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Special Issue: Polycarbonates and Green Chemistry

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EDITORIAL

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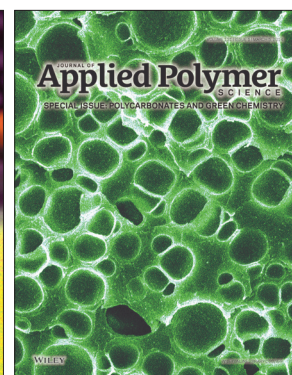
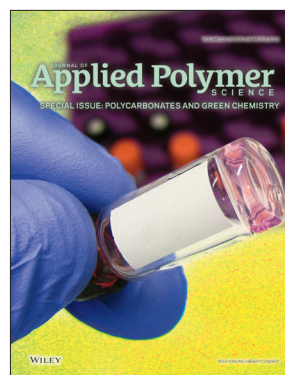
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New thermogelling poly(ether carbonate urethane)s based on pluronics F127 and poly(polytetrahydrofuran carbonate)

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Propylene Carbonate as a Source of Carbonate Units in the Synthesis of Elastomeric Poly(carbonate-urethane)s and Poly(ester-carbonate-urethane)s

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ABSTRACT: The synthesis of oligocarbonate diols from propylene carbonate (PC) and α,ω -diols with hydrocarbon chain of various length is presented and discussed. Syntheses with different catalysts and molar ratio of the reactants were performed. Novel method of the synthesis of oligo(ester-carbonate) diols based on PC, dimethyl succinate, adipate or terephthalate, and α,ω -diols was investigated. The resultant oligomerols did not contain any oxy-1,2-propylene fragments as well as other ether units in their chemical structure. Based on the obtained oligocarbonate and oligo(ester-carbonate) diols, polyurethanes were obtained according to the prepolymer method using isophorone and hexamethylene diisocyanate and water as a chain extender. The obtained products exhibited very good mechanical properties—tensile strength up to 50 MPa with 425% elongation at break [for PUR based on oligo(tetramethylene carbonate) diol] and 45 MPa, 625% [for oligo(tetramethylene succinate-co-carbonate)diol with 44 mol % of carbonate units]. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39764.

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INTRODUCTION

Polyurethanes are among the most commonly used polymers in the medical engineering. They are typically obtained in the reaction of diisocyanates and oligomerols containing ester and ether linkages in the main chain.^{1,2} However, recently more attention has been paid to the carbonate oligomerols.³ Due to the presence of carbonate linkages in the main chains, they exhibit much higher hydrolytic resistance in comparison to ester oligomerols and oxidative resistance in comparison to ether oligomerols.⁴ Moreover, polyurethanes based on oligocarbonate diols exhibit excellent mechanical properties such as high tensile strength (40 MPa) and high elongation at break (400%).⁵

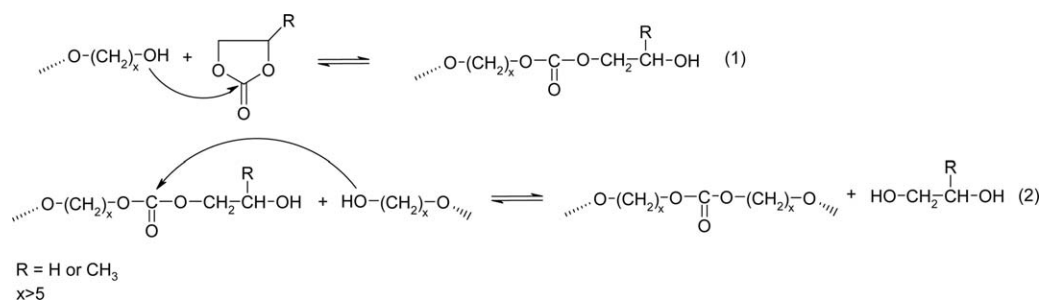
Among methods of the oligocarbonate diols synthesis, condensation of 1,6-hexanediol with phosgene or carbonate acid esters,^{6–8} copolymerization of oxiranes with carbon dioxide in the presence of organozinc compounds,⁹ or polymerization of 6-membered carbonates (such as trimethylene carbonate) have been reported.¹⁰

Five-membered alkylene carbonates, such as ethylene carbonate (EC) or propylene carbonate (PC) do not homopolymerize, due to a 1,3-dioxolan-2-one ring thermodynamic stability.^{11,12} Alkylene carbonates react with alcohols at higher temperature leading

to 2-hydroxyalkylethers.¹³ Harris et al.^{6,14} reported the synthesis of oligo(ether-carbonate) diols based on EC using 1,4-butanediol as a starter-initiator. The reaction proceeded through transesterification of 2-hydroxyethoxy-ethylcarbonate groups and formation of diethylene glycol as a by-product. The resultant oligomer contained a significant amount of ether bonds.^{11,15} Five-membered cyclic carbonates heated above 170°C in the presence of transition metal (Sn, Zn, Zr) alkoxides or carboxylates lead to oligo(ether-carbonate)s with content of ether units much higher than 50%.^{11,16,17}

Oligo(ether-carbonate)s can also be obtained by copolymerization of CO₂ and propylene oxide in the presence of Zn₃[Co(CN)₆]₂-based double metal cyanide complex.¹⁸

Our previous studies indicated that when the reaction of PC was carried out with diols containing more than five carbon atoms in a molecule, in the presence of tin-based catalyst (Bu₂SnO) aliphatic oligocarbonates practically without ether linkages can be selectively obtained.¹⁹ It was found that alkylene carbonates can react with alcohols according to two mechanisms.^{20–24} According to the first one the carbonyl carbon atom is attacked (B_{AC}2) [Scheme 1, eqs. (1) and (2)] and linear oligocarbonate diol is formed. According to the second reaction



Scheme 1. Formation of linear oligocarbonatediol without ether bonds.

pathway, the nucleophilic attack on the alkyl carbon atom takes place (B_{AL}2), resulting in decarboxylation and irreversible formation of oligo(oxyethylene) or oligo(oxy-1,2-propylene) fragments [Scheme 2, eqs. (1)–(3)]. Due to the low value of the reaction equilibrium constant (*K*) [Scheme 1, eq. (2)] by-product (ethylene glycol or 1,2-propylene glycol) should be constantly removed by distillation with azeotropic solvent.

Taking into account the high reactivity of ethylene carbonate and tendency to formation of poly(oxyethylene) units, a less basic catalyst such as NaCl was used to prevent the etherification.^{19,22}

In contrast to EC, propylene carbonate is less reactive, so a more active catalyst should be used for transesterification with diols. Due to the presence of electron donor methyl group as well as its steric hindrance effect, the etherification in the reaction with diols (Scheme 2, pathway 2) is much more suppressed even for a catalyst such as Bu₂SnO. However, it was found that it is difficult to remove the tin-based catalyst from the resultant oligocarbonate diol. The catalyst residue in the oligocarbonate diol can deteriorate the urethane prepolymer formation process.

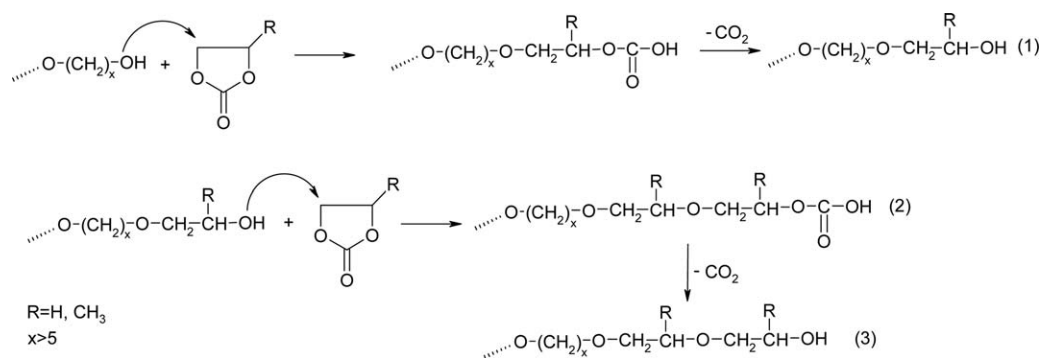
The aim of our work was to find optimal reaction conditions and a catalyst, which will promote the transesterification but not etherification reaction between PC and diol. The direct use of propylene carbonate as a source of carbonate linkages in the synthesis of carbonate oligomerols has several advantages. In contrast to trimethylene carbonate, which is used for obtaining oligocarbonate diols by ROP method,²⁵ propylene carbonate is easy to obtain by direct addition of CO₂ to propylene oxide. Dialkyl or diaryl carbonates applied in the synthesis of oligocarbonate diols by transesterification method are obtained from ethylene (propylene) carbonate or phosgene, respectively. It

means that additional step or hazardous gas should be engaged in these processes.

The second part of this work was devoted to the synthesis of oligo(ester–carbonate) diols. Methods of the synthesis of poly(ester–carbonate)s known so far include most of all copolymerization of cyclic esters (L-lactide, ε-caprolactone) with cyclic carbonate monomer—trimethylene carbonate (TMC).^{21–23,26–28} Yang et al.²⁹ reported a simple combination of polycondensation and ring-opening-polymerization (ROP) of hydroxyl terminated poly(butylene succinate) and various cyclic carbonate monomers. Poly(butylene succinate-*co*-carbonate) with low carbonate unit content (<20 mol %) was developed by Mitsubishi Gas Chemical Company.³⁰ Poly(ester–carbonate)s can also be synthesized by enzymatic polycondensation. The reactions of diethyl carbonate (DEC) with respective diester and diol carried out in the presence of *Candida antarctica* Lipase B (CALB) lead to aliphatic poly(ester–carbonate)s.³¹

To the best of our knowledge, there is no report concerning usage of alkylene carbonates (EC and PC) for the synthesis of oligo(ester–carbonate) diols. Taking into account that aliphatic polyesters are much more susceptible to hydrolytic biodegradation, we plan to use such oligomerols for the synthesis of elastomeric polyurethanes and check how the presence of ester linkages influence the PUR mechanical properties in comparison to poly(carbonate–urethane)s.

To verify the effectiveness of the catalyst removal method from the obtained oligocarbonate and oligo(ester–carbonate) diols, the synthesis of poly(carbonate–urethane)s and poly(ester–carbonate–urethane)s based on both types of the obtained oligomerols was investigated and discussed.



Scheme 2. Formation of oligo(oxyethylene) (R = H) or oligo(oxy-1,2-propylene) (R = CH₃) fragments.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) (98%), 1,10-decanediol (98%), 1,12-dodecanediol (99%), 1,6-hexanediol (97%), 1,9-nonanediol (98%), tin(II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) (95%) (Aldrich), acetonitrile (99.5%), chloroform (98.5%) (Chempur); hexamethylene diisocyanate (HMDI) ($\geq 98\%$), dimethyl terephthalate ($\geq 99\%$) (Fluka Analytical); titanium(IV) butoxide ($\text{Ti}(\text{OBu})_4$) ($\geq 97\%$), 1,5-pentanediol ($\geq 97\%$) (Fluka); propylene carbonate ($\geq 99\%$) (Merck), potassium carbonate ($\geq 99\%$), xylene (98%)—mixture of isomers (POCh); *n*-Heptane ($\geq 99\%$) (Roth); dimethyl succinate (98%) (SAFC); 1,4-butanediol (99%), dibutyltin(IV) oxide (98%), and zirconium(IV) acetylacetonate (98%) (Sigma-Aldrich) were used as received.

Characterization Techniques

FTIR spectra were recorded on a Biorad FTS-165 FTIR spectrometer as KBr pellets or Bruker ALPHA FTIR spectrometer equipped with Platinum ATR single reflection diamond ATR module operating in the spectral range of 375–4000 cm^{-1} . Samples were prepared in the form of thin layers of substances applied at ATR attachment. ^1H NMR spectra were recorded at room temperature on Varian VXR 400 MHz spectrometer using tetramethylsilane as an internal reference and CDCl_3 as solvent and analyzed with MestReNovav.6.2.0–7238 (Mestrelab Research S.L.) software. The carbonate unit content in the copolymers was calculated from ^1H NMR according to literature.³² Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF/MS) measurements were performed on a Bruker Ultra Flex MALDI TOF/TOF spectrometer (Bremen, Germany) in a linear mode using 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) software. Glass transition temperature (T_g) was calculated from the inflection point in the break in the DSC heat flow curves. DSC studies were carried out using a TA Instruments DSC Q200 apparatus. The oligocarbonatediols and oligo(ester–carbonate)-diols samples were heated in a temperature range from -80 to 100°C , then cooled backward to -80°C and heated again to 100°C . The polyurethanes were heated in a temperature range from -80 to 250°C and cooled backward to -80°C . Heating and cooling rate was $10^\circ\text{C}/\text{min}$ in all measurements. Mechanical properties of polyurethanes were determined using a testing machine Instron 5566. Head speed— 100 mm/min in case of poly(ester–carbonate–urethane)s and 50 mm/min in case of poly(carbonate–urethane)s. Samples were dog-bone shaped with 30 mm length and 1 mm thickness and 4 mm width of the measuring segment.

Synthesis of Oligo(tetramethylene carbonate) Diol

In a 250 cm^3 three-neck round-bottomed flask equipped with a magnetic stirrer, thermometer, Dean-Stark distillation trap, and reflux condenser, 50.74 g (0.5638 mol) of 1,4-butanediol, 86.26 g (0.8457 mol) of propylene carbonate, 0.13 g (0.0004 mol) of $\text{Ti}(\text{OBu})_4$, and 100 cm^3 of *n*-heptane (azeotropic solvent) were placed. The reaction was carried out at boiling point (165 –

170°C) of the reaction mixture with continuously removal of 1,2-propylene glycol by co-distillation with *n*-heptane for 6 h under atmospheric pressure. The reaction was continued till no 1,2-propylene glycol was observed in the distillate. Then, the solvent was distilled off. The second step—polycondensation was proceeded at 200°C for 2 h. The residue of propylene carbonate and 1,2-propylene diol as well as excess of 1,4-butanediol were removed from the reaction mixture by distillation under reduced pressure of 0.5 mbar. The polycondensation was continued till required molar mass of oligocarbonate was attained. Obtained product was dissolved in chloroform and washed with 3% water solution of HCl, and then with demineralized water until the conductivity of the aqueous phase was lower than 30 μS . The precipitated catalyst residue were filtrated off and organic solvent was evaporated under reduced pressure. 25.39 g of the product (CD4) with molar mass of 4690 g/mol was obtained as a white solid.

Oligocarbonates based on other diols (1,5-pentanediol, 1,6-hexanediol, 1,9-nonanediol, 1,10-decanediol, and 1,12-dodecanediol) were obtained in a similar manner.

CD4: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.15 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2$), 3.68 (4H, *t*, CH_2OH), 1.77 (4H, *m*, OCH_2CH_2).

CD5: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.11 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2$), 3.63 (4H, *t*, CH_2OH), 1.69 (4H, *m*, $(\text{O})\text{OCH}_2\text{CH}_2$), 1.57 (4H, *m*, HOCH_2CH_2), 1.45 (4H, *m*, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2$).

CD6: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.12 (4H, *t*, $(\text{O})\text{OCH}_2$), 3.65 (4H, *t*, CH_2OH), 1.67 (4H, *t*, $(\text{O})\text{OCH}_2\text{CH}_2$), 1.57 (4H, *m*, HOCH_2CH_2), 1.39 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2$).

CD9: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.10 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2$), 3.63 (4H, *t*, CH_2OH), 1.65 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2$), 1.54 (4H, *t*, HOCH_2CH_2), 1.32 (6H, *m*, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$).

CD10: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.11 (4H, *t*, $\text{C}(\text{O})\text{OCH}_2$), 3.69 (4H, *t*, CH_2OH), 1.64 (4H, *m*, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2$), 1.57 (4H, *m*, HOCH_2CH_2), 1.30 (6H, *m*, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$).

CD12: ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) = 4.11 (4H, *t*, $\text{OC}(\text{O})\text{OCH}_2$), 3.64 (4H, *t*, CH_2OH), 1.66 (4H, *m*, $\text{C}(\text{O})\text{OCH}_2\text{CH}_2$), 1.56 (4H, *m*, HOCH_2CH_2), 1.32 (8H, *m*, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$). ATR IR; λ (cm^{-1}): 3550, 2960, 1730, 1240–1160.

Reaction of Bis(4-hydroxybutyl)succinate with Propylene Carbonate

In a 250 cm^3 three-neck round-bottomed flask equipped with a magnetic stirrer, thermometer, condenser and nitrogen supply system, 73.07 g (0.5 mol) of dimethyl succinate, 90.12 g (1.0 mol) of 1,4-butanediol, and 0.18 g (0.5 mmol) of $\text{Ti}(\text{OBu})_4$ were placed. The reaction was carried out for 5 h at 150°C under inert gas flow until no distillation of methanol was observed. As a result, 101.86 g of bis(4-hydroxybutyl)succinate was obtained. In the second step, in a 150 cm^3 three-neck round-bottomed flask equipped with a magnetic stirrer, thermometer, Dean-Stark distilling trap and reflux condenser, 15.01 g (0.0909 mol) of bis(4-hydroxybutyl)succinate, 37.14 g (0.3636 mol) of propylene carbonate were placed. The reaction was carried out at 165 – 170°C with *n*-heptane under atmospheric pressure. The reaction was continued for 3 h till no distillate (beside *n*-heptane) was observed.

Table I. The Comparison of the Results of the Polycondensation α,ω -Diols with Propylene Carbonate in the Presence of Various Catalysts

Run	Catalyst ^a	Molar mass of the product ^{b/c} g/mol	Yield ^b %	Possibility of the catalyst removing	Possibility of obtaining PUR	Incorporation of the catalyst in the structure of oligomerol ^d	Presence of ether fragments ^e
1	NaCl	No reaction	0	-	-	-	-
2	K ₂ CO ₃	530/1180	- ^f	Yes	Yes	No	Yes
3	Bu ₂ SnO	420/500	55	-	-	-	-
4	Sn(Oct) ₂	540/700	65	-	Yes	Yes	No
5	Ti(OBu) ₄	450/1120	85	Yes	Yes	-	No
6	Zr(acac) ₄	470/490	50	-	-	No	No

^aConcentration of catalyst was 3 wt %/diol.

^bData refers to the reactions carried out using 1,6-hexanediol and PC in a molar ratio of 1 : 2 (mol : mol), after 8 h at 160°C under atmospheric pressure.

^cData refers to the reactions carried out using 1,6-hexanediol and PC in a molar ratio of 1 : 2 (mol : mol), after 8 h at 160°C under atmospheric pressure and 2 h under pressure of 0.5 mbar in 150–190°C.

^dCalculated from MALDI-TOF mass spectra.

^eCalculated from MALDI-TOF mass spectra and ¹H NMR spectra.

^fOligomerol contained a large amount of ether units.

Synthesis of Oligo(tetramethylene succinate-*co*-carbonate) Diol

In a 250 cm³ three-neck round-bottomed flask equipped with a magnetic stirrer, thermometer, condenser and nitrogen supply system, 73.07 g (0.50 mol) of dimethyl succinate, 157.71 g (1.75 mol) of 1,4-butanediol, and 0.20 g (0.5 mmol) of Ti(OBu)₄ were placed. The reaction was carried out for 5 h at 150°C under inert gas flow until no distillation of methanol was observed (95% of theoretical amount of methanol was collected). Then, the condenser and nitrogen supply system were replaced with a Dean-Stark distilling trap and reflux condenser and 76.58 g (0.75 mol) of propylene carbonate was added. The reaction was continued for 8 h at 165–170°C under atmospheric pressure with continuously removal of 1,2-propylene glycol by co-distillation with *n*-heptane, until no 1,2-propylene glycol was observed in the distillate. Then, the solvent was distilled off. 181.46 g of the product with molar mass of 385 g/mol containing 40 mol % of carbonate units was obtained. The final step—removal of an

excess of propylene carbonate and the post-polycondensation was proceeded under reduced pressure (0.5 mbar) at 180–200°C for 2 h—till required molar mass of oligo(ester-carbonate) was attained. About 130.45 g of final oligo(tetramethylene succinate-*co*-carbonate) diol (**SCD4**) with molar mass of 3810 g/mol and 42 mol % of carbonate units was obtained.

The catalyst was removed from the product according the same procedure as in case of oligocarbonate diol.

Poly(pentamethylene adipate-*co*-carbonate) diol (**ACD5**) was obtained in a similar manner. About 43.78 g of final oligo(pentamethylene adipate-*co*-carbonate) diol with molar mass of 3790 g/mol and 48 mol % of carbonate units content was obtained.

Poly(tetramethylene terephthalate-*co*-carbonate) diol (**TCD4**) was obtained in a similar manner. About 56.58 g of final oligo(-tetramethylene terephthalate-*co*-carbonate) diol with molar mass of 5410 g/mol and 37 mol % of carbonate units content was obtained.

SCD4: ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 4.12 (4H, *t*, OC(O)OCH₂), 4.08 (4H, *t*, C(O)OCH₂), 3.65 (8H, two overlapping triplets, CH₂OH), 2.59 (4H, *t*, CH₂C(O)O), 1.73–1.65 (8H, *m*, OCH₂CH₂). ATR IR; λ (cm⁻¹): 3550, 2960, 1730, 1240–1160.

ACD5: ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 4.11 (4H, *t*, OC(O)OCH₂), 4.05 (4H, *t*, C(O)OCH₂), 3.64 (8H, two overlapping triplets, CH₂OH), 2.30 (4H, *t*, CH₂C(O)O), 1.73–1.60 (8H, *m*, OCH₂CH₂), 1.45(2H, *m*, OCH₂CH₂CH₂). ATR IR; λ (cm⁻¹): 3550, 2960, 1715, 1240–1120, 728.

TCD4: ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.09 (4H, *s*, Ph), 4.39 (4H, *t*, CH₂OC(O)Ph), 4.34 (2H, *t*, OC(O)O(CH₂)₃CH₂OC(O)Ph), 4.21 (2H, *t*, OC(O)OCH₂(CH₂)₃OC(O)Ph), 4.16 (4H, *t*, OC(O)OCH₂), 3.74 (4H, *t*, OC(O)O(CH₂)₃CH₂OH), 3.68 (4H, *t*, PhC(O)O(CH₂)₃CH₂OH), 1.97 (4H, *t*, PhC(O)OCH₂CH₂), 1.87 (4H, *t*, OC(O)OCH₂CH₂), 1.54 and 1.77 (4H, *m*, HOCH₂CH₂). ATR IR; λ (cm⁻¹): 3550, 2963, 2902, 1744, 1716, 1247, 1119, 928, 728.

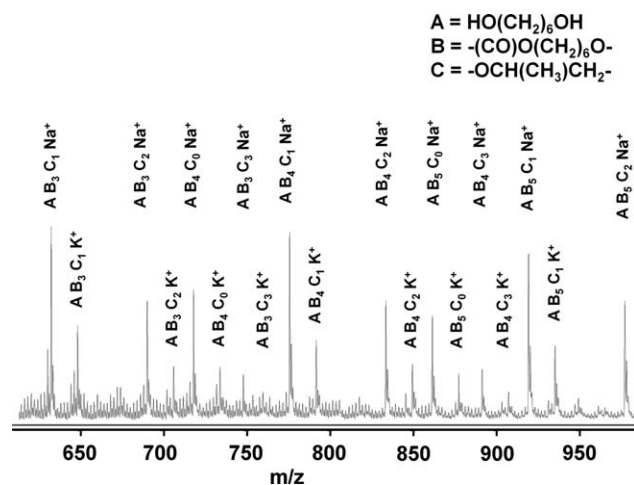


Figure 1. MALDI-TOF mass spectrum of oligo(hexamethylene carbonate-*co*-propylene oxide).

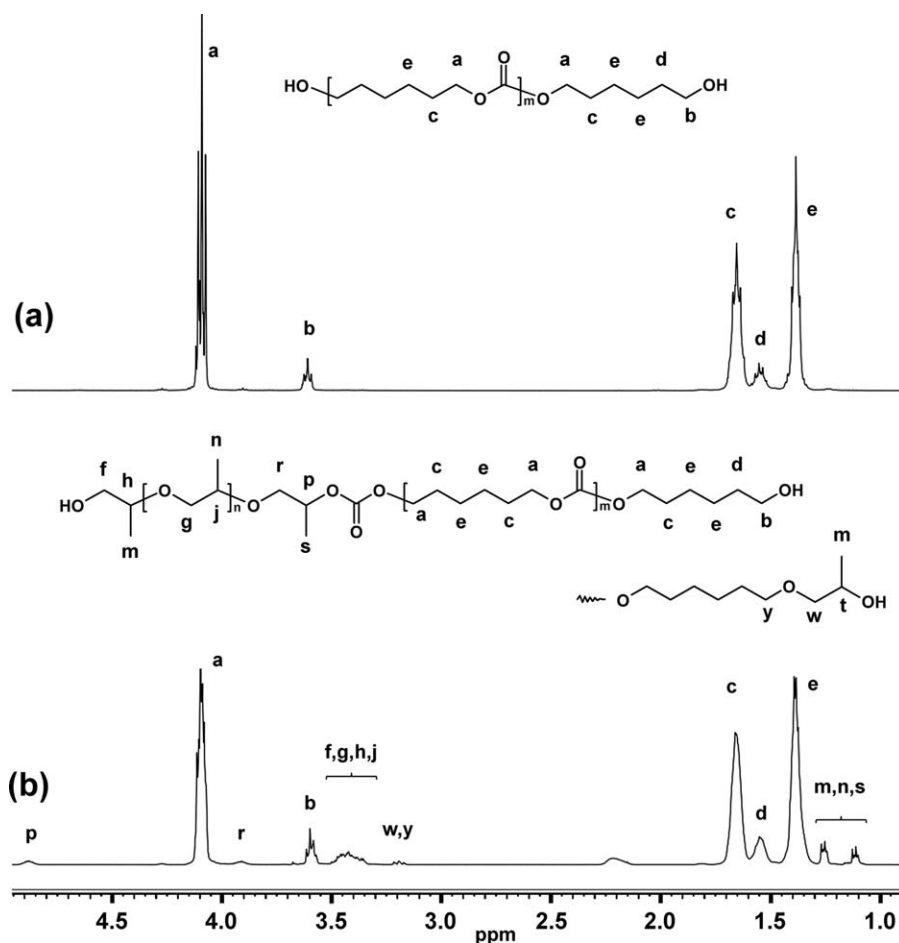


Figure 2. (a) ^1H NMR (400 MHz, CDCl_3) spectrum of oligo(hexamethylene carbonate) and (b) oligo(hexamethylene carbonate-*co*-propylene oxide); only one type of regioisomer of propylene oxide units is shown.

Synthesis of Poly(tetramethylene succinate–carbonate–urethane)

Polyurethanes were obtained according to procedure reported by us earlier.⁵

In a 50 cm^3 two-neck round-bottom flask fitted with a magnetic stirrer, thermometer and nitrogen supply system, 15.26 g

(0.0041 mol) of oligo(tetramethylene succinate-*co*-carbonate) diol with molar mass of 3750 g/mol was placed and dried under reduced pressure (0.5 mbar) at 100°C for about 1 h. Then, 2.59 g (0.0122 mol) of isophorone diisocyanate (IPDI) was added. The reaction was carried out under nitrogen atmosphere at 80°C until disappearance of absorption bands characteristic for OH groups (3500 cm^{-1}) in FTIR spectrum. Then, the product was deaerated under reduced pressure without stirring until no air bubbles formation was observed. Urethane prepolymers were colorless liquids of high viscosity.

Eleven grams of the urethane prepolymer were poured onto the open glass form (10 $\text{cm} \times 10\text{ cm} \times 0.5\text{ cm}$) to obtain polyurethane foils of ca. 1 mm thickness. The process of chain extending of urethane prepolymer was performed in a climatic chamber under controlled conditions of humidity and temperature: 3 days at 70°C, 10% of humidity, 1 day at 70°C, 20% of humidity and 3 days at 60°C, 40% of humidity.

PUR-SCD4: ^1H NMR (*d*-DMSO, 400 MHz): δ (ppm) = 4.12 (4H, *t*, OC(O)OCH_2), 4.08 (4H, *t*, C(O)OCH_2), 3.65 (8H, two overlapping triplets, CH_2OH), 2.59 (4H, *t*, $\text{CH}_2\text{C(O)O}$), 1.73–1.65 (8H, *m*, OCH_2CH_2). ATRIR; λ (cm^{-1}): 3550, 2960, 1730, 1240–1160.

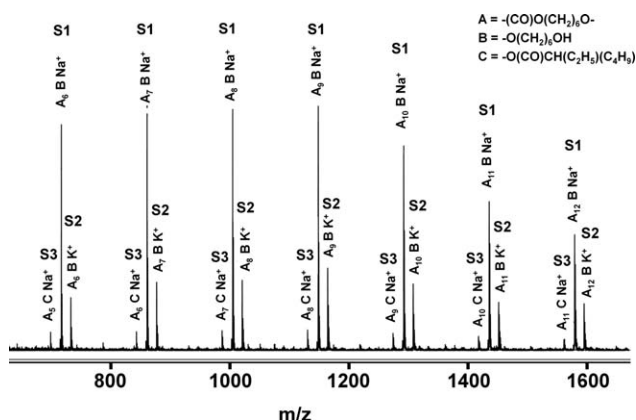
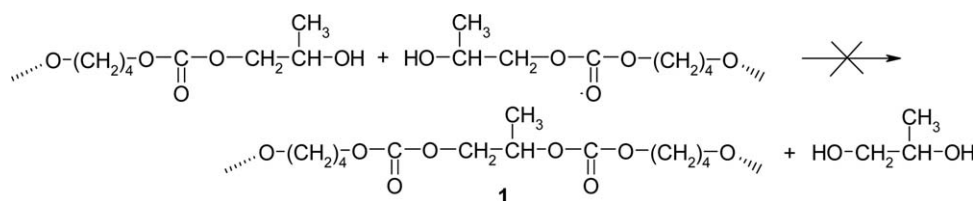


Figure 3. MALDI-TOF mass spectrum of oligo(hexamethylene carbonate) containing end groups derived from 2-ethylhexanoic acid (about 10% of the terminal groups).



Scheme 3. Potential transesterification reaction of 2-hydroxypropylcarbonate derivatives.

Other poly(ester–carbonate–urethane)s were obtained in a similar manner.

RESULTS AND DISCUSSION

Taking into account that the residue of metal-based or inorganic catalysts present in oligocarbonate diol can deteriorate the synthesis of poly(carbonate–urethane)s, the studies on the catalyst activity as well as possibility of its removal from the resultant oligomerol were undertaken.

Influence of a Catalyst on Oligocarbonate Yield and its Purification

Referring to our previous experience with transesterification reactions of alkylene carbonates, the following catalysts were selected: sodium chloride (NaCl), potassium carbonate (K_2CO_3), dibutyltin oxide (Bu_2SnO), tetrabutoxytitanium ($Ti(OBu)_4$), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$), and zirconium(IV) acetylacetonate ($Zr(acac)_4$) for the synthesis of oligocarbonate diol from propylene carbonate. The results are collected in Table I.

In contrast to ethylene carbonate, due to lower activity no reaction of propylene carbonate with 1,6-hexanediol carried out in the presence of sodium chloride was observed. On the other hand, the oligomerol obtained in the presence of K_2CO_3 contained a relatively large number of oxy-1,2-propylene units. In case of use of this alkaline catalyst, despite of lower susceptibility of propylene carbonate to etherification, the nucleophilic attack of hydroxyl groups at aliphatic carbon atom (Scheme 2) takes place and as a result the formation of ether linkages and decarboxylation was observed. The formation of oligo(oxy-1,2-propylene) fragments was confirmed by MALDI-TOF spectrometry (Figure 1), 1H NMR [Figure 2(b)] and IR spectroscopies.

Absorption band of high intensity characteristic for ether linkages was observed in the IR spectrum at 1100 cm^{-1} . The content of ether units was estimated as *ca.* 30 mol %.

It should be mentioned that the presence of ether fragments in polyurethane molecules decreases their resistance towards oxidation, as well as causes their yellowing and mechanical strength decrease.³³

It was found that when a metal-based catalyst was used (Table I, runs 2–5) oligomerols without ether linkages can be obtained [Figure 2(a)].

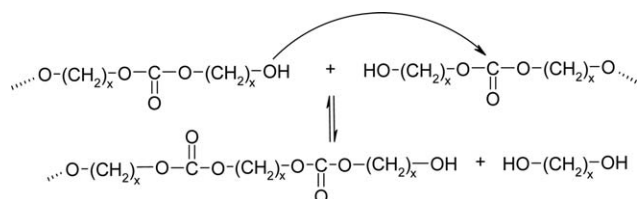
Tetrabutoxytitanium was the best among the investigated catalysts. The oligo(hexamethylene carbonate) diol obtained in the presence of $Ti(OBu)_4$ contained no ether linkages and was characterized by high yield (80%). Moreover, this catalyst can be easily removed from the post-reaction mixture by washing with acidified water and filtration. In the presence of tin-based catalysts like $Sn(Oct)_2$ and Bu_2SnO oligomerols without ether fragments also were obtained, but it was difficult to remove residual amounts of the catalysts. As a consequence it was not possible to obtain linear urethane prepolymer in the reaction of such obtained oligomerols with diisocyanate. Tin-based catalysts activate the dimerization and trimerization of diisocyanate even at relatively low temperature ($70\text{--}80^\circ\text{C}$) leading to a drastic viscosity increase of urethane prepolymer.

Additionally, it was observed that in the case of using tin(II) 2-ethylhexanoate the oligocarbonate chains were partially terminated with 2-ethylhexanoate group (up to 10% of terminal groups). In the MALDI-TOF mass spectrum there was a series of signals which can be assigned to oligo(hexamethylene carbonate)s with 2-ethylhexanoate group (Figure 3, series 3). Monofunctional

Table II. Optimization of the Oligo(tetramethylene carbonate) Diol Synthesis

Run	PC/diol molar ratio	Catalyst concentration (wt %)	Reaction time (h)	M_n after first step ^a (g/mol)	M_n after second step ^a (g/mol)
1	1.5	0.25	6	215	4690
2	2.0	0.25	6	145	770
3	2.0	0.25	8	160	2840
4	2.0	0.25	10	205	3960
5	2.0	0.5	10	475	5970
6	2.0	1.0	6	140	250
7	2.0	1.0	8	150	925
8	2.0	1.0	10	170	1090
9	2.0	3.0	10	340	2540

^aMolar masses estimated by 1H NMR spectra.



Scheme 4. Second step of the synthesis of oligocarbonate diol—polycondensation with α,ω -diol distillation.

oligomerols in the reaction with diisocyanate lead to polyurethane of smaller molar mass and as a consequence to its worse mechanical properties.

The zirconium-based catalyst gave the lowest yield and molar mass of the obtained oligomerols (Table I, run 5).

As it was discussed in our earlier article, high molar excess of propylene carbonate suppresses the formation of linear carbonate linkages.⁵ In this case, almost all molecules were terminated with 2-hydroxypropylcarbonate groups and there was no transesterification reaction leading to the formation of **1** and 1,2-propylene glycol due to the thermodynamic reason (Scheme 3).

In contrast to the reaction with ethylene carbonate,²² it was found that the transesterification process can be proceeded at relatively high temperature (even up to 180°C) without formation of ether units. The optimal concentration of $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst was 0.25 wt %. For higher concentration of the catalyst, reaction time was longer and oligomerol molar mass was lower (Table II).

Synthesis of Carbonate Oligomerols from Different α,ω -Diols

The highest molar masses of carbonate oligomerols were obtained from diols of low molar mass such as 1,4-butanediol and 1,5-pentanediol. These diols are characterized by relatively low boiling points (230 and 242°C, respectively). The molar mass increased as a results of transesterification reaction connected with removal of respective diol from the reaction mixture by distillation under reduced pressure in the second step (Scheme 4). It is worth mentioning that in case of using 1,3-propanediol, cyclic carbonate (trimethylene carbonate) is formed instead of linear oligocarbonate. The lowest molar mass (870 g/mol) was obtained for the longest 1,12-dodecanediol (b.p. = 324°C).

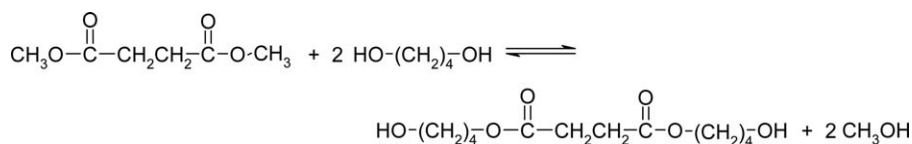
All obtained oligocarbonates were white hard waxes of melting points the range 43–75°C (Table III).

Table III. Characteristics of the Obtained Oligocarbonate Diols

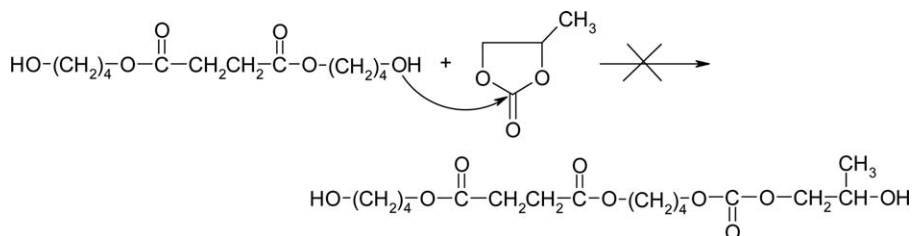
Run	Diol	B.p. (lit.) (°C)	M_n after first step ^a (g/mol)	M_n after second step ^a (g/mol)	T_m^b (°C)	Yield after first step ^b (%)	Yield after second step ^b (%)
1	1,4-Butanediol	230	215	4690	64–75	90	43
2	1,5-Pentanediol	242	430	6170	43–57	89	55
3	1,6-Hexanediol	250	495	1360	50–56	80	51
4	1,9-Nonanediol	288	700	1300	49–55	85	53
5	1,10-Decanediol	297	570	1122	50–55	87	65
6	1,12-Dodecanediol	324	545	865	59–64	81	60

^aMolar masses estimated by ¹H NMR spectra

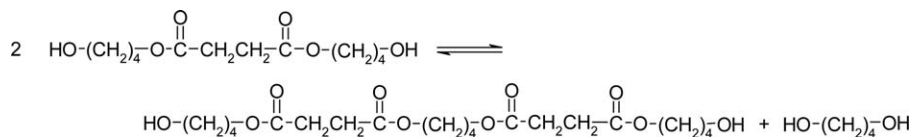
^bData refers to the reactions carried out using diol and PC in a molar ratio of 1 : 1.5 (mol : mol), for 6 h at 160°C under atmospheric pressure (first step) and 2 h at 200°C under reduced pressure of 0.5 mbar (second step).



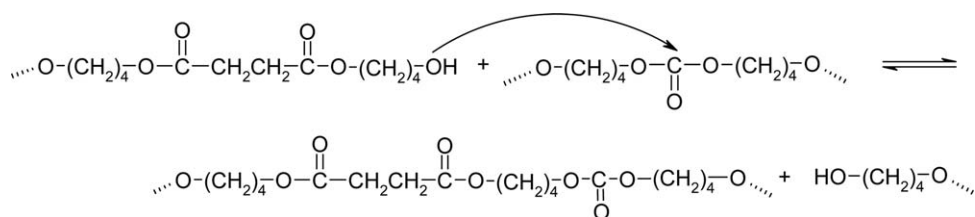
Scheme 5. Synthesis of bis(4-hydroxybutyl)succinate.



Scheme 6. Potential reaction of bis(4-hydroxybutyl)succinate with propylene carbonate.



Scheme 7. Equilibrium of bis(4-hydroxybutyl)succinate with 1,4-butanediol and succinate dimer.



Scheme 8. Synthesis of oligo(ester-carbonate)s.

Synthesis of Oligo(tetramethylene succinate-co-carbonate)

Diol

It was found that to obtain oligo(tetramethylene succinate-co-carbonate) diol based on propylene carbonate, bis(4-hydroxybutyl)succinate should be prepared first in the reaction of dimethyl succinate with two-fold molar excess of 1,4-butanediol (Scheme 5).

When the reaction was carried out in one pot and all ingredients were mixed together, by-product, methanol deteriorated the lin-

ear carbonate formation. The same problem appeared when succinic acid was used instead of dimethyl succinate. By-product, water caused the hydrolysis of carbonate linkages resulting in decarboxylation and decrease of the amount of carbonate units in the product. Moreover, the presence of unreacted carboxylic group also can promote further decarboxylation as a result of subsequent esterification reactions and water formation.

In our first attempt of the synthesis of oligo(ester-carbonate), bis(4-hydroxybutyl)succinate was treated with propylene

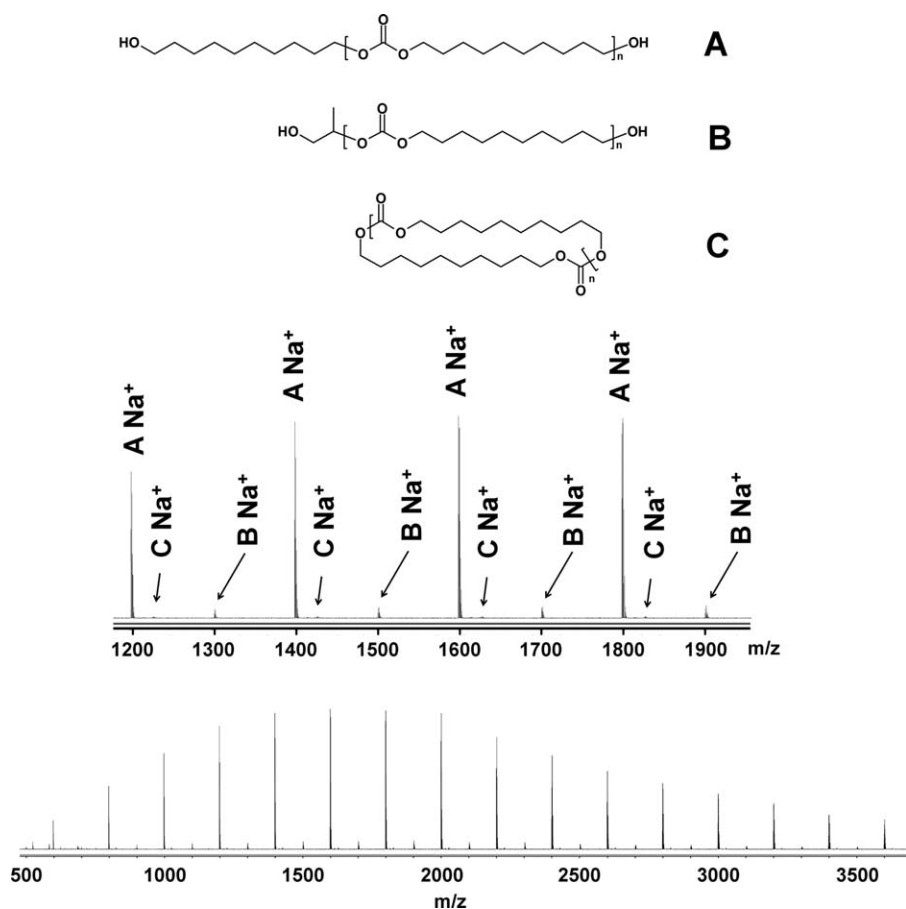


Figure 4. MALDI-TOF mass spectrum of oligo(decamethylene carbonate) containing 2-hydroxypropylcarbonate terminal groups.

Table IV. Characteristics of the Obtained Oligomerols

Run	Sample	Molar mass ^a (g/mol)	T_m (°C)	$\Delta H_m S$ (J/g)	T_g (°C)	T_c (°C)	$\Delta H_c S$ (J/g)
1	SCD4-42 ^b	3810	c	c	c	c	c
2	SCD4-44	2730	50.3	67.4	-45.4	7.0	65.1
3	SCD4-57	3750	- ^e	- ^e	-42.7	- ^d	- ^d
5	SCD5-46	2385	- ^e	- ^e	-52.7	- ^d	- ^d
6	SCD5-51	1515	- ^e	- ^e	-55.0	- ^d	- ^d
7	SCD5-62	2075	- ^e	- ^e	-51.9	- ^d	- ^d
9	ACD5-43	2385	- ^e	- ^e	-54.1	- ^d	- ^d
10	ACD5-51	2405	0.2	41.8	0.2	-29.85	40.8
11	TCD4-37	5410	176	c	4.0	c	c
12	CD4	2200	59.1	103.6	-32.2	15.1	56.4
13	CD5	2400	36.9	113.6	-45.9	- ^d	- ^d

^aMolar masses estimated from ¹H NMR spectra.

^bNames of the samples were given according to the rule: SCD4-42 means (tetramethylene succinate-co-carbonate) diol with 42 mol % of carbonate units, ACD5-43 (pentamethylene adipate-co-carbonate) diol with 43 mol % of carbonate units and TCD4-37 (tetramethylene terephthalate-co-carbonate) diol with 37 mol% of carbonate units.

^cNo measurement.

^dCrystallization of the sample was not observed.

^eMelting point of the sample was not observed.

carbonate in the presence of Ti(OBu)₄ and *n*-heptane as an azeotropic solvent. The azeotropic distillation was carried out for 8 h at 160–180°C, but no 1,2-propylene glycol was observed in the distillate. It means that the ester group at position 4 of butyl alcohol suppresses the opening of a 1,3-dioxolane-4-one ring (Scheme 6).

Small number (*ca.* 10 mol %) of carbonate units in the product can be formed due to the presence of small amount of 1,4-butanediol and succinate dimer which are in equilibrium with bis(4-hydroxybutyl)succinate (Scheme 7).

When additionally, 1,4-butanediol was added into the reaction system we observed the formation of 1,2-propylene glycol as

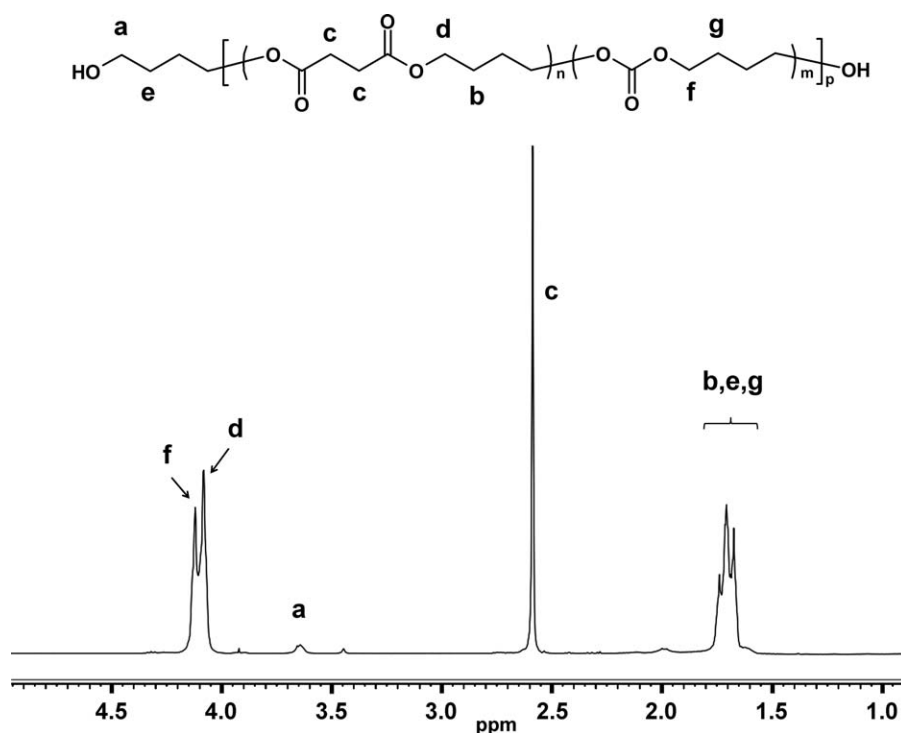


Figure 5. ¹H NMR (400 MHz, CDCl₃) spectrum of the obtained oligo(tetramethylene succinate-co-carbonate) diol.

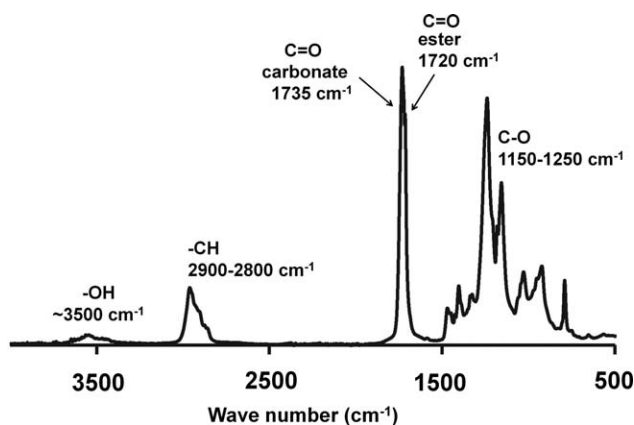


Figure 6. FTIR spectrum of oligo(tetramethylene succinate-*co*-carbonate) diol.

well as linear carbonate linkages in substantial amount [Scheme 1, eqs. (1) and (2)].

The final oligo(ester-carbonate)s are formed in the transesterification reaction of linear carbonates and bis(4-hydroxybutyl)succinate (Scheme 8).

It should be mentioned that when oligo(decamethylene carbonate) diol, containing longer hydrocarbon chains between carbonate linkages, was used in the reaction with propylene carbonate under similar conditions to that above discussed, the presence of 2-hydroxypropylcarbonate terminal groups can be observed in the MALDI-TOF mass spectrum (Figure 4). It means that diols with longer hydrocarbon chain enable the reaction of their oligocarbonate with propylene carbonate.

Based on the investigations described above, the three-step polycondensation procedure of the oligo(ester-carbonate) diols synthesis was performed for the synthesis of aliphatic and aliphatic-aromatic oligo(ester-carbonate)s. In the first step, bis(hydroxyalkyl)succinate (adipate or terephthalate) was obtained in the alcoholysis reaction of dimethyl ester with

respective α,ω -diol used in the amount calculated for both ester and carbonate units (Scheme 5). In the second step, the obtained bis(hydroxyalkyl)succinate (adipate or terephthalate) was used as an ester monomer together with α,ω -diol in the reaction with propylene carbonate to obtain low molar mass of oligo(alkylene succinate-*co*-carbonate) diols. The final step—removal of an excess of α,ω -diol and propylene carbonate and the polycondensation was proceeded under reduced pressure (0.5 mbar) at 200°C (Scheme 8).

Oligo(tetramethylene succinate-*co*-carbonate) diol of molar mass 3810 g/mol containing 42 mol % of carbonate units was obtained (Table IV, run 1).

Figure 5 shows the ^1H NMR spectra of oligo(tetramethylene succinate-*co*-carbonate) diol. Taking into account the signals intensity ratio of protons corresponding to CH_2OH (a) and $\text{CH}_2\text{OC(O)}$ (d), $\text{CH}_2\text{OC(O)O}$ (f), $\text{CH}_2\text{C(O)O}$ (c) groups, a number-average molar mass of oligomerol was calculated [eq. (1)] and the molar content of carbonate units was estimated [eq. (2)].

$$M_n = ((f+d)-c)M_{\text{carbonate repeating unit}} + cM_{\text{ester repeating unit}} + M_{\text{diol}} \quad (1)$$

$$\text{Molar fraction of carbonate units} = ((f+d)-c)/(f+d) \quad (2)$$

The IR spectra (Figure 6) and MALDI-ToF analysis (Figure 7) also confirmed the structure of the obtained oligo(tetramethylene succinate-*co*-carbonate) diols. There were no characteristic signals for ether bonds in the spectra, what indicates that etherification is suppressed when polycondensation is proceeded under the above-mentioned conditions.

It was found that it is possible to use dimethyl terephthalate instead of dimethyl succinate and as a result aliphatic-aromatic oligo(ester-carbonate) diol can be obtained. Oligo(tetramethylene terephthalate-*co*-carbonate) diol of molar mass 5410 g/mol containing 37 mol % of carbonate units was obtained (Table IV, run 11). Oligo(pentamethylene adipate-*co*-carbonate) diol of molar mass 2385 g/mol containing 43 mol % of carbonate units also was obtained (Table IV, run 9).

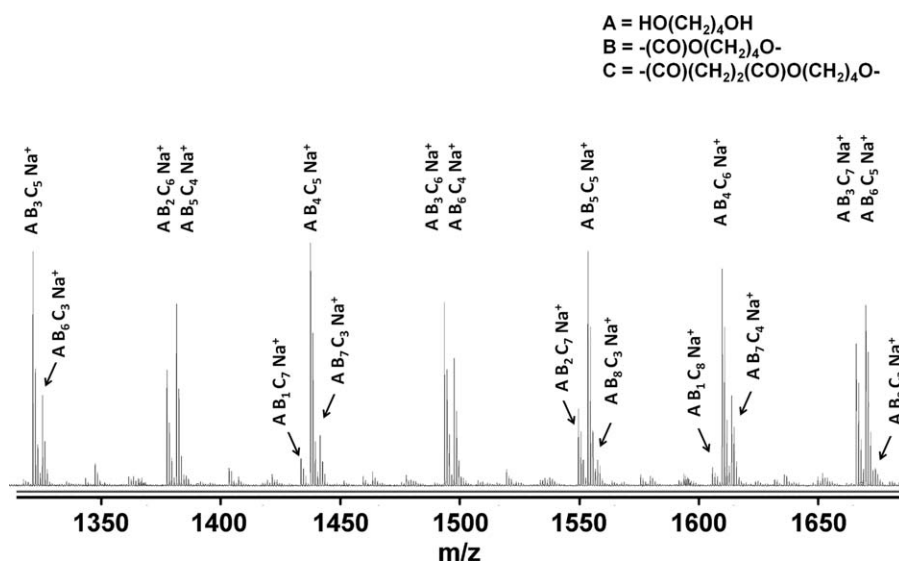


Figure 7. MALDI-TOF mass spectrum of oligo(tetramethylene succinate-*co*-carbonate) diol. Small signals can be assigned to cyclic products and potassium adducts.

Table V. Characteristics of the Obtained Polyurethanes

Run	Sample	Diisocyanate	Tensile strength MPa	Elongation at break %	T_m °C	$\Delta H_m S$ J/g	T_g °C
1	PUR-IP-SCD4-44	IPDI	29.0 ± 0.4	460 ± 15	46.1	2.4	-30.9
2	PUR-HM-SCD4-44	HMDI	43.2 ± 5.0	630 ± 14	44.6	7.2	-35.8
3	PUR-HM-SCD4-57	HMDI	34.3 ± 2.2	545 ± 20	43.5	2.3	-35.8
4	PUR-IP-SCD4-57	IPDI	b	b	- ^a	- ^a	-32.3
5	PUR-HM-SCD5-46	HMDI	25.0 ± 3.2	575 ± 26	39.2	5.0	-40.8
6	PUR-IP-SCD5-46	IPDI	21.6 ± 1.0	760 ± 47	- ^a	- ^a	-37.1
7	PUR-HM-SCD5-51	HMDI	26.8 ± 1.5	560 ± 13	41.7	5.0	-38.0
8	PUR-IP-SCD5-51	IPDI	16.9 ± 1.7	530 ± 11	- ^a	- ^a	-31.1
9	PUR-IP-ACD5-43	IPDI	19.9 ± 1.0	440 ± 20	- ^a	- ^a	-40.5
10	PUR-HM-ACD5-51	HMDI	b	b	45.4	0.6	-48.4
11	PUR-IP-ACD5-51	IPDI	30.4 ± 4.8	485 ± 17	- ^a	- ^a	-49.2
12	PUR-IP-CD4	IPDI	49.5 ± 4.5	425 ± 13	- ^a	- ^a	-20.4
13	PUR-IP-CD5	IPDI	24.5 ± 4.9	265 ± 12	- ^a	- ^a	-24.7

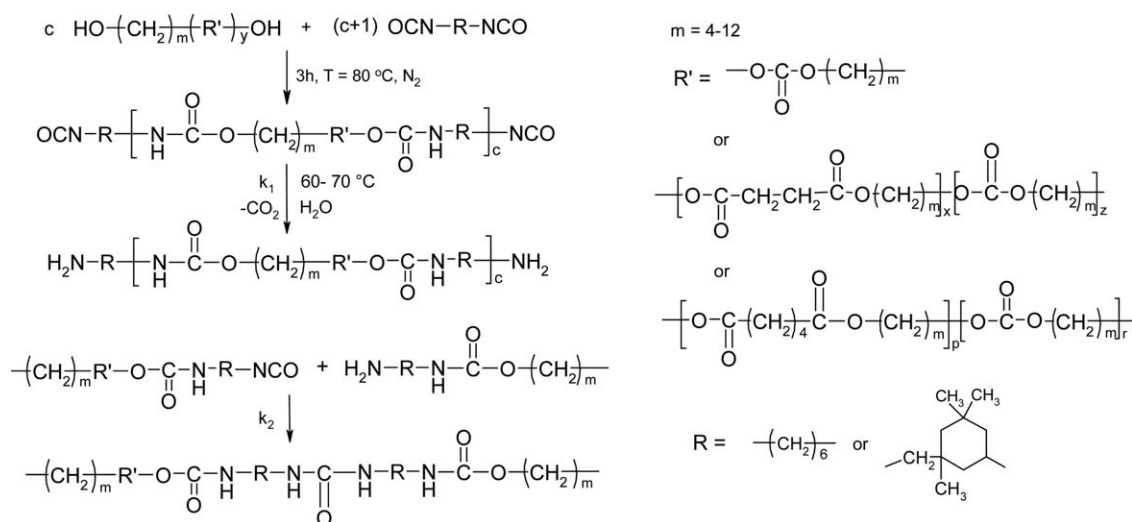
^aA melting point of the sample was not observed.^bNo measurement.

Synthesis of Poly(carbonate-urethane)s and Poly(ester-carbonate-urethane)s

In the synthesis of polyurethanes based on carbonate and ester-carbonate oligomerols (molar mass of 1500–3000 g/mol) were used (Table V). The polyurethane film was obtained according to procedure published by us earlier (Scheme 9).⁵ In the synthesis of urethane prepolymer, a three-fold molar excess of diisocyanate was used. The reaction was carried out at 80–85 °C under nitrogen atmosphere. Progress of the reaction was controlled by IR spectroscopy—disappearance of absorption bands characteristic for terminal OH groups (3500 cm⁻¹) and the appearance of absorption bands characteristic for NH group (3360 cm⁻¹) of the urethane bond were monitored. The process of obtaining poly(ester-carbonate-urethane) films was

proceeded in a climatic chamber using water vapor as a chain extender. Polymers were characterized by DSC analysis and mechanical testing—tensile strength and elongation at break were measured (Table V). In the case of oligo(tetramethylene terephthalate-*co*-carbonate), it was not possible to obtain polyurethane according to the above mentioned procedure due to high value of its melting point (176 °C).

Higher elongation at break of poly(ester-carbonate-urethane)s in comparison to that of poly(carbonate-urethane)s (Table V, runs 1–11) was observed. In case of samples based on 1,4-butanediol, decrease of tensile strength also is observed. (However, this tendency is not observed for PUR based on 1,5-pentanediol.) Also the glass transition temperature of obtained

**Scheme 9.** Synthesis of poly(carbonate-urethane)s and poly(ester-carbonate-urethane)s.

poly(ester–carbonate–urethane)s is lower than those of poly(carbonate–urethane)s, especially in case of the poly(ester–carbonate–urethane) obtained from 1,5-pentanediol (Table V, runs 5–10 and 12). It should be noticed that PUR based on oligo(pentamethylene carbonate) diol and IPDI do not contain any crystalline phase, in contrast to all samples based on HMDI. This effect is possibly caused by regular structure of PUR based on HMDI that enables polymer crystallization. T_m of all these samples were very similar—in the range of 39.2 to 46.1°C.

CONCLUSIONS

Oligocarbonate diols can be selectively obtained by polycondensation of propylene carbonate with α,ω -diols of different molar mass in the presence of tetrabutoxytitanium(IV), the catalyst which can be easily removed from the resultant oligomerol by washing and filtration of the organic layer. Similar procedure can be applied for the synthesis of oligo(ester–carbonate)s. However, prior to the reaction with cyclic carbonate, bis(ω -hydroxyalkyl) ester should be obtained and the polycondensation proceeded in the presence of neat α,ω -diol. In contrast to ethylene carbonate, propylene carbonate can be used in a one-pot synthesis of oligo(ester–carbonate) diols in the presence of one catalyst. As it was previously presented by us the synthesis of oligocarbonate diols from ethylene carbonate less active catalyst such as NaCl should be used to avoid etherification.²² This catalyst is inactive in the synthesis of oligo(ester–carbonate) diols. The polyurethanes based on the obtained oligocarbonate and oligo(ester–carbonate) diols exhibited excellent mechanical properties—mechanical strength up to 50 MPa with 425% elongation at break [for PUR based on oligo(tetramethylene carbonate) diol] and 45 MPa, 630% [for (oligo(tetramethylene succinate-*co*-carbonate) with 44% of carbonate units)].

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