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Synthesis of oligocarbonate diols from a “green monomer” — dimethyl carbonate — as soft segments for poly(urethane-urea) elastomers

Summary — Results from the investigation of a two-step synthesis of oligocarbonate diols from a “green monomer” — dimethyl carbonate (DMC) are presented and discussed. In the first step 1,6-hexanediol or 1,10-decanediol was reacted with DMC to obtain bis(methylcarbonate)hexamethylene (**1h**) or bis(methylcarbonate)decamethylene (**1d**), respectively which were further reacted in the next step with appropriate diol at a intended molar ratio to obtain the final product. The solvent — 1,4-dioxane — served as a suppressant of the evaporation of both the diol and low molecular weight oligomers, while facilitating the removal of residual amount of methanol and full conversion of methylcarbonate groups. This method allows for the synthesis of oligocarbonate diols without ether linkages containing exclusively terminal hydroxyl groups and of desired molecular weights. It was shown that such oligomerols can be applied for the preparation of poly(urethane-urea) elastomers. The obtained elastomers based on oligocarbonate diols of molecular weights ranging from 1700 to 2700 exhibited very good mechanical properties.

Key words: oligocarbonate diols, dimethyl carbonate, poly(urethane-urea)s, “green monomer”.

SYNTEZA OLIGOWĘGLANODIOLI Z „ZIELONEGO MONOMERU” — WĘGLANU DIMETYLU — JAKO SEGMENTÓW GIĘTKICH W ELASTOMERACH POLI(URETANO-MOCZNIKOWYCH)

Streszczenie — Przedstawiono wyniki badań dwustopniowego procesu wytwarzania oligowęglanodiolu z wykorzystaniem „zielonego monomeru” jakim jest węglan dimetylu (DMC). Na pierwszym etapie otrzymano bis(metylowęglan)alkilenu (**1h** lub **1d**) (schemat B, tabela 1, rys. 1), który następnie poddano polikondensacji z odpowiednim diolem [1,6-heksanodiolem (**h**) lub 1,10-dekanodiolem (**d**)] użytym w założonych stosunku molowym (schemat C, tabela 2, rys. 2). Zastosowanie w tej syntezie 1,4-dioksanu jako rozpuszczalnika ogranicza odparowywanie diolu lub małowcząstkowych oligomerów, ułatwia usuwanie resztek metanolu i sprzyja obustronnemu przereagowaniu końcowych grup metylowęglanowych. Wykazano, że za pomocą tej metody można otrzymać oligowęglanodiole o założonych ciężarach cząsteczkowych (rys. 3), bez wiązań eterowych w makrocząsteczce oraz zawierających wyłącznie hydroksylowe grupy końcowe. Wykazano, że opisane oligomerole można z powodzeniem zastosować do otrzymywania elastomerów poli(uretano-mocznikowych) (rys. 4). Uzyskane elastomery z udziałem oligowęglanodiolu o ciężarach cząsteczkowych od 1700 do 2700 charakteryzowały się bardzo dobrymi właściwościami mechanicznymi (tabela 3).

Słowa kluczowe: oligowęglanodiole, węglan dimetylu, poli(uretano-moczniki), “zielony monomer”.

Polyurethanes have generated widespread interest due to their good biocompatibility and mechanical properties [1, 2]. They have found application, among others, in implantable devices such as artificial hearts, cardiovascular catheters, pacemaker lead insulation [3]. Typical polyurethane polyols are based on polyesters and polyethers. Polyesters are unstable on hydrolysis [4], generating additionally acidic degradation products, while polyethers are hydrolytically stable, but suscepti-

ble to oxidation [5]. Oligocarbonate diols, on the contrary, are stable on hydrolysis and resistant to oxidation and so constitute promising soft segments for polyurethanes used for biomedical applications [6, 7].

Toxic phosgene or its derivatives were used as a carbonate linkages source in the oldest known method of obtaining oligocarbonate diols [8, 9]. Moreover, a large amount of chlorides is generated as by-products in this process.

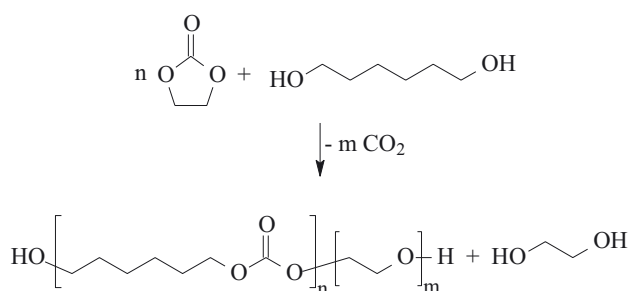
More efficient methods are based on CO₂ or simple carbonic acid esters as a source of carbonate linkages. Oligocarbonate diols can be obtained by the copolymerization of oxiranes with CO₂ in the presence of organozinc compounds [10, 11]. Oligocarbonate diols can also be obtained through the ring-opening polymerization of

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six- [12, 13] or seven-membered cyclic carbonates [14]. However the transesterification of five-membered alkylene carbonate with diols is a more convenient method (Scheme A) [15]. In this approach, the product is terminated exclusively with OH groups. The main disadvantage of this method is a partial decarboxylation which takes place, depending on the diol used, leading to the formation of a copolymer containing carbonate as well as ether linkages [16]. The presence of ether linkages in polyurethane elastomer causes a decrease in strength and the formation of cracks on contact with the oxidizing medium [3].



Scheme A. Transesterification reactions of ethylene carbonate with 1,6-hexanediol

Oligocarbonate diols can be also obtained by carbonate interchange reaction of dimethyl carbonate (DMC) with respective diols. This method was originally presented by Pokharkar *et.al.* [17]. However, due to the proximity of the boiling points of both the by-product, that is methanol (64 °C) and DMC (90 °C), some amount of DMC is removed from the reaction mixture during condensation making it difficult to obtain the oligomer of the desired molecular weight. Moreover, a small amount of methylcarbonate groups can be found in the product in addition to terminal hydroxyl groups. This in turn leads to a lowering of the molecular weight of the polyurethanes obtained from these polyols.

In spite of this, the method utilizing DMC remains convenient because it is a cheap and easily available green monomer [18]. The advantage of DMC application is further enhanced by the fact that it is obtained in stoichiometrical amounts in the production of ethylene glycol from methanol and ethylene carbonate thanks to production costs are significantly reduced.

Our strategy for synthesis of oligocarbonate diols from DMC is based on a two-step process. In the first step an intermediate — bis(methylcarbonate)alkylene is obtained and in the second step the intermediate is reacted with an appropriate diol leading to oligomers of defined molecular weight terminated exclusively with hydroxyl groups. The properties of the synthesized oligocarbonate diols and poly(urethane-urea)s obtained using these polyols have also been examined.

EXPERIMENTAL PART

Materials

— 1,6-Hexanediol (97-proc.), 1,10-decanediol (98-proc.), dimethyl carbonate, isophorone diisocyanate (IPDI) 98-proc., Bu_2SnO (all from Aldrich); anhydrous K_2CO_3 , Na_2CO_3 , CaCO_3 , NaHCO_3 and dichloromethane (all from POCh, Gliwice) were used as received, 1,4-dioxane (POCh, Gliwice) was purified by distillation over sodium.

Synthesis

Bis(methylcarbonate)hexamethylene (**1h**) (intermediate product)

59 g (0.5 mol) of 1,6-hexanediol was placed in a 1 dm³ flask fitted with magnetic stirrer, Vigreux column and distillation condenser and then 450 g (5.0 mol) of dimethyl carbonate and 2.1 g (0.015 mol) of potassium carbonate as catalyst added to it. The mixture was heated under reflux for 2 hours, after which the methanol/DMC azeotrope was slowly removed using a 1.2 m distillation column. The reaction was monitored by measuring the refractive index of the distillate. After the removal of the methanol content, the excess of dimethyl carbonate was removed under reduced pressure.

¹H NMR (400 MHz, CDCl_3); δ (ppm) = 4.11 (t, 4.36H, CH_2O , $J=6.6$ Hz), 3.76 (s, 6H, CH_3), 1.66 (m, 4.36H, $\text{CH}_2\text{CH}_2\text{O}$), 1.39 (m, 4.36H, CH_2).

FT-IR (KBr); ν (cm^{-1}) = 2963, 2911, 2862, 1749, 1444, 1260, 941, 793.

Bis(methylcarbonate)decamethylene (**1d**) (intermediate product)

1d was obtained analogically to **1h**, using 87 g (0.5 mol) of 1,10-decanediol instead of 1,6-hexanediol.

¹H NMR (400 MHz, CDCl_3); δ (ppm) = 4.12 (t, 4.56H, CH_2O , $J=6.7$ Hz), 3.77 (s, 6H, CH_3), 1.65 (m, 4.56H, $\text{CH}_2\text{CH}_2\text{O}$), 1.35 (m, 6.84H, CH_2).

FT-IR (KBr); ν (cm^{-1}) = 2934, 2923, 2856, 1754, 1445, 1289, 951, 790.

Oligo(hexamethylene carbonate) diol (**2h**)

12.836 g (0.1087 mol) of 1,6-hexanediol was placed in a 100 cm³ three-necked flask equipped with a magnetic stirrer, thermometer and distillation condenser, and then 25.001 g (0.1020 mol, $M_n = 245$) of bis(methylcarbonate)hexamethylene (**1h**), 0.45 g (0.0033 mol) of dry potassium carbonate and 20 cm³ of 1,4-dioxane were added. The mixture was initially heated to 115 °C and methanol was removed from the reaction mixture by distillation. The temperature was raised gradually for about 6 hours up to 155 °C, until all methanol was removed. The reaction was monitored by measuring the refractive index of the distillate. The residual amount of 1,4-dioxane was removed by maintaining the temperature at 155 °C under reduced pressure (2 mm Hg) for additional 2 h. The product was dissolved in dichloromethane and then

washed three times with 80 cm³ of demineralized water. The solvent was evaporated to yield 31 g of oligo(hexamethylene carbonate) diol as a waxy white solid ($M_n = 2200$, yield 82 %).

¹H NMR (400 MHz, CDCl₃); δ (ppm) = 4.09 (t, 56H, CH₂O, J=6.6 Hz), 3.61 (dt, 4H, CH₂OH, J=6.6 Hz), 1.65 (m, 56H, CH₂CH₂O), 1.55 (m, 6H, OH + CH₂CH₂OH), 1.38 (m, 60H, CH₂).

FT-IR (KBr); ν (cm⁻¹) = 3446, 2940, 2871, 1736, 1483, 1409, 1349, 1261, 1071, 958, 792, 736.

Oligo(decamethylenecarbonate) diol (**2d**)

The procedure for obtaining **2d** was similar to that of **2h**, but in this case 14.580 g (0.0838 mol) of 1,10-decanediol was used, followed by 25.002 g (0.0786 mol, $M_n = 318$) of bis(methylcarbonate)decamethylene (**1d**) and then 0.35 g (0.0025 mol) of K₂CO₃ as a catalyst. Yield 80-proc. ($M_n = 2660$).

¹H NMR (400 MHz, CDCl₃); δ (ppm) = 4.11 (t, 48H, CH₂O, J=6.8 Hz), 3.64 (dt, 4H, CH₂OH, J=6.6 Hz), 1.65 (m, 48H, CH₂CH₂O), 1.57 (m, 6H, OH + CH₂CH₂OH), 1.34 (m, 52H, CH₂CH₂CH₂O), 1.27 (m, 104H, CH₂).

FT-IR (KBr); ν (cm⁻¹) = 3459, 2924, 2855, 1741, 1474, 1411, 1342, 1281, 1258, 1093, 940, 792.

Oligo(hexamethylene carbonate) diol (**2h**) in a one-step method

30.002 g (0.2542 mol) of 1,6-hexanediol, 21.258 g (0.2362 mol) of dimethyl carbonate and 1.05 g (0.0076 mol) of K₂CO₃ were placed in a 100 cm³ flask fitted with a magnetic stirrer, Vigreux column and distillation condenser. The mixture was initially heated to 105 °C and methanol was removed from the reaction mixture by distillation. Then the temperature was increased gradually up to 150–160 °C for about 7 h, until traces of the methanol were removed. The reaction progress was monitored by measuring the refractive index of the distillate. Yield 65-proc. ($M_n = 670$).

¹H NMR (400 MHz, CDCl₃); δ (ppm) = 4.09 (t, 24H, CH₂O, J=6.5 Hz), 3.73 (s, CH₃), 3.59 (dt, CH₂OH, J=6.5 Hz), 1.64 (m, 24H, CH₂CH₂O), 1.53 (m, 6H, OH + CH₂CH₂OH), 1.37 (m, 28H, CH₂).

FT-IR (KBr); ν (cm⁻¹) = 3450, 2940, 2871, 1737, 1484, 1409, 1348, 1260, 1071, 957, 792, 736.

Urethane prepolymers

20.04 g (0.0113 mol) of oligo(hexamethylene carbonate) diol ($M_n = 1770$) and 7.55 g (0.0339 mol) isophorone diisocyanate (IPDI) were placed in a 100 cm³ two-necked flask equipped with a magnetic stirrer, thermometer and a nitrogen inlet. The reaction was carried out at 85 °C under nitrogen. The reaction progress was monitored by FT-IR spectroscopy until a complete decay of the absorption band corresponding to hydroxyl groups.

FT-IR (KBr); ν (cm⁻¹) = 3675, 3384, 2964, 2910, 2260, 1746, 1717, 1244, 792.

Curing of urethane prepolymers with water vapor

Obtained prepolymer was poured into an open glass mold (10 × 10 × 0.3 cm) and placed in a climatic chamber at 70 °C in air at 10-proc. relative humidity for 3 days and then at 60 °C in air at 40-proc. relative humidity for a further 3 days. The curing process was monitored by means of FT-IR spectroscopy observing the decay of the 2260 cm⁻¹ absorption band characteristic for urethane prepolymer isocyanate groups. A flexible transparent film was removed from the mold after 6 days and specimens of dumb-bell shape were cut for the determination of mechanical properties.

Methods of testing

— ¹H NMR spectra were recorded on a Varian VXR (400 MHz, CDCl₃) Spectrometer using tetramethylsilane as an internal standard.

— FT-IR spectra were recorded on a Biorad FT-IR Spectrometer FTS165.

— Mechanical properties of poly(urethane-urea)s were determined using Instron 5566 testing machine.

— DSC studies were performed over the temperature range from -100 °C to +120 °C using a Perkin Elmer Pyris 1 Calorimeter at a heating rate of 20 °C/min for samples of 10–25 mg mass.

— Glass transition temperature (T_g) was calculated from the inflexion point in the break in the heat flow curves in DSC curves.

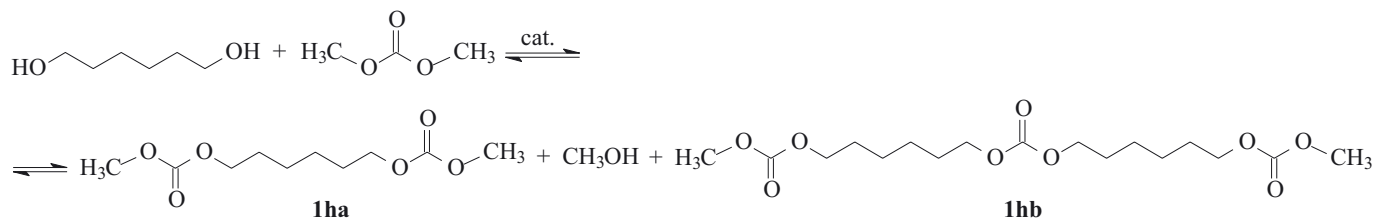
— Viscosity of the oligocarbonate diols was measured using a Mettler RM180 Rheomat at 50 °C with shear rate 129 s⁻¹.

RESULTS AND DISCUSSION

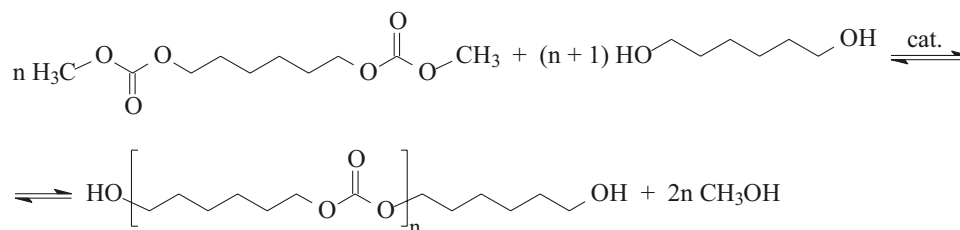
The main problem encountered in the synthesis of oligocarbonate diols from dimethyl carbonate is the co-distillation of the starting material with the by-product (methanol) which distorts the molar ratio of the desired monomers. Even a slight change in the molar ratio can drastically alter the molecular weight of the resultant oligomer and could lead to the formation of oligomers containing methylcarbonate end groups. In order to avoid the uncontrolled distillation of dimethyl carbonate with methanol, a new two-step method is hereby proposed [19].

Bis(methylcarbonate)hexamethylene (**1h**)

In the first step the intermediate product **1h** was obtained in the reaction of an appropriate diol with DMC used in a high molar excess (Scheme B). It was found that in spite of the high molar ratio of DMC: diol — 10:1, the intermediate product contained some amount (9 mol.%) of the dimer (**1hb**) apart from the desired product **1h** (Table 1).



Scheme B. Synthesis of bis(methylcarbonate)hexamethylene



Scheme C. Synthesis of oligo(hexamethylene carbonate) diol (2h)

Table 1. Influence of DMC:diol molar ratio on the dimer content

Kind of diol	DMC:diol molar ratio	Catalyst content mol. %	Dimer content mol. %	Melting point °C	Yield %
1,6-hexanediol	10 : 1	3.0 ^{a)}	9	42.5—43.5	98
	8 : 1	3.0 ^{a)}	17	42.5—43.5	99
	6 : 1	2.9 ^{a)}	25	43.0—44.0	98
	8 : 1	3.1 ^{b)}	15	43.0—44.0	97
1,10-decanediol	8 : 1	3.0 ^{a)}	14	63.0—64.0	97

^{a)} K₂CO₃ was used as catalyst.

^{b)} Na₂CO₃ was used as catalyst.

The amount of the dimer was calculated from the ¹H NMR spectrum of the product taking into account the areas of signals corresponding to CH₃ protons (3.76 ppm) and CH₂O protons (4.11 ppm) adjacent to carbonate linkages, respectively (Fig. 1):

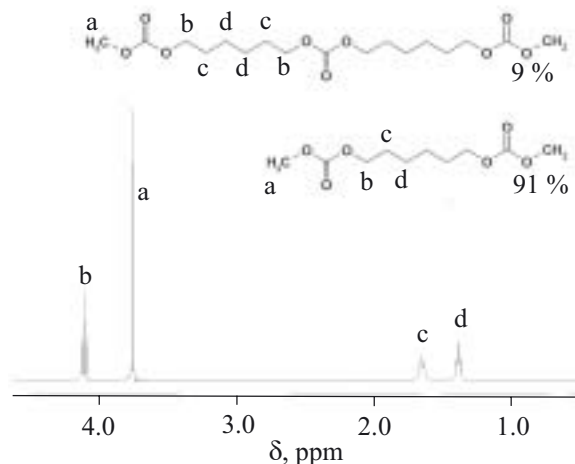
$$[\text{dimer}], \text{ mol. \%} = \frac{6b - 4a}{24} \cdot 100\% \quad (1)$$

where: *a* — area of signals corresponding to CH₃ protons = 6, *b* — area of signals corresponding to CH₂O protons.

It was also observed that the dimer content depended on the DMC:diol molar ratio changing from 9 to 25 mol. % for 10-fold and 6-fold excess of DMC, respectively.

Oligocarbonate diols

In the second step the intermediate product was reacted with the appropriate diol to obtain the corresponding oligocarbonate diols (Scheme C). The two-stage reactions led to the formation of oligomers molecular weights from 1190 to 2870 (Table 2). The reactions were carried out in the presence of 1,4-dioxane and various

Fig. 1. ¹H NMR spectrum of the intermediate product (1h) obtained from DMC and 1,6-hexanediol in molar ratio 10:1

catalysts and then carefully methanol was removed from the reaction products by distillation. It is worth noting that no DMC was detected in the distillate.

The obtained lower molecular weight (1200—1500) oligocarbonate diols were of the form of soft waxy solids, whereas oligomers of higher molecular weight (above 2200) had the form of hard waxes.

The molecular weights of the oligocarbonate diols were calculated taking into account the areas of the signals corresponding to CH₂OH (3.61 ppm) and CH₂O protons (4.09 ppm) adjacent to carbonate linkages (Fig. 2).

$$M_n = \frac{g \cdot M_r}{b} + M_t \quad (2)$$

where: *g* — area of signals corresponding to CH₂O protons, *b* — area of signals corresponding to CH₂OH protons, *M_r* — molecular weight of the constituent repeating unit, *M_t* — molecular weight of the terminal unit.

Table 2. Characteristics of obtained oligocarbonate diols ^{a)}

Run	1	diol/1 (mol/mol)	Catalyst	Catalyst content mol. %	Oligocarbonate diol		
					M_n ^{b)}	viscosity Pa · s ^{c)}	state
1 ^{d)}	1h	1.074	K ₂ CO ₃	3.0	670	0.61	soft
2	1h	1.120	Bu ₂ SnO	3.0	1190	2.16	waxy
3 ^{e)}	1h	1.103	K ₂ CO ₃	3.0	1210	2.19	white
4	1h	1.100	NaHCO ₃	3.0	1380	2.94	solid
5	1h	1.078	CaCO ₃	3.0	1770	4.14	waxy white solid
6	1h	1.073	NaHCO ₃	1.0	1850	4.42	
7	1h	1.069	CaCO ₃	5.0	2040	5.14	
8	1h	1.065	K ₂ CO ₃	3.0	2200	5.75	
9 ^{f)}	1h	1.061	K ₂ CO ₃	3.0	2220	5.79	
10	1h	1.062	Na ₂ CO ₃	6.0	2460	6.55	hard
11	1h	1.050	K ₂ CO ₃	3.0	2870	7.86	waxy
12	1d	1.062	Na ₂ CO ₃	3.0	2450	—	white
13	1d	1.066	K ₂ CO ₃	3.0	2650	—	solid

^{a)} Reaction was carried out in the presence of purified 1,4-dioxane as a solvent.

^{b)} Calculated from ¹H NMR spectra.

^{c)} Measured at 50 °C.

^{d)} Reaction was carried out in a one step mode using DMC directly.

^{e)} Reaction was carried out in the presence of non-purified 1,4-dioxane as a solvent.

^{f)} Reaction was carried out without solvent.

Figure 3 illustrated the influence at the molar ratio of the reagents on the molecular weight of oligo(hexamethylene carbonate) diol. It can be noticed that the dependence of the molecular weight on the excess of one of the monomers is typical for the polycondensation process. Described here two-step method is characterized by good repeatability and appears convenient for obtaining oligocarbonate diols of desired molecular weights.

In order to estimate molecular weights of the oligocarbonate diols, their dynamic viscosity was measured

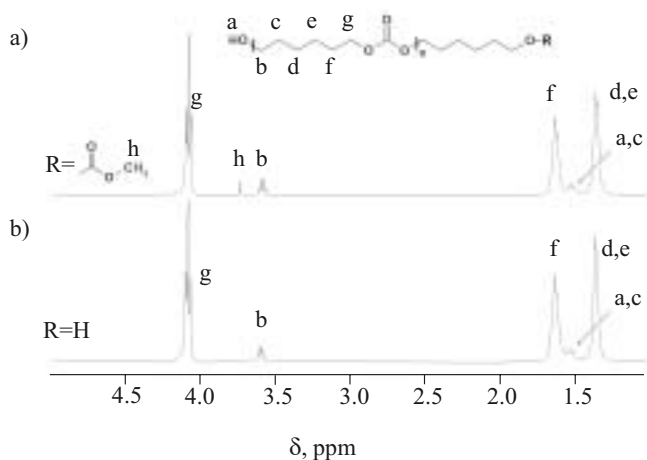


Fig. 2. ¹H NMR spectra of oligo(hexamethylene carbonate) diol: a) containing some terminal methylcarbonate groups (Table 2, run 9); b) containing only terminal hydroxyl groups (Table 2, run 10)

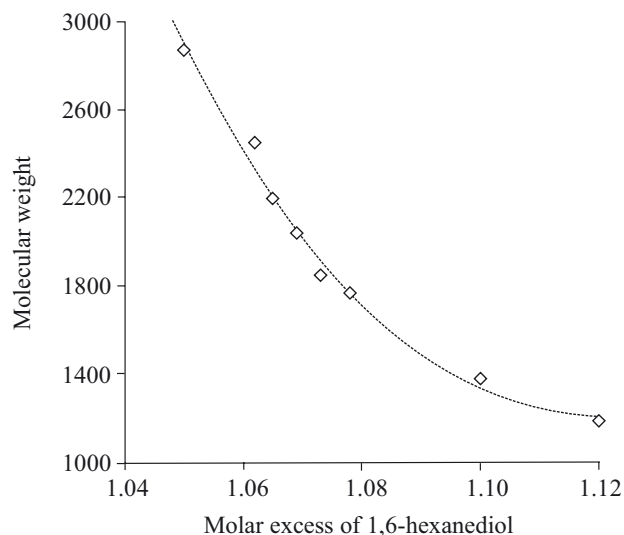


Fig. 3. Influence of 1,6-hexanediol molar excess in the reaction with **1h** on the oligo(hexamethylene carbonate) diol molecular weight

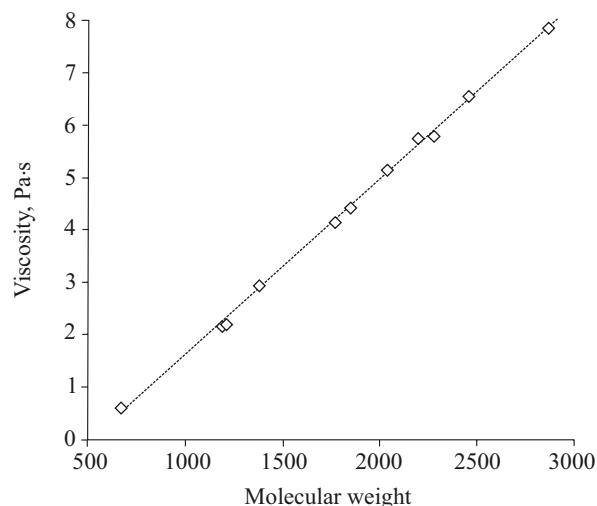


Fig. 4. Dependence of viscosity (at 50 °C) on molecular weights of oligo(hexamethylene carbonate) diol

(Fig. 4). The correlation between viscosity and molecular weight is linear and viscosity measurement can be used for molecular weight estimation in technical applications.

The synthesis oligocarbonate diols were carried out over various amounts of different catalysts such as K₂CO₃, Na₂CO₃, CaCO₃, NaHCO₃, Bu₂SnO. A minimal influence of the kind of catalyst used on the reaction kinetics as well as oligocarbonate molecular weight was also observed.

Similar results were also obtained when 1,10-decanediol was substituted for 1,6-hexanediol (Table 2, runs 12 and 13). It was found that 1,4-dioxane inhibits the evaporation of 1,6-hexanediol or low molecular weight oligomers from the reaction mixture but enhances methanol removal. 1,4-Dioxane has a higher boiling point than methanol and does not form any azeo-

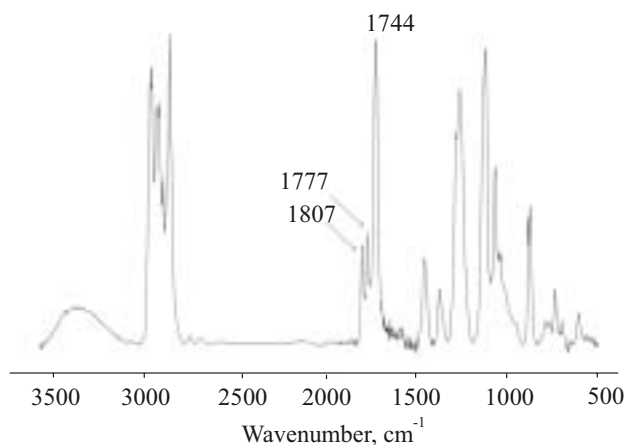


Fig. 5. FT-IR spectrum of the post-reaction mixture when 1,4-dioxane containing an ethylene glycol impurity was used as a solvent

trope with methanol. It usually contains traces of ethylene glycol, which must be removed before the reaction. In event of synthesis carried out with 1,4-dioxane contaminated with ethylene glycol (Table 2, run 3), ethylene carbonate was formed which causes changes in the molar ratio of the intended reagents. In the FT-IR spectrum of the product from run 3 the absorption band characteristic for carbonyl group of five-membered cyclic carbonate of 1777–1807 cm^{-1} was observed (Fig. 5).

Moreover, it was found that when the synthesis was carried out without a solvent (Table 2, run 9) some oligomers were terminated with methylcarbonate groups despite using vacuum distillation. In the ^1H NMR spectrum of the product a signal corresponding to $\text{CH}_3\text{OC}(\text{O})\text{O}$ protons (3.71 ppm) appeared beside the signals corresponding to terminal CH_2OH groups (3.61 ppm) (see Fig. 2). Such monofunctional oligomers with methylcarbonate end groups can terminate polymer chains during the synthesis of polyurethanes thereby to worsening their mechanical properties.

For comparison purposes, the synthesis of oligocarbonate diols was performed in a one-step mode using DMC directly in the reaction with 1,6-hexanediol. It was found that in this case, the molecular weight of the resultant oligomer was much lower than expected (670) and it was difficult to obtain repeatable results (Table 2, run 1).

Urethane prepolymers

The obtained oligocarbonate diols were used as substrates for poly(urethane-urea) synthesis. Firstly, urethane prepolymer was synthesized using isophorone diisocyanate (IPDI) and the diols. Taking into account that the presence of residual catalyst (alkali metal salts or stannate) in the obtained diols can invoke side reactions such as isocyanate dimerization or trimerization, a methylene chloride solution of the diols should be washed with deionized water in order to remove the

catalyst prior to the prepolymer synthesis. The washing was maintained until the a water conductance lower than 50 μS is reached.

The urethane prepolymers synthesis was carried out at 85 $^\circ\text{C}$ with three-fold molar excess of the diisocyanate. In this synthesis the different reactivity of the isocyanate groups in IPDI is utilized as presented earlier in [20]. Despite the different reactivity of NCO groups the reactions should be carried out with an excess of the diisocyanate monomer. Under such conditions the probability of the the second IPDI isocyanate group reacting with the diol as well as the formation of high molecular weight prepolymers is lowered.

Poly(urethane-urea) films

In order to avoid the formation of CO_2 bubbles the curing of urethane prepolymers was carried out in a climatic chamber under optimized conditions in two steps as mentioned above.

The obtained poly(urethane-urea) films based on oligocarbonate diols with molecular weight less than 2500 were transparent and colorless whereas in the case of oligomers of $M_n > 2500$ the films were also colorless, but hazy which indicated a crystallization process.

Table 3. Mechanical properties of poly(urethane-urea) films

Run	Diol	M_n of diol	Elongation at break %	Tensile strength MPa	Stress at 100-proc. of elongation MPa	T_g $^\circ\text{C}$
5	2h	1770	530	34.2	20.1	-28.6
6	2h	1850	550	33.6	19.6	-29.8
8	2h	2200	640	30.2	17.5	-34.0
13	2d	2650	710	30.8	18.0	-35.9

The mechanical properties of the elastomer films are presented in Table 3. The tensile strength depends on the molecular weight of the oligocarbonate diols used. Elastomers obtained from oligocarbonate diols of lower molecular weights exhibit a greater tensile strength (34.2 MPa) in comparison to those obtained from oligocarbonate diols of higher molecular weights (30.2 MPa). This is due to the greater concentration of hard segments (urethane and urea units). However, an increase in the oligocarbonate diol molecular weight from 1770 to 2200 leads to a decrease in the elongation at break from 640 to 530 %.

CONCLUSIONS

The presented two-step method enables the synthesis oligocarbonate diols of desired molecular weights up to 2900. It should be emphasized that these oligocarbonate diols contain exclusively terminal OH groups and can be

used as soft segments for the preparation poly(urethane-urea) elastomers. Poly(urethane-urea) films obtained from these oligocarbonate diols are characterized by high transparency, good mechanical strength and high elongation at break.

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