compared to the previous results found in the literature (Table S1, Supporting information), and especially those with the aliphatic diisocyanate, hexamethylene diisocyanate (HDI), the first addition of glycidyl functions on the isosorbide before the synthesis of bis-carbonate can explain the lower T_g observed and the increase softness of PHUs.

Table 3
Thermal properties of **PHU2** and **PHU4-6.**

Oligomer	Amines	PHUs	Td 5% (°C)	T_g (°C)
DC2	IPDA	**PHU4**	255	59
	DA10	**PHU2**	243	15
	DETA	**PHU5**	234	0
	JEFF400	**PHU6**	242	−8

TGA analysis shows a 5% mass loss (Td 5%) at 243 and 237 °C for **PHU2** and **PHU3** respectively. The thermal degradation with formation of volatiles of the two PHUs is similar and proceeds in three steps under air as well as under nitrogen atmosphere (Fig. 3).

For example, for **PHU2**, the first step between 180 and 310 °C corresponds to a 28% weight loss. Then the second step, between 342 and 379 °C corresponds to a 48% weight loss. The third step between 420 and 451 °C corresponds to a 48% weight loss and the residue represents 11 wt.% of the initial weight at 500 °C. In both cases, no difference between oxidative or inert atmosphere was found so that no oxidation phenomenon occurs. The weakest bond is supposed to be the urethane one (E_{C-NH} = 98 kJ/mol) and its degradation is supposed to be the same under oxygen and nitrogen atmosphere [53].

The next part of this article is devoted to the study of the diamine structure effect. Since the oligomer length shows no evidence in modifying the final polymer properties, the next part of the study will focus on PHUs obtained from **DC2** and three other diamines e.g. Jeffamine D-400, diethylenetriamine and isophoronediamine (Scheme 3 and Table 2).

We first studied the thermal properties (Td 5% and T_g) of **PHU4–6**. Due to the rigid structure of IPDA, the T_g obtained for **PHU4** (59 °C) is higher than the one obtained with DA10 and other diamines. Then DETA, a soft aliphatic triamine, allows **PHU5** to reach a T_g of 0 °C. The last amine, Jeffamine D-400, is a long polyether chain diamine which confers high flexibility and toughness to **PHU6** so that its T_g is the lowest (−8 °C) (Table 3).

This result is compatible with a use in coatings. DMF and DMSO appear to be the best solvent as all materials are soluble in it whereas none of them are soluble in water (Table S3, Supporting information).

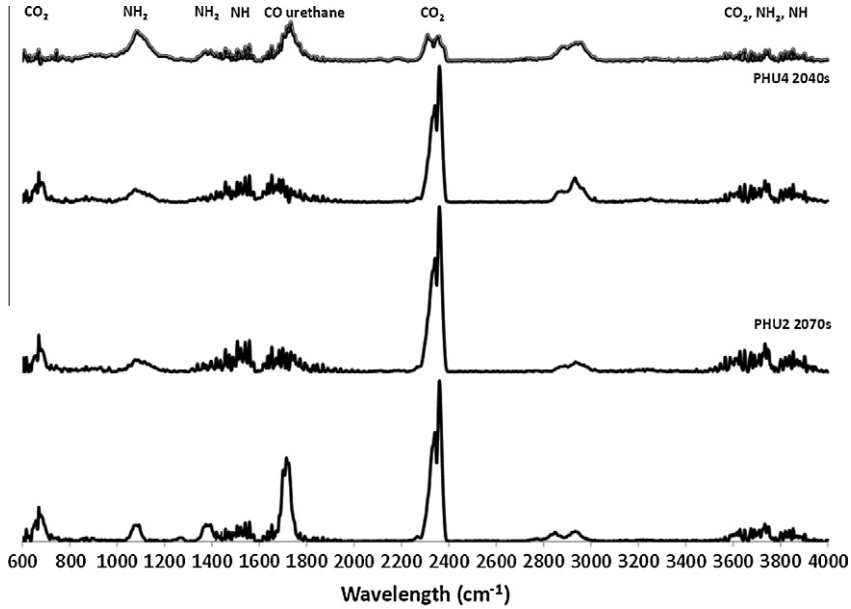


Fig. 4. ATG-IR analysis of **PHU2** and **PHU4**.

The last part of our study is dedicated to the characterization of the released compounds during the degradation process of PHUs by the ATR-IR technique (Fig. 4). The decomposition of urethane bonds is depending on the structures of the reactants which were used for their synthesis. If the first decomposition is due to hard segments, the second and third decompositions were attributed to soft segments. Javni et al. have demonstrated that the first degradation step for polyurethanes from functionalized vegetable oils was the production of carbon dioxide. This carbon dioxide was suspected to come from the formation of carbodiimides but more credibly from the disruption of the urethane bond following mechanisms 2 and 3 [54].

PHU2 and **PHU4** were typically introduced into an ATG instrument and the released gases were analyzed by an infra-red apparatus after a given time (Fig. 4). After only 495s, the first degraded bond is the carbonyl of the urethane function ($\nu_{\mathrm{COurethane}}$ = 1720 - cm^{-1}) as expected [53]. Carbon dioxide and secondary amine bands (ν_{CO_2} = 670, 2320, 3700 cm^{-1} and ν_{NH} = 1095, 1490, 3800 cm^{-1}).

Alkane groups, probably PHUs spacers, were detected by the presence of two large bands between 2800 and 3000 cm^{-1}. Except the carbonyl urethane group, the same bands can be observed along the thermal analysis (i.e. CO_2 and NH bands). **PHU4** gave same results as **PHU2** concerning the degradation products. Moreover, we can clearly see that no isocyanate, alcohol or alkene were formed during the degradation process so that we can clearly demonstrate that PHUs degradation products are CO_2 and secondary amines. This result is of importance since it shows that not only PHUs are synthesized without isocyanates, but also they do not lead to isocyanate during thermal degradation.

4. Conclusions

Isosorbide was functionalized with glycidyl ether groups and the quantity of epoxide groups was determined by a titration. Results obtained by titration were in agreement with those obtained by ^{1}H NMR spectroscopy. Then functionalized oligoisosorbides were carbonated for the first time using mild conditions with a total conversion. This work led to the synthesis of new biobased PHUs using the cyclocarbonate-aliphatic amine chemistry in the presence of a catalyst. This reaction was found to be very effective as the reaction of cyclocarbonate groups is completed within 12 h. Linear and branched PHUs were obtained with T_g values in the range from −8 to 59 °C, and low T_g PHUs are suitable for coatings application. An acceptable thermal stability (Td between 234 and 255 °C) was determined owing to TGA for all PHUs. This work demonstrates that biobased PHUs can be obtained easily from isosorbide as hard segment and with ether bonds. Works are in progress for a better control of molecular weight and polydispersity. Last but not least, the compounds released by the degradation of PHUs were analyzed and found to be carbon dioxide and secondary amines. Interestingly, these new PHUs do not release isocyanates during thermal degradation. Choices of other aliphatic biobased diamines, shorter one like C5 or longer one like C36 will permit to prepare hard and soft PHUs.

Acknowledgements

This work was supported by ANR project GreenCoat. The authors also thank Specific Polymers for the synthesis of isosorbide diglycidyl ether compounds under the reference SP 9S-5-001.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2013.01.002.

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