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Facile route to multigram synthesis of environmentally friendly non-isocyanate polyurethanes

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ABSTRACT

Non-isocyanate poly(hydroxyurethanes) (NIPUs) are a fast growing class of polymers prepared by an environmentally friendly method without the use of toxic phosgene and isocyanates. In this work, we report a one-step procedure to synthesize bis(2,3-dihydroxypropyl)ether dicarbonate from a commercially available diglycerol. The product was characterized by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopies and for the first time by X-Ray diffraction measurements. Enantiomers RR and SS of the obtained monomer were observed in the single crystal structure. The bis(cyclic carbonate) monomer was used as a precursor for the synthesis of various NIPUs. The NIPUs were prepared in a non-solvent process. Spectral, thermal and rheological properties of the NIPUs formed from ten various diamines were compared.

1. Introduction

Polyurethanes (PU) are polymers widely used in many applications, i. e. foams, coatings, adhesives and isolations [1]. Conventional polyurethanes are prepared in the polyaddition reaction of isocyanates and polyols. Common isocyanates such as 4,4′-methylenediphenyl diisocyanate (MDI) and toluidene diisocyanates (TDI) are reported to be harmful. Most of isocyanates are carcinogenic, reprotoxic, mutagenic and some of them are in the Annex 17 of REACH. They can enter the body through inhalation, open wounds, eye contact, or mouth by swallowing or with contaminated food and drink or by smoking [2,3]. Moreover, the isocyanates are produced with the use of harmful phosgene. Due to the stringent regulations of the European Union to ensure a high level of protection of health and the environment, many of these processes are required to adapt to the new rules [4] Taking into account awareness of the need to ensure the safety of the staff as well as consumers, there is a demand for environment-friendly processes and products. Those concerns have led to the development of alternative ways of polyurethane synthesis. A majority are based on carbon dioxide as a sustainable feedstock that can be applied directly or indirectly [2].

Alternatives to conventional polyurethane non-isocyanate polyurethanes (NIPUs) are obtained by the polyaddition of poly(cyclic carbonate)s with polyamines, typically bi-functional monomers [5–9]. During this reaction, in theory, no by-products are produced [10], which is also desirable from the ecological point of view. Therefore, NIPUs are safe alternative to conventional polyurethanes derived from toxic and unstable isocyanates [11]. Furthermore, NIPUs can be characterized by greater thermal stability and higher chemical resistance [12].

As a result of the addition of amine species to cyclic carbonate, urethane and hydroxyl groups are formed. The pendant hydroxyl groups present in each repeating unit of the NIPU allow for further modifications and enable tailoring of a polymer's properties for a specific purpose [13–23]. Another advantage of NIPUs is their lack of chemically unstable alophanate and biuret end-groups [24]. On the other hand, the application of NIPUs is limited by a 15–35 fold higher absorption of water in comparison to conventional PUs [25].

NIPUs can be prepared from bis(cyclic carbonate)s consisting of five-, six- and seven-membered carbonate rings of the same or different types. Cyclic carbonates are known from 1930s [26–28] and nowadays they are the subject of intensive research [29]. Among them, five-membered rings are the least reactive, while six- and seven-membered cyclic carbonates react readily [25]. Usually five-membered bis(cyclic carbonate)s react slowly with diamines under moderate conditions leading to poly(hydroxyurethanes) of

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lower average molecular weight in comparison to commercial PUs. Five-membered carbonates are thermodynamically stable and do not homopolymerize [30,31]. Due to their stability, five-membered bis(cyclic carbonate)s can be easily obtained in high yields. They are commonly synthesized by transesterification of 1,2-diols with dialkyl carbonates, the addition of CO_2 to oxiranes or 1,2-halohydrins with bicarbonates [32,33]. A number of methods are known for the preparation of five-membered bicyclic carbonates [33,34].

Among them some are based on environmentally benign glycerol carbonate. Bis(cyclic carbonate)s containing terephthalic acid have been synthesized in two different ways. Steblyanko et al. reacted terephthalic acid chloride with glycidol yielding a diglycidyl terephthalate that was further reacted with CO_2 under atmospheric pressure using LiCl (5 mol%) as a catalyst at 100 °C [35,36]. A newer one-step synthetic procedure for this compound used terephthalic acid, glycerol carbonate and *N*,*N*'-dicyclohexylcarbodiimide (DCC) as starting materials [37]. An allyl ether of glycerol carbonate was used for the synthesis of bis(cyclic carbonate)s *via* a thiol-ene coupling reaction [38]. Hanada et al. elaborated several cyclic carbonate terminated polydimethylsiloxane resins for the preparation of NIPUs [39]. Annunziata et al. synthesized a series of α,ω-bis(glycerol carbonate) telechelic polymers based on poly(propylene glycol) (PPG), poly(ethylene glycol) (PEG), poly(ester ether) (PEE), and poly(butadiene) (PBD) through chemical modification of the corresponding α,ω-dihydroxy telechelic polymers [14]. A simple method to synthesize biodegradable poly(trimethylene carbonate) based five membered bis(cyclic carbonate)s was also presented by Guillaume et al. [40,41]. Biobased bis(cyclic carbonates) synthetized from sugars or vanillin and then used as a monomer for non-isocyanate polyurethanes synthesis has been also reported [42,43].

Glycerol is a by-product of biodiesel preparation. However, nowadays the worldwide production of glycerol is more than 1.5 million tones and the global demand is much lower [44]. Diglycerol is the simplest derivative of cheap glycerol. It founds application in food, cosmetics such as soaps, tooth pastes and chemical applications, i.e performance additives for printing inks [44,45]. Glycerol and diglycerol are cheap intermediate used for obtaining bio-based materials. Moreover, the main advantage of glycerol and its derivative is low price, biodegrability and environmental friendliness. Diglycerol offered by Solvay S.A. is technical grade (>90%) containing the isomers of diglycerol: *α*,*α*-diglycerol, *α*,*β*-diglycerol *β*,*β*-diglycerol and cyclic diglycerols. Furthermore, no procedure of obtaining pure fractions of diglycerol have been reported.

NIPUs obtained from five-membered bis(cyclic carbonate)s have already been studied in the literature; however the monomers were expensive and recovered by multistep reactions, often with low yield [25,46]. In this work, we present a simple, one-step synthesis of bis(cyclic carbonate) that can be adapted on the industrial scale and subsequently applied for the preparation of non-isocyanate polyurethanes. The proposed bis(2,3-dihydroxypropyl) ether dicarbonate was prepared from a bio-based raw material — diglycerol. The bis(cyclic carbonate) monomer was then reacted with various aliphatic and aromatic diamines yielding NIPUs. The spectral, thermal and rheological properties of the obtained polymers were investigated.

2. Materials and methods

2.1. Chemicals

Diglycerol (*α*,*α*-diglycerol ~84%, *α*,*β*-diglycerol ~14%, *β*,*β*-diglycerol <1%, cyclic diglycerols ~0.2%) was a gift from Solvay S.A. (Brussels, Belgium). 1,2-Diaminoethane (99.5%), 1,4-diaminobutane (99%), 1,6-diaminohexane (98%), 1,8-diaminooctane (98%), 1,12-diaminododecane (98%), 1,8-diamino-3,6-dioxaoctane (98%), 4,7,10-trioxa-1,13-tridecanediamine (97%), poly(propylene glycol) bis(2-aminopropyl ether) M_n~230 (total amines 8.1 meq/g), poly(propylene glycol) bis(2-aminopropyl ether) M_n~400 (total amines 1.64 meq/g), and 1,3-bis(aminomethyl)benzene (99%) were purchased from Aldrich Chemical (Poznan, Poland) and used as received. Solvents were purchased from POCh (Gliwice, Poland) and dried prior to use.

2.2. Instrumentation

FTIR spectra were recorded on a Biorad FTS-165 FTIR spectrometer as KBr pellets or an Bruker ALPHA FTIR spectrometer equipped with a Platinum ATR single reflection diamond ATR module. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal standard and deuterated solvents ($CDCl_3$, DMSO-d_6) and analyzed with MestReNova v.6.2.0—7238 (Mestrelab Research S.L) software. The X-ray measurement was performed at 100(2)K on a Bruker D8 Venture Photon 100 CMOS diffractometer equipped with a mirror monochromator and a CuKα INCOATEC IμS micro-focus source (λ = 1.54178 Å). The raw frame data were collected using the Bruker APEX2 program [47], while the frames were integrated with the Bruker SAINT software package [48] using a narrow-frame algorithm integration of the data and were corrected for absorption effects using the multi-scan method (SADABS) [49]. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in their calculated positions and refined within the riding model. The atomic scattering factors were taken from the International Tables [50]. Molecular graphics was prepared using the Diamond 3.2 program [51]. Thermal ellipsoid parameters were presented at a 50% probability level. MALDI-TOF measurements were performed on a Bruker UltraFlex MALDI TOF/TOF spectrometer (Bremen, Germany) in a linear or reflectron mode using a DHB (2,5-dihydroxybenzoic acid) or HABA (2-(4'-hydroxybenzeneazo) benzoic acid matrix and Bruker Peptide Calibration Standard (1047.19—3149.57 Da) as a calibrant and analyzed with flexAnalysis v.3.3 (Bruker Daltonik GmbH) and Polymerix v. 2.0 (Sierra Analytics Inc.) software.

Calorimetric studies of obtained **2** and NIPUs were carried out with differential scanning calorimetry (DSC) on TA Instruments Q2000 apparatus and with thermogravimetric analysis (TGA) on TA Instruments SDT Q600 apparatus, with the heating rate in both cases equal to 10 K min^{-1}.

Polymer viscosity measurements were performed on a Malvern Kinexus Pro rheometer (Malvern, England) in the parallel plate geometry (gap 0.3 mm). A standard mass of the sample (0.3 g) was placed symmetrically in the center of the plate. The shear stress was measured at a constant shear rate, $\gamma = 4\ s^{-1}$ in 2 min. The measurements were repeated twice with new sampling at 120 °C.

2.3. Synthesis procedure

2.3.1. Synthesis of five-membered bis(cyclic carbonate), (**2**)

1000 g (6.02 mol) of diglycerol (a mixture of isomers) was placed in a 5 L three neck round bottom flask equipped with a magnetic stirrer, a thermometer and a reflux condenser, followed by 3210 g (35.6 mol, 3 L) of dimethyl carbonate and 5 g (36 mmol) of K_2CO_3. The reaction mixture was heated at 70 °C for 24 h. Then 1.8 L of the mixture of dimethyl carbonate and methanol was distilled off at atmospheric pressure at 65 °C over a period of 6 h. Then the reaction mixture was cooled down to room temperature. The precipitated catalyst was filtered off and washed with dimethyl carbonate. The combined organic phases were evaporated to dryness and crystallized from ethyl acetate. A total of 876 g (4.01 mol) of **2** was obtained as a white solid with 79% yield (with respect to *α,α*-diglycerol).

Yield 876 g (79%); mp 66–67 °C (lit [52]. 62–64 °C); density 1.4981 ± 0.022 g/mL. ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 4.98–4.89 (m, 2H, $\mathrm{CH_2C\underline{H}CH_2}$), 4.52 (t, 2H, J = 8.5 Hz, $\mathrm{OC\underline{H}_{2\ cycl.}}$), 4,28–4.20 (m, 2H, $\mathrm{OC\underline{H}_{2\ cycl.}}$), 3.79–3.72 (m, 2H, $\mathrm{OC\underline{H}_2}$), 3.71–3.64 (m, 2H, $\mathrm{OC\underline{H}_2}$)); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 154.8 ($\mathrm{\underline{C}{=}O}$), 75.4 ($\mathrm{\underline{C}H}$), 70.4 ($\mathrm{\underline{C}H_{2\ cycl.}}$), 65.9 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 2994, 2927, 2886, 1785, 1486, 1372, 1343, 1252, 1177, 1148, 1113, 1057, 959, 855, 770, 714, 598.

Crystal data for **2** (enantiomers): orthorombic, P b c a, $a = 7.6790(8)$ Å, $b = 11.7916(12)$ Å, $c = 20.679(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 1872.4(3)$ Å^3 $Z = 8$, $\mu = 1.219$ mm^{-1}, $D_{\mathrm{calc}} = 1.548$ g/cm^3, 13 108 reflection measured ($4.28 \le 2\Theta \le 70.05°$), 1783 independent ($\mathrm{R_{(int)}} = 0.0444$). The final R_1 was 0.0396 ($I > 2\sigma(I)$) and wR2 was 0.1065 (all data).

2.3.2. Hydrolysis of five-membered bis(cyclic carbonate)

(1a) In a 100 mL round bottom flask equipped with a magnetic stirrer and a reflux condenser, 10 g (45.9 mmol) of bis(cyclic carbonate) **2** was placed followed by 50 mL of methanol, 50 mL of water and 2 g (14.5 mmol) of potassium carbonate. The resulting mixture was stirred at reflux for 2 h. The mixture was evaporated to dryness. The residue was dissolved in methanol. The solid salt was filtrated off and the solution evaporated to dryness yielding 7.54 g (99%) of tetrol **1a** as a light viscous oil.

Yield 7.54 g (99%); density 1.2961 ± 0.022 g/mL.; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 4.65 (d, 2H, J = 4.8 Hz, $\mathrm{O\underline{H}}$), 4.51 (t, 2H, J = 5.8 Hz, $\mathrm{O\underline{H}}$), 3.60–3.49 (m, 2H, $\mathrm{CH_2C\underline{H}CH_2}$), 3.45–3.22 (m, 8H, $\mathrm{OC\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 72.9 ($\mathrm{O\underline{C}H_2}$), 70.5 ($\mathrm{\underline{C}H}$), 63.1 ($\mathrm{\underline{C}H_2OH}$); FTIR (KBr): ν (cm^{-1}) = 3364, 2922, 2880, 1659, 1130, 1042, 931, 867.

*2.3.3. Synthesis of model adduct of bis(cyclic carbonate) 2 with butylamine, (**3**)*

21.8 g (0.1 mol) of bis(cyclic carbonate) was placed in a 250 mL round bottom flask equipped with a mechanical stirrer and a nitrogen inlet. The solid was melted under nitrogen atmosphere at 70 °C. Then 36.6 g (0.5 mol) of *n*-butylamine was added in portions during 30 min. The reaction mixture was stirred at 80 °C for 8 h. The reaction mixture was cooled down, the excess amine was evaporated and the product was crystalized from diethyl ether.

Yield 31.4 g (86%); mp 107–108 °C; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.11 (t, $\mathrm{N\underline{H}_{(E)}}$, 1.8H, J = 5.7 Hz), 6.7 (bs, 0.2H, $\mathrm{N\underline{H}_{(Z)}}$), 4.92 (d, 2H, $\mathrm{O\underline{H}}$, 5.1 Hz), 3.92 (dd, 2H, $\mathrm{C\underline{H}_2O(CO)}$, J_1=11.0 Hz, J_2=4.7 Hz), 3.84 (dd, 2H, $\mathrm{C\underline{H}_2O(CO)}$, J_1=11.0 Hz, J_2=6.2 Hz), 3.78–3.68 (m, 2H, $\mathrm{C\underline{H}}$), 3.41–3.30 (m, 4H, $\mathrm{C\underline{H}_2OCH_2}$), 2.95 (q, 2H, $\mathrm{C\underline{H}_2NH}$, J = 6.7 Hz), 1.41–1.20 (m, 8H, $\mathrm{C\underline{H}_2}$), 0.85 (t, 6H, $\mathrm{C\underline{H}_3}$, J = 7.3 Hz); ^{13}C NMR (DMSO-d_6, 100 MHz); δ (ppm) = 156.3 ($\mathrm{\underline{C}{=}O}$), 72.7 ($\mathrm{\underline{C}H_2O\underline{C}H_2}$), 67.9 ($\mathrm{\underline{C}H}$), 65.5 ($\mathrm{\underline{C}H_2O(CO)}$), 40.0 ($\mathrm{\underline{C}H_2NH}$), 31.6 ($\mathrm{\underline{C}H_2}$), 19.5 ($\mathrm{\underline{C}H_2}$), 13.8($\mathrm{\underline{C}H_3}$); FTIR (KBr): ν (cm^{-1}) = 3320, 2958, 1690, 1673, 1555, 1283, 1260.

2.3.4. General procedure for the preparation of non-isocyanate polyurethanes (NIPUs)

NIPUs were synthesized by the reaction of five-membered bis(cyclic carbonate) **2** with various diamines. 54.5 g (0.25 mol) of bis(cyclic carbonate) was placed in a 250 mL round bottom flask equipped with a mechanical stirrer and a nitrogen inlet. The solid was melted under nitrogen atmosphere at 80 °C. Then 0.25 mol of an appropriate diamine (see Table 1) was added in portions during 30 min and the temperature increased up to 150 °C. The reaction mixture was stirred at this temperature for 8 h. Then the reaction mixture was cooled down and the polymers analyzed without further purification.

NIPU 1; Yield 99.5%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.08 (bs, 1.82H, $\mathrm{N\underline{H}_{(E)}}$), 6.76 (bs, 0.18H, $\mathrm{N\underline{H}_{(Z)}}$), 4.98 (bs, 1.4H, $\mathrm{O\underline{H}}$), 4.79 (bs, 0.6H, $\mathrm{O\underline{H}}$), 4.68 (bs, 0.8H, $\mathrm{C\underline{H}O(CO)N}$), 3.98–3.78 (m, 2.5H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.78–3.66 (m, 1.4H, $\mathrm{C\underline{H}OH}$), 3.56–3.21 (m, 5.3H, $\mathrm{C\underline{H}_2O}$), 3.00 (bs, 4H, $\mathrm{C\underline{H}_2NH}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.4, 156.0 ($\mathrm{\underline{C}{=}O}$), 73.3, 72.6, 72.5, 69.9, 69.8, 67.8, 65.6, 60.1 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.2 ($\mathrm{\underline{C}H_2NH}$); FTIR (KBr): ν (cm^{-1}) = 3337, 2944, 2878, 1786, 1697, 1533, 1262, 1140, 776.

NIPU 2; Yield 99%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.11 (bs, 1.82H, $\mathrm{N\underline{H}_{(E)}}$), 6.75 (bs, 0.18H, $\mathrm{N\underline{H}_{(Z)}}$), 4.91 (bs, 1.3H, $\mathrm{O\underline{H}}$), 4.76 (bs, 0.7H, $\mathrm{O\underline{H}}$), 4.62 (bs, 0.8H, $\mathrm{C\underline{H}O(CO)N}$), 3.95–3.77 (m, 2.5H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.77–3.66 (m, 1.4H, $\mathrm{C\underline{H}OH}$), 3.60–3.20 (m, 5.3H, $\mathrm{C\underline{H}_2O}$), 2.93 (bs, 4H, $\mathrm{C\underline{H}_2NH}$), 1.34 (bs, 4H, $\mathrm{C\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.3, 156.0 ($\mathrm{\underline{C}{=}O}$), 73.3, 72.7, 72.6, 70.0, 67.9, 65.5, 60.1 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.0 ($\mathrm{\underline{C}H_2NH}$), 29.6 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 3341, 2932, 2869, 1786, 1698, 1534, 1452, 1254, 1136, 775.

NIPU 3; Yield 98%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.09 (bs, 1.83H, $\mathrm{N\underline{H}_{(E)}}$), 6.73 (bs, 0.17H, $\mathrm{N\underline{H}_{(Z)}}$), 4.95 (bs, 1.5H, $\mathrm{O\underline{H}}$), 4.77 (bs, 0.5H, $\mathrm{O\underline{H}}$), 4.66 (bs, 0.7H, $\mathrm{C\underline{H}O(CO)N}$), 3.96–3.78 (m, 2.7H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.78–3.67 (m, 1.5H, $\mathrm{C\underline{H}OH}$), 3.55–3.25 (m, 5.1H, $\mathrm{C\underline{H}_2O}$), 2.97–2.86 (m, 4H, $\mathrm{C\underline{H}_2NH}$); 1.35 (bs, 4H, $\mathrm{C\underline{H}_2}$), 1.20 (bs, 4H, $\mathrm{C\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.4, 156.0 ($\mathrm{\underline{C}{=}O}$), 73.1, 73.0, 72.7, 72.6, 70.5, 70.0, 69.8, 67.9, 65.5, 63.0, 60.2 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.3 ($\mathrm{\underline{C}H_2NH}$), 29.5, 26.1 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 3338, 2933, 2861, 1786, 1699, 1538, 1458, 1258, 1137, 777.

NIPU 4; Yield 98%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.10 (bs, 1.82H, $\mathrm{N\underline{H}_{(E)}}$), 6.75 (bs, 0.18H, $\mathrm{N\underline{H}_{(Z)}}$), 4.92 (bs, 1.6H, $\mathrm{O\underline{H}}$), 4.75 (bs, 0.4H, $\mathrm{O\underline{H}}$), 4.61 (bs, 0.8H, $\mathrm{C\underline{H}O(CO)N}$), 3.97–3.76 (m, 2.7H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.78–3.67 (m, 1.5H, $\mathrm{C\underline{H}OH}$), 3.58–3.23 (m, 5.0H, $\mathrm{C\underline{H}_2O}$), 2.97–2.86 (m, 4H, $\mathrm{C\underline{H}_2NH}$); 1.35 (bs, 4H, $\mathrm{C\underline{H}_2}$), 1.20 (bs, 8H, $\mathrm{C\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.3, 155.9 ($\mathrm{\underline{C}{=}O}$), 73.0, 72.9, 72.7, 72.6, 70.5, 70.4, 69.9, 67.8, 66.0, 65.5, 60.1 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.8 ($\mathrm{\underline{C}H_2NH}$), 29.3, 28.8, 26.5 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 3335, 2927, 2857, 1786, 1699, 1533, 1464, 1255, 1136, 779.

NIPU 5; Yield 98%^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.08 (bs, 1.85H, $\mathrm{N\underline{H}_{(E)}}$), 6.73 (bs, 0.15H, $\mathrm{N\underline{H}_{(Z)}}$), 4.92 (bs, 1.55H, $\mathrm{O\underline{H}}$), 4.74 (bs, 0.45H, $\mathrm{O\underline{H}}$), 4.65 (bs, 0.6H, $\mathrm{C\underline{H}O(CO)N}$), 3.94–3.77 (m, 2.9H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.77–3.65 (m, 1.5H, $\mathrm{C\underline{H}OH}$), 3.54–3.23 (m, 5.0H, $\mathrm{C\underline{H}_2O}$), 2.99–2.86 (m, 4H, $\mathrm{C\underline{H}_2NH}$); 1.35 (bs, 4H, $\mathrm{C\underline{H}_2}$), 1.22(bs, 12H, $\mathrm{C\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.3, 155.9 ($\mathrm{\underline{C}{=}O}$), 73.1, 72.7, 72.5, 70.2, 70.4, 69.9, 67.8, 66.3, 60.1 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.3 ($\mathrm{\underline{C}H_2NH}$), 29.5, 29.1, 28.8, 26.3 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 3335, 2921, 2851, 1788, 1697, 1538, 1468, 1245, 1143, 778.

NIPU 6; Yield 96%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.12 (bs, 1.81H, $\mathrm{N\underline{H}_{(E)}}$), 6.76 (bs, 0.19H, $\mathrm{N\underline{H}_{(Z)}}$), 4.94 (bs, 1.3H, $\mathrm{O\underline{H}}$), 4.74(bs, 0.7H, OH), 4.65 (bs, 0.7H, $\mathrm{C\underline{H}O(CO)N}$), 3.99–3.79 (m, 2.6H, $\mathrm{C\underline{H}_2O}$), 3.79–3.65 (m, 1.5H, $\mathrm{C\underline{H}OH}$), 3.56–3.21 (m, 13.2H, $\mathrm{C\underline{H}_2O}$), 3.16–3.04 (m, 4H, $\mathrm{C\underline{H}_2NH}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.3, 156.0 ($\mathrm{\underline{C}{=}O}$), 73.3, 72.6, 72.5, 69.9, 69.8, 69.5, 69.1, 67.7, 65.5, 60.1 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 40.1 ($\mathrm{\underline{C}H_2NH}$); FTIR (KBr): ν (cm^{-1}) = 3339, 2938, 2875, 1787, 1699, 1533, 1458, 1257, 1121, 1049, 776.

NIPU 7; Yield 97%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.10 (bs, 1.83H, $\mathrm{N\underline{H}_{(E)}}$), 6.75 (bs, 0.17H, $\mathrm{N\underline{H}_{(Z)}}$), 4.88 (bs, 2H, $\mathrm{O\underline{H}}$), 4.65 (bs, 0.7H, $\mathrm{C\underline{H}O(CO)N}$), 3.97–3.78 (m, 2.7H, $\mathrm{C\underline{H}_2O}$), 3.78–3.66 (m, 1.6H, $\mathrm{C\underline{H}OH}$), 3.57–3.23 (m, 17H, $\mathrm{C\underline{H}_2O}$), 3.16–3.04 (m, 4H, $\mathrm{C\underline{H}_2NH}$), 1.65–1.54 (m, 4H, $\mathrm{C\underline{H}_2}$); ^{13}C NMR (DMSO-$d_6$, 100 MHz); δ (ppm) = 156.1, 155.8 ($\mathrm{\underline{C}{=}O}$), 73.0, 72.9, 72.6, 72.4, 70.4, 68.0, 67.7, 67.5, 65.4, 63.0, 60.0 ($\mathrm{\underline{C}H_2O}$ and $\mathrm{\underline{C}HO}$), 37.6 ($\mathrm{\underline{C}H_2NH}$), 29.7 ($\mathrm{\underline{C}H_2}$); FTIR (KBr): ν (cm^{-1}) = 3335, 2932, 2874, 1787, 1699, 1538, 1446, 1257, 1118, 1049, 775.

NIPU 8; Yield 99%; ^{1}H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.01 (bs, 1.79H, $\mathrm{N\underline{H}_{(E)}}$), 6.64 (bs, 0.21H, $\mathrm{N\underline{H}_{(Z)}}$), 4.92 (bs, 2H, $\mathrm{O\underline{H}}$), 4.67 (bs, 0.8H, $\mathrm{C\underline{H}O(CO)N}$), 4.00–3.75 (m, 2.9H, $\mathrm{C\underline{H}_2OC\underline{H}_2}$), 3.75–3.69 (m, 1.5H, $\mathrm{C\underline{H}OH}$), 3.69–2.85 (m, 29.8H, $\mathrm{C\underline{H}_2O}$ and

Table 1
Amounts of amines used for NIPU synthesis.

Entry	NIPU	Diamine	Amount (g)
1	NIPU1	1,2-Diaminoethane	15.1
2	NIPU2	1,4-Diaminobutane	22.3
3	NIPU3	1,6-Diaminohexane	29.6
4	NIPU4	1,8-Diaminooctane	36.8
5	NIPU5	1,12-Diaminododecane	51.1
6	NIPU6	1,8-Diamino-3,6-dioxaoctane	37.8
7	NIPU7	4,7,10-trioxa-1,13-tridecanediamine	56.7
8	NIPU8	Poly(propylene glycol) bis(2-aminopropyl ether) M_n~230	61.7
9	NIPU9	Poly(propylene glycol) bis(2-aminopropyl ether) M_n~400	121.8
10	NIPU10	1,3-Bis(aminomethyl)benzene	34.4

$C\underline{H}_2NH$), 1.1–0.85 (m, 21H, $C\underline{H}_3$); ^{13}C NMR (DMSO-d_6, 100 MHz); δ (ppm) = 155.7, 155.4 ($\underline{C}{=}O$), 75.0–72.9(m), 73.2–71.3(m), 70.5, 69.9, 67.8, 65.5, 63.1, 60.1 ($\underline{C}H_2O$ and $\underline{C}HO$), 46.5, 46.3, 46.0, 44.9, 44.7, 44.5 ($\underline{C}H_2NH$), 19.9, 18.3, 17.6, 17.1 ($\underline{C}H_3$); FTIR (KBr): ν (cm^{-1}) = 3348, 2971, 2932, 2874, 1787, 1699, 1651, 1551, 1452, 1371, 1254, 1108, 779.

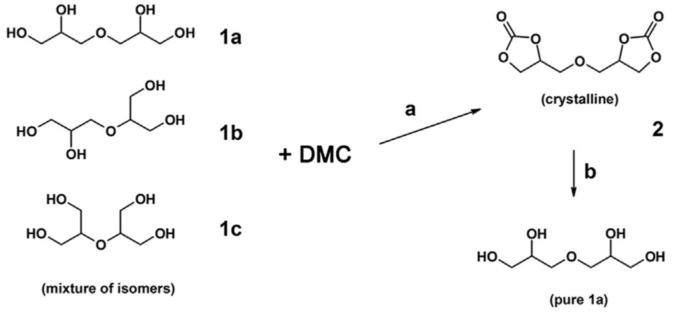
NIPU 9; Yield 99%; ^1H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.00 (bs, 1.92H, $N\underline{H}_{(E)}$), 6.60 (bs, 0.08H, $N\underline{H}_{(Z)}$), 4.95 (bs, 1.5H, $O\underline{H}$), 4.81 (bs, 0.5H, $O\underline{H}$), 4.67 (bs, 0.7H, $C\underline{H}O(CO)N$), 3.94–3.76 (m, 2.8H, $C\underline{H}_2OC\underline{H}_2$), 3.76–3.65 (m, 1.5H, $C\underline{H}OH$), 3.65–2.80 (m, 40.9H, $C\underline{H}_2O$ and $C\underline{H}_2NH$), 1.2–0.83 (m, 32H, $C\underline{H}_3$); ^{13}C NMR (DMSO-d_6, 100 MHz); δ (ppm) = 155.6, 155.3 ($\underline{C}{=}O$), 74.7–74.0(m), 73.3–71.3(m), 70.5, 69.9, 67.8, 65.5, 63.1, 60.0 ($\underline{C}H_2O$ and $\underline{C}HO$), 46.5, 46.4, 46.2, 44.9, 44.7, 44.6 ($\underline{C}H_2NH$), 19.9, 18.2, 17.6, 17.3, 17.1 ($\underline{C}H_3$); FTIR (KBr): ν (cm^{-1}) = 3332, 2971, 2932, 2873, 1788, 1706, 1534, 1457, 1374, 1242, 1107, 778.

NIPU 10; Yield 96%; ^1H NMR (DMSO-d_6, 400 MHz); δ (ppm) = 7.69 (bs, 2H, $\underline{H}_{Ar}$), 7.34–7.04 (m, 3.81H, $\underline{H}_{Ar}$ and $N\underline{H}_{(E)}$), 6.43 (bs, 0.19H, $N\underline{H}_{(Z)}$), 4.99 (bs, 1.2H, $O\underline{H}$), 4.82(bs, 0.8H, $O\underline{H}$), 4.71 (bs, 0.6H, $C\underline{H}O(CO)N$), 4.23–4.11 (m, 4H, $C\underline{H}_2NH$), 4.01–3.83 (m, 2.8H, $C\underline{H}_2O$), 3.83–3.67 (m, 1.4H, $C\underline{H}OH$), 3.52–3.31 (m, 5.2H, $C\underline{H}_2O$); ^{13}C NMR (DMSO-d_6, 100 MHz); δ (ppm) = 156.5, 156.2 ($\underline{C}{=}O$), 139.8, 128.3, 125.8, 125.5 ($\underline{C}_{Ar}$), 73.4, 72.6, 70.5, 69.9, 67.8, 65.7, 63.0, 60.2 ($\underline{C}H_2O$ and $\underline{C}HO$), 43.9 ($\underline{C}H_2NH$); FTIR (KBr): ν (cm^{-1}) = 3335, 3061, 2926, 1788, 1699, 1609, 1533, 1258, 1134, 776.

3. Results and discussion

3.1. Synthesis of bis(cyclic five-membered carbonate)

Bis(2,3-dihydroxypropyl)ether dicarbonate, **2**, was prepared by a reaction of commercially available diglycerol (Solvay) and dimethyl carbonate (Scheme 1). Typically, the starting diglycerol is a mixture containing $\alpha,\alpha-$, $\alpha,\beta-$ and $\beta,\beta-$diglycerols and a cyclic glycerol. The reaction of such a mixture with dimethyl carbonate in the presence of potassium carbonate yields a mixture of bis(cyclic carbonate)s. However, a simple crystallization from ethyl acetate allowed the selective separation of a single isomer, an $\alpha,\alpha-$diglycerol derivative **2**. It was possible to obtain **2** with a 79% yield. In contrast, the multistep procedure described previously in the literature yielded 32% of the product [52] or 56% [53]. Moreover, **2** can be achieved using as-synthesized hydrotalcites with varying magnesium-to-aluminum ratios or lanthanide oxide as catalyst materials with comparable yield as presented by us [54,55]. The method presented in this paper is based on cheap, harmless and easily accessible potassium carbonate as catalyst. Furthermore, this method allows us to obtain **2** at lower temperatures in contrast to the method presented in Ref. [53].



Scheme 1. Synthesis and hydrolysis of 2. Reaction conditions: a) DMC, K_2CO_3; b) MeOH, H_2O, K_2CO_3.

Subsequent hydrolysis of the product provided pure $\alpha,\alpha-$diglycerol. The simplicity of this procedure allows for a large-scale, selective separation of one of the diglycerol isomers.

The formation of the five-membered cyclic carbonates was followed by FTIR spectroscopy. The FTIR spectrum of the final bis(-cyclic carbonate) **2** is shown in Fig. 1. It shows a characteristic absorption band corresponding to the five-membered cyclic carbonate carbonyl group at 1785 cm^{-1} and no absorption band for the hydroxyl groups.

The ^1H NMR spectrum of **2** showed a pattern characteristic of mono-substituted 1,3-dioxolan-2-one rings. The methine proton signals are located at approx. 4.95 ppm and appear as a multiplet.

The endo-cyclic methylene group protons have different chemical surroundings and appear as two pairs of doublets. Due to the overlapping, one of them resembles a triplet (4.5 ppm). The other one is located at approx. 4.25 ppm. Similarly, the exo-cyclic methylene group signals appear as two pairs of doublets in the range of 3.8–3.6 ppm. The spectrum also contains a second set of signals of lower intensity (marked in Fig. 2), since diastereoisomers are possible. The low intensity signals can be assigned to a *R,S*-isomer.

The ^{13}C NMR spectrum consisting of four signals confirmed the presence of a carbonyl group carbon and three carbons located next to an oxygen atom.

The structure of the product **2** was further determined by single-crystal X-ray diffraction. The crystallographic details can be found in the Electronic Supplementary Materials file. Single crystals of **2** were obtained by recrystallization from the ethyl acetate solution. Interestingly, enantiomers (*R,R* and *S,S*) of **2** were observed. **2** crystallized in a centrosymmetric, orthorhombic system with space symmetry Pbca as a colorless prism for enantiomers *R,R* and *S,S*, respectively. The X-Ray crystal structure of **2** is presented in Fig. 3. The r.m.s. deviations from planarity for the five-membered cyclic carbonate ring was equal to 0.060 Å. The bond lengths C=O varied from 1.1947(18) to 1.1968(18) Å.

The thermal properties of **2** were characterized by DSC and TGA (see in Figs. 3S and 4S in Supplementary Materials). **2** exhibited stability up to about 200 °C; the melting point of **2** was 65.9 °C. Two

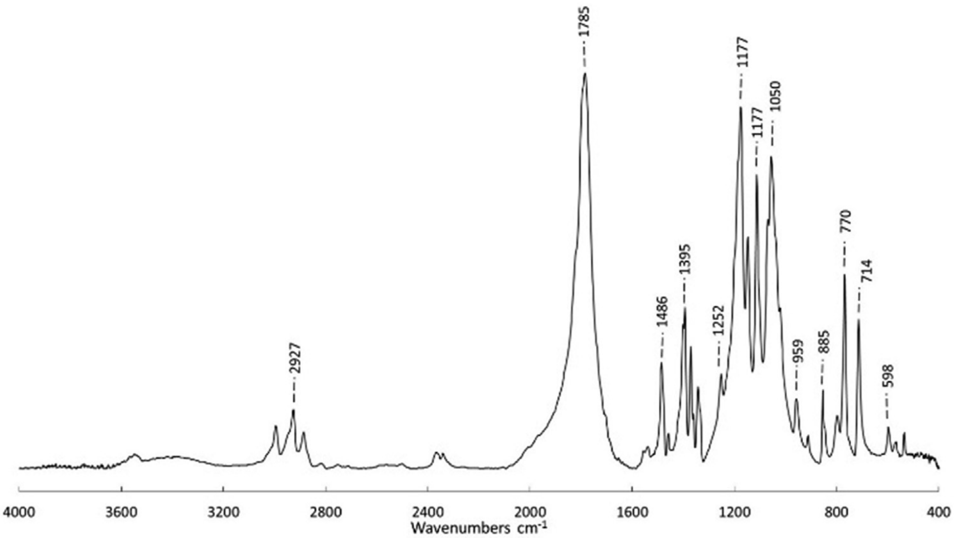


Fig. 1. FT-IR spectrum of bis(2,3-dihydroxypropyl)ether dicarbonate **2**.

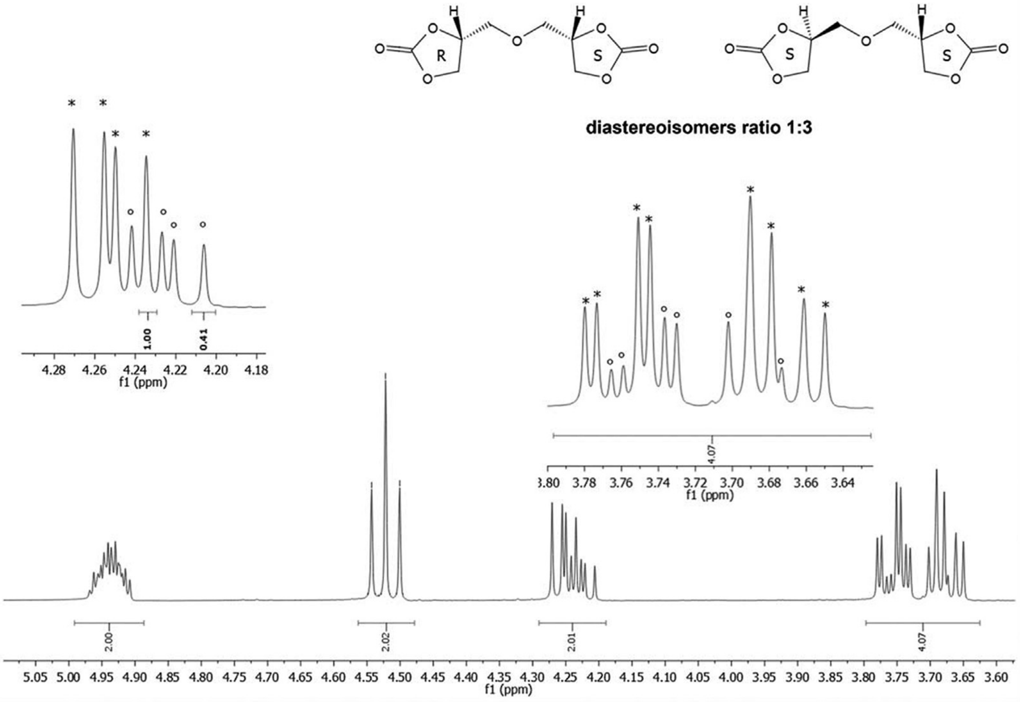


Fig. 2. ^{1}H NMR spectra of bis(2,3-dihydroxypropyl)ether dicarbonate **2** diastereoisomers.

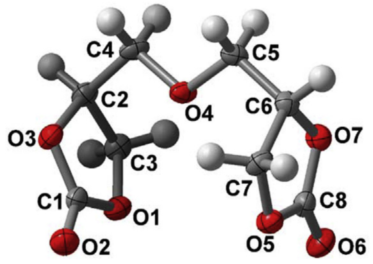
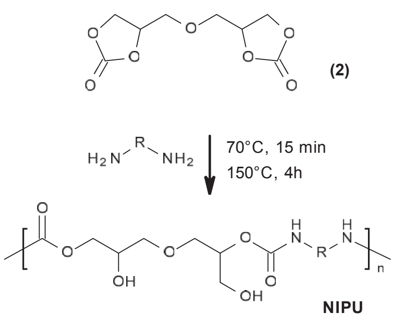


Fig. 3. X-Ray structure of bis(2,3-dihydroxypropyl)ether dicarbonate **2**.



Scheme 2. Synthesis of NIPUs from 2 and various diamines.

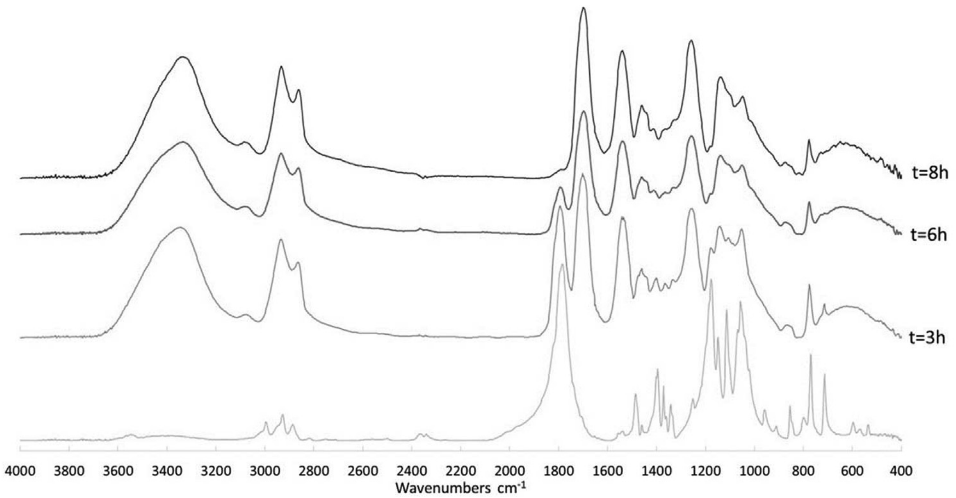
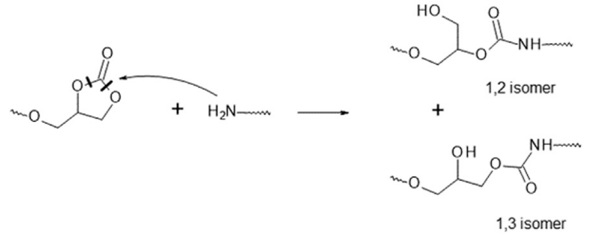


Fig. 4. FT-IR spectra of formation of NIPU3 from 2 and hexamethylenediamine.

different regions can be observed on the TGA curve. The first step of decomposition observed from 200 to 265 °C is endothermic, accompanied by a 77% mass loss and with T_{onset} 259 °C and a maximum decomposition temperature $T_{\max} = 284$ °C. The second step observed from 300 to 450 °C refers to a 22% mass loss. The two-step decomposition of **2** indicates that there are a minimum of two competitive or consequential reactions. In order to accurately determine the melting temperature of **2,** measurements by



Scheme 3. Reaction of cyclic carbonate with an amine. Formation of isomers.

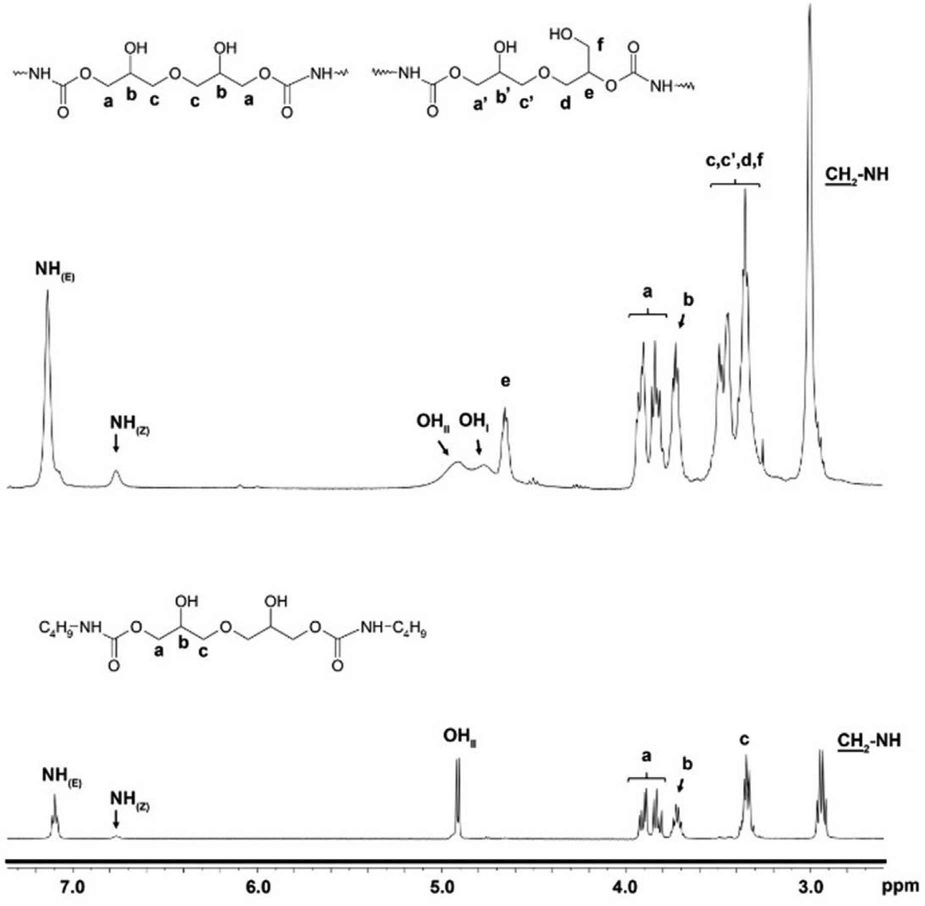


Fig. 5. The ^{1}H NMR (DMSO-d$_6$, 400 MHz) spectrum of the NIPU1 polymer compared to the model compound **3**.

differential scanning calorimetry were performed. The melting process started at temperature T_{onset} = 65.7 °C with a maximum temperature T_{max} = 65.9 °C.

3.2. Synthesis and properties of NIPUs

The obtained bis(cyclic carbonate) **2** was used as a monomer for the synthesis of non-isocynate poly(hydroxyurethane)s *via* a polyaddition reaction with various diamines: aliphatic ones, oligoetherdiamines and, for comparison, aromatic diamines (Scheme 2). The polyaddition reactions were carried out by a solvent-free and catalyst-free method, resulting in various polyurethanes with different backbones. Furthermore, the advantage of the obtained NIPUs was their complete or partial solubility in water in contrast to the NIPUs already presented in the literature [4]. NIPUs, obtained by us, may have find potentials application in environmentally friendly water-based, VOCs free, coatings varnishes or inks.

The reaction of **2** with diamines was monitored by IR spectroscopy. Fig. 4 shows the FT-IR spectra before and after the polyaddition. During the reaction the strongest peak at 1785 cm^{-1} assigned to the cyclic carbonyl group disappeared and new peaks appeared that are typical of hydroxyurethane (3350, 1700 and 1540 cm^{-1}) and N—H deformation of urethane groups (1540 cm^{-1}).

Five-membered cyclic carbonates react with primary amines yielding β-hydroxyurethanes. In this reaction two isomers are formed. They are presented in Scheme 3. Thus, in the case of bis(cyclic carbonate)s, three different structures are possible. They can contain two isomers of the same type (1,3 isomers or 1,2 isomers) or be built of one 1,3 isomer and one 1,2 isomer. The ^1H NMR spectra showed that the majority of the bis β-hydroxyurethane units contained two 1,3-isomers. In the case of the small molecule model compound 3-(2,3-dihydroxypropoxy)propane-1,2-diol bis(butylcarbamate) (**3**) it was possible to obtain product consisting solely of 1,3-isomers. However, in the case of polymers, units containing one 1,3 and one 1,2 isomer were also obtained in large amounts. The signals of the most sterically hindered units containing two 1,2 isomers in the repeating unit are barely visible.

Fig. 5 shows the diglycerol repeating unit region of the ^1H NMR spectrum typical for all of the synthesized poly(β-hydroxyurethanes). The spectra showed the presence of the urethane NH protons. They appear as two singlets due to the hindered rotation of the (CO)-N bond and they are not sensitive to the means of substitution of the diglycerol units. The free hydroxyl groups appear in the range of 5.2 to 4.8 ppm as two broad separate signals for secondary and primary OH groups. In some cases the OH protons are not distinguishable and appear as a single broad peak. In the spectrum separate groups of peak signals of methylene groups **a** and methine groups **b** and **e** can also be seen. The rest of the diglycerol unit peaks appear as a multiplet in the range of 3.55 to 3.20 ppm. The methylene group next to the urethane nitrogen atom

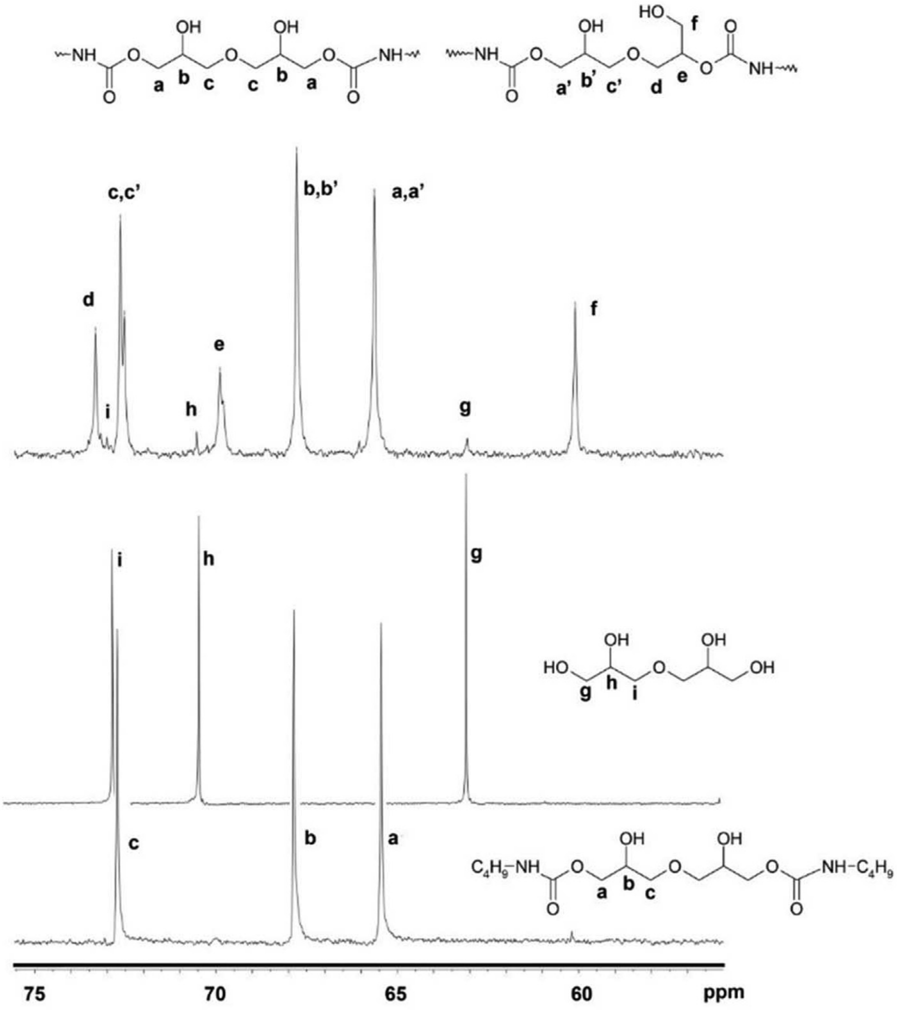


Fig. 6. NIPU1 Typical pattern of ^{13}C NMR signals of the diglycerol unit depending on the method of substitution.

usually appears at approx. 2.9 ppm. Other signals are related to the type of diamine used.

Fig. 6 presents the signal assignments for the diglycerol peaks in the range of the ^{13}C NMR spectra of the poly(β-hydroxyurethanes). It confirms that the polymer contains diglycerol units substituted by urethane bonds in both the primary and secondary OH group positions (1,3 and 1,2 isomers, see Scheme 1). In addition, the polymers show two carbonyl carbon signals for the 1,3 and 1,2 isomeric structures.

Fig. 7 shows a typical pattern of the MALDI-TOF spectra of non-isocyanate polyurethane NIPU1. The polymer sample was intentionally treated with water to allow the polymer to solubilize in the THF/water mixture. The spectrum shows four sets of signals that can be assigned to: one amine and one triol terminated macromolecule (Fig. 7, A), one amine and one cyclic carbonate terminated macromolecule (Fig. 7, B), and molecules with two amines ((Fig. 7, C) and two triol (Fig. 7, B) terminal groups. The figure shows only the simplified structures of the polymer and the terminal groups (no regioisomers are shown). The presence in the spectrum of the triol terminal groups in the product most probably is a result of earlier hydrolysis.

It is interesting that the molecular weights of the statistically most probable molecules containing one amino and one cyclic carbonate terminal group (Fig. 7, B) are the same as those of cyclic products. So it is not possible to estimate the degree of cyclization during the NIPU synthesis.

The thermal properties of the obtained NIPUs were characterized by DSC and TGA (see Table 2). It was expected that the T_g values depend on the chemical structure of the NIPU, specifically on the structure of the diamine used. The T_g of NIPU1 – NIPU5 decreased when the spacer length in the NIPU increased (See Fig. 6S in Supplementary Materials). The highest value of T_g was exhibited by NIPU10 polymer (38 °C) because of the presence of an aromatic group that limits the flexibility and mobility of the poly(hydroxyurethane) chain. Moreover, the T_g of NIPU10 was much higher than the T_g of NIPU1 (31 °C), in which the ethylodiamine was used. This effect can be explained by the π-stacking effect of aromatic rings. The obtained NIPUs exhibited initial degradation (at 5% weight loss) between 222 and 247 °C and maximum decomposition rates between 260 and 335 °C, values comparable to those shown previously in the literature [4]. NIPU9 showed the highest thermal stability. Its maximum rate of degradation occurred at 335 °C due to the presence of the polyoxypropylene chain in the macromolecule. In the group of NIPU1–NIPU5 wherein aliphatic diamines where used, in general the initial degradation and maximum decomposition rate increased as the length of the alkyl chain in the NIPU increased; however, the values of initial and maximum decomposition temperatures for those polymers were comparable. In this group, NIPU5 possessed the highest initial (at 5% weight loss) and maximum degradation temperatures, 229 and 267 °C, respectively, due to the presence of the longest flexible carbon chain in the poly(hydroxyurethane) macromolecule.

The viscosity of the obtained NIPUs is collected in Table 2. The highest viscosity was exhibited by NIPU1 and NIPU10, due to the presence of short aliphatic chains and aromatic groups in the macromolecule, respectively. Moreover, the viscosity of NIPU decreased when the length of the alkyl chain between the urethane groups increased. The lowest viscosity was observed for NIPU8 and

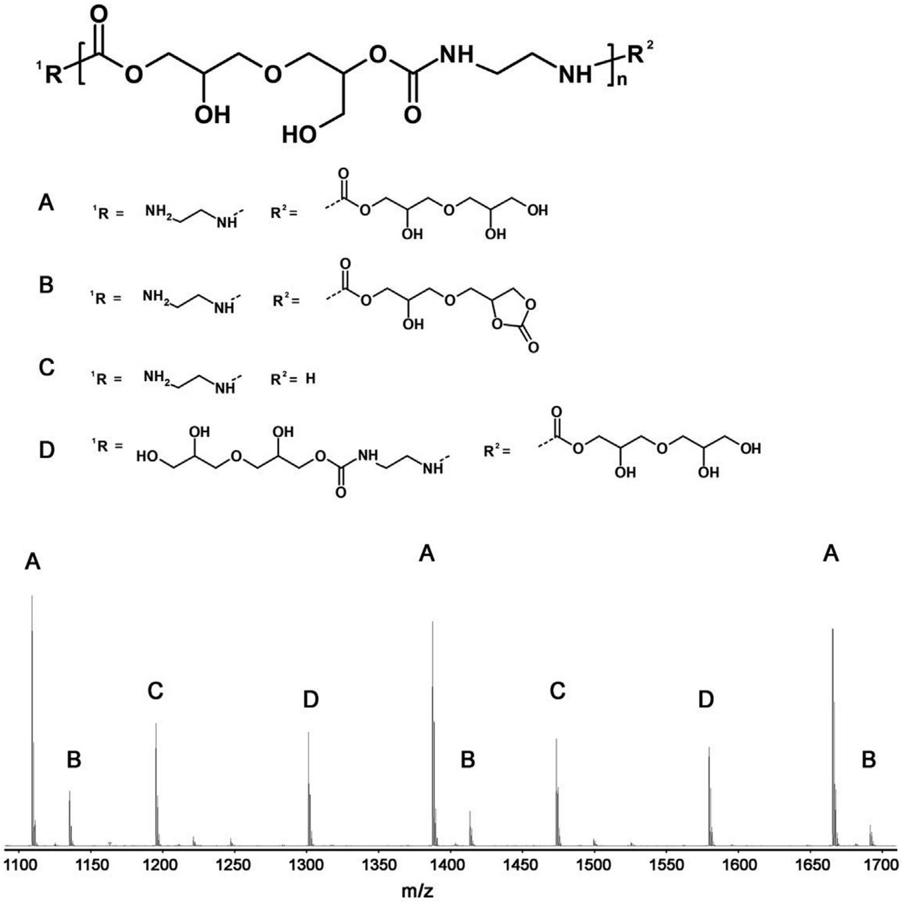


Fig. 7. NIPU1 Typical pattern of MALDI-TOF series signals depending on the terminal units.

Table 2
Thermal properties and viscosity of the obtained NIPUs: T_g – glass transition temperature, $T_{d,5\%}$ – temperature of initial degradation (at 5% weight loss), $T_{d\ max}$ – temperature of maximum decomposition and η – viscosity.

Entry	NIPU	T_g (°C)	$T_{d,5\%}$ (°C)	$T_{d\ max}$ (°C)	η (Pa s)
1	NIPU1	31	222	260	1230
2	NIPU2	26	228	264	124
3	NIPU3	18	226	265	30.2
4	NIPU4	8	231	264	18.6
5	NIPU5	−2	229	267	14.6
6	NIPU6	−1	234	268	232
7	NIPU7	−7	228	309	70.4
8	NIPU8	−8	237	297	1.4
9	NIPU9	−20	247	335	1.2
10	NIPU10	38	237	271	993

NIPU9, 1.4 and 1.2 Pa s, respectively. In this NIPU, polyglycerol amines were used and the flexibility of the macromolecular chain is quite high. The molecular weight and molecular weight distributions were not determined by a GPC because of the lack of solubility of the polymers in typical solvents.

4. Conclusions

In this study, an easy, one-step procedure of synthesis of five-membered bis(cyclic carbonate) – bis(2,3-dihydroxypropyl)ether dicarbonate from commercially available diglycerol was presented. Highly efficient synthesis of **2** with very high selectivity and high yield (79%) was achieved. The obtained products were comprehensively characterized (FT-IR, ^{1}H NMR, ^{13}C NMR. Furthermore, the X-ray structure of **2** showed that the obtained bis(cyclic carbonate) was a pair of enantiomers. **2** was further used as a monomer for the preparation of poly(hydroxyurethanes) in a reaction with various diamines by a green route without the use of toxic phosgene or isocyanates. The obtained NIPUs exhibited high thermal stability accompanied by low T_g.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2015.10.055.

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