

Oligocarbonate diols obtained from carbonate „green monomers” as soft segments of polyurethanes

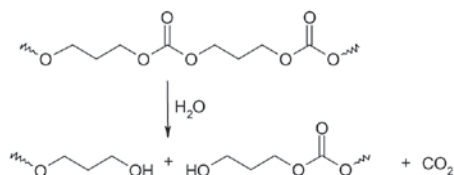
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Introduction

Polyurethane elastomers are polymeric materials exhibiting high mechanical strength and flexibility, combined with chemical resistance and biocompatibility in contact with living organisms. This segmented polyurethane is produced from diisocyanates and oligomerols as precursors of hard and soft segments, respectively. As oligomerols oligoesters, oligoethers, and recently oligocarbonate diols are usually applied. Polyurethanes based on oligoethers are resistant to hydrolysis, whereas susceptible to oxidation [1], what is disadvantageous in case of biomedical applications, especially when used as implants being in contact with blood. Polyurethanes obtained with oligoesters readily undergo hydrolytic degradation [2]. As a result of the hydrolysis of the ester bond carboxylic acid is formed which catalyzes the further hydrolysis, as well as leads to a local decrease in pH, which is an additional disadvantage of this type of implant.

It was found that poly(carbonate-urethanes) obtained from oligocarbonate diols, unlike poly(ether-urethanes) commonly used in medicine, were successfully applied as biomedical materials resistant to oxidation. Such polyurethanes offer very good properties, particularly convenient for coating materials and assuming their good biostability, for implants. It should be noted that in hydrolysis of the carbonate bond only alcohol groups and carbon dioxide are formed and no autocatalytic effect for further hydrolysis was observed (Scheme 1). The hydrolytic stability of polycarbonate containing more than 6 carbon atoms in the repeating unit is related to low water permeability. In contrast, aliphatic polycarbonates containing a repeating unit with two or three carbon atoms separated from carbonate bonds are susceptible to hydrolytic biodegradation [3,4].

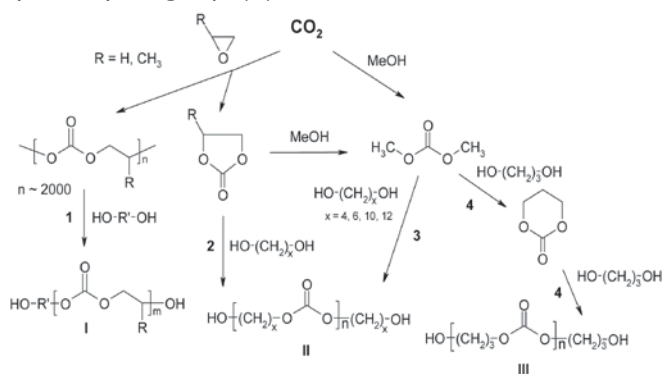


Scheme 1. Hydrolytic degradation of oligocarbonatediols

For synthesis of oligocarbonate diols it is possible to use carbon dioxide and its derivatives such as: phosgene, alkylene carbonates, dialkyl or diphenyl carbonates as a source of carbonate linkages. CO_2 is one of the cheapest materials containing multiple bonds which can be applied as co-monomer in polymerization processes. Older methods based on phosgene or its derivatives (diphosgene, triphosgene, alkyl chloroformate) [5,6] are less convenient because of the materials toxicity and formation of chlorides as by-products which are burdensome for the environment.

Taking into consideration low price, availability of raw materials, and efficiency of the process, our attention was focused on methods of obtaining oligocarbonate diols using carbon dioxide and simple carbonic acid esters. On Scheme 2 four reaction pathways leading to oligocarbonate diols with different number of carbon atoms in the repeating unit starting from carbon dioxide as a renewable

material are summarized. Oligocarbonate diols received according to the reaction pathway I contain carbonate linkages separated by two carbon atoms (I). Oligomerols synthesized according to the pathways 2 and 3 contain carbonate linkages separated by 4-12 carbon atoms depending on the used diol (II). However, in oligomers obtained according to pathway 4 carbonate linkages are separated by 3 methylene groups (III).



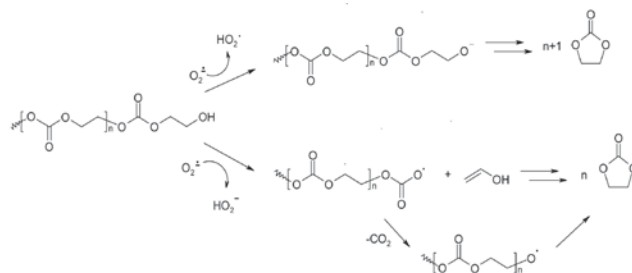
Scheme 2. Carbon dioxide as a starting material in the synthesis of oligocarbonate diols with different number of carbon atoms in the repeating unit

Oligocarbonate diols obtained directly from carbon dioxide and propylene oxide

Developed in Warsaw University of Technology in the 70s. last century by Prof. W. Kuran's group method of obtaining oligocarbonate diols at the first stage relies on copolymerization of carbon dioxide and propylene oxide in the presence of organo-zinc coordination catalysts (diethylzinc/pyrogallol 3:1) leading to high molecular weight poly(propylene carbonate). Resultant polymers of molecular weight ca. 200 000 - 300 000 were subjected to glycolysis using 1,4-butanediol. As a result oligomers of molecular weight

2000 - 3000 were obtained. Glycolysis reaction was carried out in the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ as a catalyst (Scheme 2, pathway 1) [7÷9]. The disadvantage of this method is the necessity to use high-pressure apparatus and expensive organozinc catalysts sensitive to moisture and oxygen. In addition, the products of glycolysis may contain besides the primary, less reactive secondary hydroxyl groups.

In the method of direct copolymerization of CO_2 with oxiranes polycarbonates can be obtained, in which the carbonate linkages are



Scheme 3. Degradation mechanism of polycarbonates, in which carbonate groups are separated by two carbon atoms

Oligocarbonate diols obtained from propylene carbonate

For the oligocarbonate diols production other alkylene carbonate which is propylene carbonate can be used (Scheme 2, pathway 2, $R=CH_3$). In this case, due to its lower reactivity synthesis should be carried out at higher temperature: 165-170°C and in the presence of more active catalyst, such as dibutyltin oxide (Bu_2SnO). In the presence of NaCl or NaBr transesterification reaction does not occur even at high temperatures. For azeotropic distillation of 1,2-propylene glycol because of co-distillation of the propylene carbonate with aromatic hydrocarbons we applied n-heptane instead of xylene.

We have shown that oligocarbonate diols obtained by this method do not contain ether fragments despite the higher reaction temperature, what was confirmed by the results of FTIR and 1H NMR spectroscopic analysis and mass spectrometry MALDI-TOF. The presence of a methyl group in a propylene carbonate molecule (electron-donor substituent) leads to sterical hindrance, which impedes an attack on an alkyl carbon atom belonging to a 1,3-dioxolan-2-one ring. The disadvantage of this method was the difficulty in removing tin catalyst, which created a problem at the stage of the synthesis of polyurethanes. Obtained oligomers were characterized by similar number average molecular weight (to 1300), as obtained from ethylene carbonate.

Co-oligocarbonate diols obtained from ethylene carbonate

Oligocarbonate diols easily crystallize and depending on molecular weight they form soft or hard waxes. Crystallization of oligomerol can be a disadvantage both in the transport of raw materials in industrial installations, as well as in the process of producing polyurethanes by a prepolymer method conducted at room temperature using water vapor as a chain extender. Therefore, we consider the synthesis of the oligocarbonate diols exhibiting the irregular structure. In order to disturb a regular structure of oligocarbonate diols the synthesis was carried out with a diols mixture of different chain length (Table 2). In case of obtaining co-oligocarbonate diols in the reaction of ethylene carbonate with 1,6-hexanediol and 1,4-butanediol (1:1 or 1:3) a significant content of oxyethylene units in the structure of co-oligomer was observed. This follows from the fact that the diols attack on the carbonyl carbon atom in a molecule of five-membered carbonate is a reversible process, while the attack on the alkyl carbon atom is an irreversible process due to the high speed of decarboxylation reaction.

Oligocarbonate diols obtained from dimethyl carbonate

Dimethyl carbonate (DMC) is inexpensive and easily available „green” monomer, which recently became popular as a reagent in organic synthesis. It is obtained from methanol and carbon monoxide or carbon dioxide in the process carried out in the presence of aluminosilicate as a catalyst. In an alternative method ethylene carbonate

Table 2

Characteristics of (co) oligocarbonate diols obtained by using alkylene carbonates

Diols (mol/mol)	Alkylene carbonates	M_n^a	M_n^b	Physical state
1,6-HD	propylene	1300	1820	wax
1,6-HD	propylene	750	1230	wax
1,6-HD	ethylene	1660	2150	wax
1,6-HD	ethylene	1500	1880	wax
1,6-HD/1,4-BD (1/1)	ethylene	1400	1750	liquid ^c
1,6-HD/1,4-BD (3/1)	ethylene	1450	2100	liquid ^c

a) estimated from 1H NMR spectra

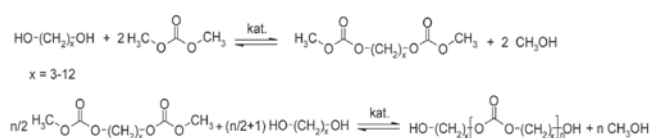
b) estimated from MALDI-TOF mass spectra

c) contained oxyethylene groups

and methanol are used as raw materials. During selective method of monoethylene glycol production from ethylene carbonate and methanol stoichiometric amount of dimethyl carbonate is formed as a by-product (Scheme 2).

Dimethyl carbonate can be also used for synthesis of aliphatic polycarbonates. However, direct transesterification of DMC with diol leads to product which molecular weight is difficult to adjust. During methanol distillation uncontrolled amount of DMC is removed from the reaction system and monomers molar ratio is disturbed.

Recently, we have developed two-stage method of oligocarbonate diols synthesis applying DMC as a source of carbonate linkages. In this method the molecular weight of oligomers can be easily controlled and the product molecules are exclusively terminated with OH groups and do not contain ether linkages [18, 19]. It was found that the polycondensation can be carried out in the presence of simple, nontoxic catalyst such as K_2CO_3 , which can be easily removed by washing the oligomer methylene chloride solution with distilled water. Firstly, the low molecular weight intermediate product - bis(methylcarbonate)alkylene is obtained in the reaction of diol with molar excess of DMC. In the second stage the resultant intermediate product is reacted with the same or different diol leading to oligocarbonate of planned molecular weight (Scheme 4).



Scheme 4. Two-step synthesis of oligocarbonate diols from DMC and α,ω -diols

Applying this method oligocarbonates of molecular weights from 1000 to 3000 without ether linkages and terminated exclusively with hydroxyl groups were synthesized by us.

Table 3

Characteristics of oligocarbonate diols obtained in two-step method using DMC

Diols (mol/mol)	M_n^a	Physical state
1,6-HD	1600	wax
1,6-HD	2200	wax
1,6-HD/1,4-BD (1/2)	1400	liquid
1,6-HD/1,4-BD (1/3)	1740	liquid

a) determined from 1H NMR spectra

According to this procedure (Scheme 2, pathway 3) oligocarbonates of higher molecular weights in comparison to the method based on alkylene carbonates (pathway 2) can be obtained. Depending on diol used in oligomer carbonate linkages are divided by hydrocarbon fragments containing 4 to 12 carbon atoms.

Co-oligocarbonate diols obtained from dimethyl carbonate

In contrast to the method based on ethylene carbonate, co-oligocarbonates obtained from dimethyl carbonate do not contain oxyethylene fragments. The synthesis was carried out similarly to the way presented above. Firstly, two intermediate products bis(methylcarbonate)-hexamethylene and bis(methylcarbonate)tetramethylene were obtained and in the second stage condensation with 1,6-hexanediol (used in required molar ratio) was carried out. It was found that for content of 1,4-butanediol higher than 20% in macromolecules the regular chemical structure is disturbed in a such degree that co-oligocarbonates are liquid at room temperature (Table 3).

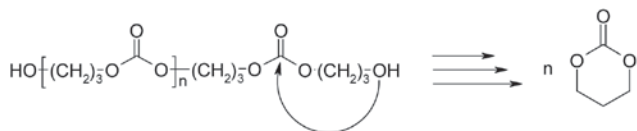
Preparation of oligocarbonate diols from trimethylene carbonate

The last presented method bases on trimethylene carbonate polymerization. In contrast to five-membered ethylene carbonate, six-

membered trimethylene carbonate (TMC) can be easily polymerized. The polymerization can proceed according to different mechanisms. It was found that for obtaining oligomers of molecular weights up to 2500 polymerization can be carried out at high temperature (110°C) without using catalyst in the presence of required amount of typical diol which play a role of initiator-starter.

Preparation of trimethylene carbonate monomer

Trimethylene carbonate (TMC) was obtained by the method using oligocarbonate as a starting material. At the first step bis(methylcarbonate)trimethylene was obtained in the reaction of dimethylcarbonate with 1,3-propanediol (Scheme 4, x = 3). Then the resultant product was reacted with 1,3-propanediol to obtain a high molecular weight poly(trimethylene carbonate). In the next step, polycarbonate was depolymerized and simultaneously cyclic monomer was distilled out of the reaction system (Scheme 5). Depolymerization process was carried out at 235-240 °C under reduced pressure (2 mmHg) [20]. This process is characterized by relatively high yield (73%) in comparison to known methods in which ethyl chloroformate or phosgene [21] are used. Additionally, no burdensome for environment chlorides are formed, and side products (linear dimers, trimers and unreacted 1,3-propanediol) can be reused.



Scheme 5. Synthesis of TMC by depolymerization of poly(trimethylene carbonate) combined with distillation under reduced pressure

Thermal polymerization of trimethylene carbonate

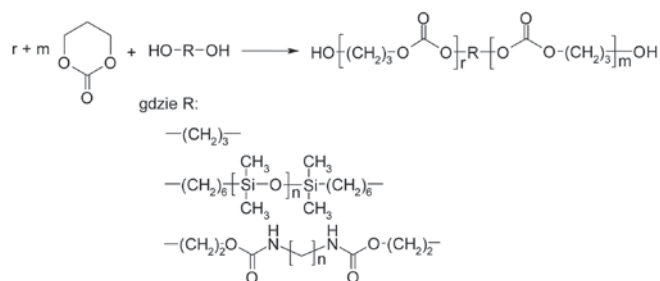
Oligocarbonate diols based on 1,3-propanediol of predictable molecular weight can be obtained by thermal polymerization of TMC using various diols as starters in proper molar ratio (Scheme 6). Polymerization was carried out at 110°C under inert gas for 24 ÷ 36 h.

As initiators: 1,3-propanediol, 1,6-bis(2-hydroxyethoxy-carbonylamino)hexane (1,6-DH DU), α,ω -bis(6-hydroxyhexyl)poly(dimethylsiloxane) (OSD) were applied.

When the product of the reaction of 1,6-diaminehexane with ethylene carbonate was used as a starter (Scheme 7) urethane fragments were introduced into the structure of oligocarbonate diol without use of diisocyanates.

When α,ω -bis(6-hydroxyhexyl)poly(dimethylsiloxane) (OSD) was used as a starter co-oligomer containing oligocarbonate and oligo(dimethylsiloxane) blocks were obtained (Scheme 6, Table 4).

Developed (co)-oligocarbonate diols were used for preparation of polyurethanes. At first step they were reacted with isophorone diisocyanate leading to urethane prepolymers which were in second step cured with water vapor in a climatic chamber. Obtained colorless and transparent foils exhibited elastomeric properties (Fig. 4). Independently on obtaining method, oligocarbonate diols exhibited good mechanical properties (Table 5). Depending on chemical structure and



Scheme 6. The ring-opening polymerization of trimethylene carbonate using various initiator-starters



Scheme 7. Synthesis of the starter - 1,6-bis(2-hydroxyethoxycarbonylamino)hexane in the reaction of ethylene carbonate with 1,6-diaminohexane

Table 4

Characteristics of the obtained (co)-oligocarbonate diols

Diols	M _n ^{a)}	Physical state
1,3-PD	1500	liquid
1,3-PD	1950	liquid
1,6-DH DU 8% _{wag.}	1520	soft wax
1,6-DH DU 6% _{wag.}	1980	soft wax
OSD	1910	soft wax
OSD	1720	soft wax

a) determined from ¹H NMR spectra.

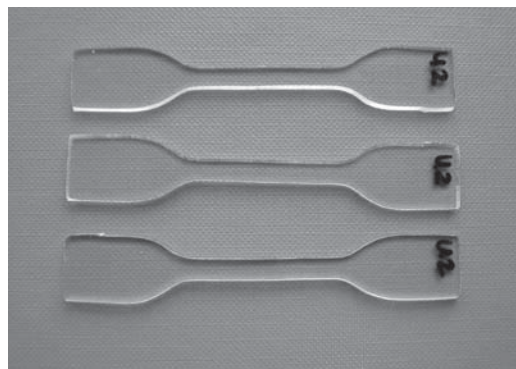


Fig. 4. Specimens for testing of mechanical properties prepared from polyurethane obtained from oligo(hexamethylene carbonate) diol (M_n = 1600)

molecular weight of the used oligocarbonate diol, tensile strength of polyurethanes were in the range from 35 MPa (oligo(trimethylene carbonate) diol of M_n = 1500) up to 50 MPa (oligocarbonate diol based on 1,6-HD/1,4-BD (1/2) of M_n = 1400), and ultimate elongation from 420% (OWD + OSD of M_n = 1720) up to 750% (oligo(carbonate trimethylene) diol of M_n = 1500).

Unexpectedly, the highest mechanical strength exhibited polyurethane elastomers obtained from co-oligocarbonate diols based on 1,6-HD/1,4-BD (1/2). It should be underlined that their ultimate elongation was greater than 600%.

Table 5

Dependence of mechanical properties and T_g of polyurethanes on the chemical structure and molecular weight of oligocarbonate diols

Diols (mol/mol)	Carbonate	M _n	ε _r ^{a)} , %	δ _r ^{b)} , MPa	δ _{100%} ^{c)} , MPa	elastomers T _g , °C
1,6-HD	ethylene	1660	510	38,5	-	-
1,6-HD/1,4-BD (1/1)	ethylene	1500	460	38,5	20,5	-19,1
1,3-PD	trimethylene	1500	750	35,0	5,0	-19,7
1,6-DH DU	trimethylene	1980	580	45,5	6,0	-
OSD	trimethylene	1720	420	39,5	11,5	-47,3
1,6-HD	dimethyl	1600	440	43,5	20,0	-
1,6-HD/1,4-BD (1/2)	dimethyl	1400	630	50,0	33,0	-

a) ultimate elongation b) stress at break c) stress at 100% elongation

It was also found that polyurethanes based on oligocarbonate obtained from diols of longer hydrocarbon chains and characterized by molecular weight higher than 2500 do not exhibit elastomeric properties and can remain new shape after deformation at room temperature. Such polyurethane specimens after heating above melting point (T_m) of crystallites recover primary shape. At temperature below T_m conformational movements of polymer chains are confined. Due to the restricted relaxation the polyurethane shape recovery is almost 100%. The method of obtaining of the polyurethanes exhibiting shape memory was described in detail in [22].

Conclusions

The methods of oligocarbonate diols preparation developed by us are based on carbon dioxide as primary renewable starting material. Depending on requirement, for synthesis of oligomers containing from 2 to 12 carbon atoms in hydrocarbon fragment (between carbonate linkages) different reaction pathways can be selected. Oligocarbonate diols containing 2 or 3 carbon atoms in hydrocarbon fragment are susceptible for hydrolytic biodegradation. Larger number of carbon atoms in hydrocarbon fragment leads to better hydrolytic stability of such polycarbonates.

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The 17th International Symposium on Homogeneous Catalysis SHC-17

For the Polish chemists of catalysis the year 2010 is definitely going to be special as in July 4-9, 2010 in Poznań the 17th International Symposium on Homogeneous Catalysis will take place. This important event is organized under the auspices of the Polish Academy of Sciences. The chairman of the organizing committee is Prof. Bogdan Marciniak from the Adam Mickiewicz University in Poznań. The fact that Poland has been appointed to organize the Symposium confirms the recognition of the high position of Polish chemistry, especially those working on catalysis in a board sense of the word.

The success of SHC-17 depends considerably on participation of a wide range of representatives of the scientific and industrial circles. It is expected that this Symposium will host about 500 participants from the whole world and we count on large participation of Polish chemists.

The information on the Symposium is given on a continuously updated website www.ishc17.amu.edu.pl In case of any questions or problems please contact the Symposium Secretariat at the following address: ishc@amu.edu.pl