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Synthesis of oligocarbonate diols from ethylene carbonate and aliphatic diols catalyzed by alkali metal salts

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Abstract

The influence of alkali metal salt catalysts and reaction conditions on the oxyethylene units formation in the synthesis of oligocarbonate diols from five-membered cyclic carbonates and aliphatic diols is presented. The reaction mechanism, involving the alkoxide group formation from cyclic carbonate and alkali metal salts has been proposed and discussed. The oligomeric products were analyzed by means of MALDI-TOF mass spectrometry and NMR spectroscopy.

Keywords: Oligocarbonate diols; Ethylene carbonate; Alkali metal salts

1. Introduction

Polyurethanes are important biomedical polymers, and are used in implantable devices such as artificial hearts, cardiovascular catheters, pacemaker lead insulation, etc. Polyether polyurethanes exhibit greater biostability than polyester polyurethanes, and are therefore generally preferred biopolymers. However, there is some problem with stress cracking of polyether polyurethane materials, which can cause the material failure. Polyether polyurethanes are susceptible to oxidation in the body, particularly in areas that are under stress [1,2]. When oxidized, polyether polyurethane elastomers lose strength and form cracks. It is believed that the ether linkages degrade, perhaps due to the metal ion catalyzed oxidative attack at α-methylene groups in the material [3].

New polyurethanes have been developed that are more resistant to an oxidative attack. Such polyurethanes include only hydrocarbon- and carbonate-based flexible segments that are resistant to metal induced oxidation [4]. These polyurethanes are substantially free of ether and ester linkages [5,6].

Aliphatic polycarbonates can be obtained from diols and phosgene. A more convenient method is that, in which polycarbonates are synthesized directly from carbon dioxide by the copolymerization of CO_2 with oxiranes (propylene oxide) [7] or via ring-opening polymerization of six- (trimethylene carbonate) [8] and seven-membered cyclic carbonates (tetramethylene carbonate) [9]. Oligocarbonates can be also synthesized from dialkyl carbonate and respective diol according to the transesterification mode [10]. However, in the latter method inactive alkyl groups can terminate the oligomer chains instead of OH group.

The application of carbon dioxide or another simple form of CO_2—cyclic carbonate, as a cheap and easy available raw material in the polycarbonate synthesis is an additionally attractive method taking into account that carbon dioxide is a renewable material and its consumption leads to the reduction of the greenhouse effect.

In contrast to six- and seven-membered cyclic carbonates, it is not possible to homopolymerize five-membered cyclic carbonates. The reaction carried out at above 170 °C in the presence of transition metal alkoxides leads to a product containing less than 50 mol% of carbonate linkages in the polymer chain [11]. The ring-opening polymerization of ethylene carbonate proceeds with partial decarboxylation, resulting in the formation of a copolymer comprising of ethylene oxide and ethylene carbonate repeated units—poly(ethylene ether-carbonate). The synthesis of such polymers has been reported by several authors. Soga et al. have found that when $Al(acac)_3$ or $Ti(OBu)_4$ were used as catalysts, the structure of poly(ether-carbonate) is mostly an

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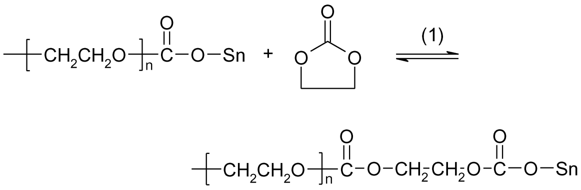
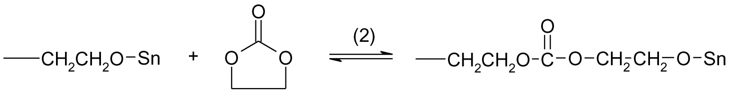
alternating one, resulting from the evolution of carbon dioxide from every other repeated unit. They proposed the mechanism in which 1,4,6,9-tetraoxaspiro[4.4]nonane is an intermediate for ethylene carbonate polymerization [12]. Vogdanis et al. [13,14] have found that when organotin compounds were used as catalysts, diethylene glycol with smaller amounts of higher glycols was the major hydrolysis product of poly(ether-carbonate), but no ethylene glycol was identified. They also reported that the composition of poly(ether-carbonate) was strongly dependent on the catalyst chosen and that the degree of CO_2 retention decreased from 50 mol% fraction, as the relative basicity of the catalyst increased. Their explanation was that the polymerization occurred above the ceiling temperature (T_c) for pure poly(ethylene carbonate) formation and that propagation occurred via monomer insertion between the growing polymer chain end and a catalyst fragment (Scheme 1).



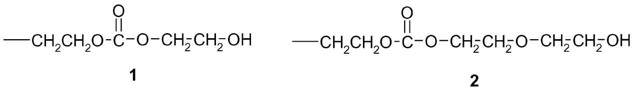
Scheme 1.

Above T_c the equilibrium (1) must be shifted to the left since the sequence length of ethylene carbonate units cannot exceed one. The reaction can proceed to either type of the alkoxide chain end presented in Scheme 2.



Scheme 2.

Harris and McDonald used GC analysis in conjunction with ^{13}C NMR to elucidate the structure of the polymer and other intermediates formed during the ring-opening polymerization of ethylene carbonate [15]. They observed that both 2-hydroxyethylcarbonate (**1**) and 2-hydroxyethylether (**2**) end groups are present initially (Scheme 3).



Scheme 3.

However, only (**2**) was present during the latter stages of the polymerization. They also found that diethylene glycol was an important reaction intermediate and was present in steady-state concentration, independent of which glycol was used as the starter [15,16].

There is little information concerning the synthesis of polycarbonates from diols and ethylene carbonate proceeding without the loss of CO_2. Although the previous authors have contributed greatly to the understanding of the EC polymerization, in particular Storey [17] and Harris's [16], no mechanism which explains the results of the transesterification reaction proceeding without the formation of oxyethylene fragments was proposed.

Recently, we have revealed that the reaction of diols containing more than five carbon atoms in a molecule with propylene carbonate, carried out under atmospheric pressure using azeotropic solvents in the presence of the coordination catalysts (Bu_2SnO) leads to pure oligocarbonate diols [18]. The main drawback of that method was the use of a relatively high amount of the tin-based catalyst (5%) which was difficult to remove from the product. In the case of using ethylene carbonate the resulting macrodiols, obtained under the same conditions, contained a significant amount of oxyethylene units.

The aim of our work were the investigations on oligocarbonate diol synthesis by the transesterification of ethylene carbonate with aliphatic diols carried out in the presence of alkali metal salts, as simple non-toxic catalysts. It is our goal to propose a mechanism which would explain the formation of a polycarbonate without oxyethylene fragments, particularly this involving the role of the reaction temperature, excess of ethylene carbonate, as well as kind of alkali metal salt in the selective catalysis. Alkali metal salts are easy to remove from the oligocarbonate diols by washing with water, and the polyurethanes obtained using these diols not containing toxic additives can be applied for biomedical purposes.

Oligocarbonate diols are also potential solid rocket propellant binders due to possessing a high oxygen content. Moreover, aliphatic polycarbonates display a low heat of combustion and incorporate CO_2 as a cheap building block [17].

2. Experimental

2.1. Materials

Hexane-1,6-diol (HD), decane-1,10-diol (DD), propylene carbonate (Fluka), and ethylene carbonate (Aldrich) were used as received. Solvents: xylene, *n*-hexane and *n*-octane (Polish Chemical Reagents, Gliwice) were distilled, and the middle fraction was used for polycondensation as an azeotropic medium.

Li_2CO_3, Na_2CO_3, K_2CO_3, NaCl, KCl, NaBr, KBr, NaI, KI, NaF, Na_2SO_4, NaH_2PO_4, CH_3COONa (Polish Chemical Reagents, Gliwice), CsF, LiCl, RbCl, CsCl, LiI (Fluka), LiBr (BDH), were used after drying under reduced pressure at 120 °C. Bu_2SnO (Aldrich) was used without additional purification.

2.2. Measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. Deuterated solvents were used and tetramethylsilane served as internal standard.

IR spectra were recorded on a Biorad FTIR spectrometer as KBr pellets. Polycarbonate oligodiols MALDI-TOF spectra were recorded on a Kratos Kompact MALDI 4 V5.2.1 apparatus equipped with a 337 nm nitrogen laser with a 3 ns pulse duration. The measurements were carried out in the linear mode of the instrument at an acceleration voltage of +20 kV. For each sample, spectra were averaged over 200 laser shots. The samples were dissolved in THF (5 mg/ml) and mixed with a solution of the MALDI-TOF matrix (2,5-dihydroxybenzoic acid, 0.2 M in THF). The laser power was moderated in the range 120–130 units, characteristic for this apparatus in order to avoid distortion of the mass spectrum. DSC thermograms over the temperature range, −120 to 60 °C were recorded on a Perkin Elmer Pyris 1 calorimeter. The measurements were carried out at a heating rate of 20 °C/min. Sample weights were 10–25 mg. The hydroxyl number of macrodiols was determined by the phthalic anhydride method according to the ASTM D 2849 standard.

Solubility of alkali metal salts in the reaction mixture was measured using Atomic Absorption Spectrometer Avanta.

2.3. Macrodiol synthesis

The synthesis of the oligocarbonate diols was carried out using a monomer mixture consisting of diol and ethylene carbonate in the molar ratio of 1:1.5. A typical procedure is as follows.

In a 100 ml three-necked flask, equipped with a mechanical stirrer, reflux condenser, thermometer and Barrett type receiver, ethylene carbonate (6.6 g, 0.075 mol), hexane-1,6-diol (5.9 g, 0.05 mol), 15 ml of xylene as the azeotropic solvent, and NaCl (0.01 g, 0.2 mmol) as a catalyst were placed. The transesterification reaction was carried out at 142–145 °C under reflux collecting ethylene glycol in a Barret receiver. The progress of the polycondensation reaction was monitored analyzing samples of the reaction mixture by IR spectroscopy measuring the absorption band characteristic for OH and C=O groups using the calibration curve. Additional information was obtained from the amount of ethylene glycol collected. After 6 h the azeotropic solvent was evaporated from the post-reaction mixture and next the post-reaction mixture was heated at 132–135 °C under vacuum (2 mmHg) for additional 6 h to continue the transesterification reaction with ethylene glycol as well as hexane-1,6-diol removal. The residual amount of ethylene carbonate and catalyst were removed by washing the CH_2Cl_2 solution of the post-reaction mixture three times with 50 ml of water and then the solvent was distilled off under reduced pressure. The yield of the oligocarbonate diol was 6.1 g.

^1H NMR ($CDCl_3$): δ(ppm) = 4.11 (t, $OC(O)OCH_2$), 3.64 (m, $HOCH_2CH_2$), 2.00 (b, HO), 1.69 (m, $OC(O)OCH_2CH_2$), 1.58 (m, $HOCH_2CH_2$), 1.41 (m, $CH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ(ppm) = 25.4–25.5 $C(O)OCH_2CH_2CH_2$, 28.5–28.6 $C(O)OCH_2CH_2$, 32.5 $HOCH_2CH_2$, 62.7 $HOCH_2$, 67.8 $C(O)OCH_2$, 155.4 C=O FTIR (KBr): 3400, 2930, 1745, 1470, 1400, 1260, 1020, 930, 770 cm^{-1}.

2.4. Oligocarbonate synthesis with diol excess

To a similar reaction vessel equipped with a dropping funnel hexane-1,6-diol (5.9 g, 0.05 mol), 12 ml of xylene as the azeotropic solvent, and NaCl (0.01 g, 0.2 mmol) were introduced. Ethylene carbonate (6.6 g, 0.075 mol) as a solution in xylene (8 ml) was added dropwise to the boiling reaction mixture.

2.5. Oligocarbonate synthesis using a Soxhlet apparatus

The synthesis of oligocarbonate diols was carried out analogously to the above procedure but at the end, when no ethylene glycol was distilled off, instead of a Barret receiver, a Soxhlet apparatus containing molecular sieves A5 was used. The reaction was continued with circulating xylene at 141–143 °C for additional 5 h.

2.6. Macrocyclization of oligocarbonate diols under diluted conditions

Oligocarbonate diols (M_n = 3900) (1.44 g, 0.36 mmol) dissolved in *o*-dichlorobenzene (72 ml) were heated at 176–178 °C for 96 h in the presence of Bu_2SnO (0.075 g, 0.3 mmol) as a catalyst. The solvent was evaporated off under reduced pressure at 120 °C and the product was analyzed by MALDI-TOF mass spectrometry.

3. Results and discussion

It was found that the reaction of ethylene carbonate with hexane-1,6-diol carried out at 142–145 °C under atmospheric pressure in the presence of NaCl (1 mol%), as a catalyst with xylene as an azeotropic solvent, removing ethylene glycol from the reaction system leads to α-hydroxyhexamethylene-ω-hydroxypoly(oxycarbonyloxyhexamethylene) [poly(hexamethylene carbonate) diol] (Table 1, run 6).

In the MALDI-TOF spectrum of the product, there are two series of signals corresponding to oligocarbonate diols

Table 1
Characteristics of macrodiols obtained from hexane-1,6-diol and ethylene carbonate under various reaction conditions

Run no	Catalyst	Temperature (°C)	Time (h)	Yield (g)[a]	Content of oxyethylene units in macrodiols (mol%)	MALDI-TOF	
						M_n	M_w/M_n
1	Li_2CO_3	142–145	3	6.1	<5	1600	1.16
2	Na_2CO_3	142–145	5.5	6.5	72	1270	1.19
3	K_2CO_3	142–145	4.5	6.7	73	1220	1.22
4	K_2CO_3	170–172	5	6.5	89	2500	1.25
5	LiCl	142–145	4	6.1	6	1000	1.18
6	NaCl	142–145	4	6.1	<2	1150	1.13
7	NaCl	170–173	4	6.3	45	1280	1.18
8	NaCl	168–170[b,c]	6	–	<5	1110	1.18
9	KCl	142–145	4.5	6.1	7	1020	1.14
10	RbCl	142–145	2	6.2	10	1010	1.16
11	CsCl	142–145	4	6.1	6	1100	1.18
12	LiBr	142–145	4	6.1	<5[d]	1100	1.14
13	NaBr	142–145	4	6.1	<2	1160	1.13
14	KBr	142–145	5	5.9	3	1400	1.16
15	LiI	142–145	4	5.3	<5	750	1.20
16	NaI	142–145	5.5	5.5	<5	800	1.23
17	KI	142–145	5	5.4	<5	850	1.23
18	NaF	140–145	5.5	–	–	–[e]	–
19	CsF	142–145	4	–	–	–[e]	–
20	CsF	170–175	4	6.0	82	1200	1.32
21	NaH_2PO_4	165–170	4.5	6.1	65	1050	1.35
22	Na_2SO_4	140–145	4	–	–	–[e]	–
23	Na_2SO_4	165–170	7	6.1	58	1400	1.29
24	CH_3COONa	140–145	4.5	6.2	77	2100	1.32
25	Bu_2SnO	140–145	4	–	–	–[e]	–
26	No catalyst	140–145	12	–	–	–[e]	–
27	No catalyst	175–185	5	5.5	>90	1450	1.31

[a] Starting from 5.9 g of hexane-1,6-diol.
[b] Decane-1,10-diol was used.
[c] Propylene carbonate was used.
[d] With hexamethylene ether units.
[e] No reaction.

terminated with hexane-1,6-diol and ethylene glycol, respectively. The peaks are characterized by a mass increment of 144 Da. This mass increment equals the mass of repeating unit in the poly(hexamethylene carbonate). The residual masses correspond to 118 and 62 Da which can be assigned to hexane-1,6-diol and ethylene glycol, respectively (Fig. 1). Molecular weight of each macromolecule as a sodium ion adduct (M) can be calculated from the Eq. (1).

$$M = Q + nX + Y + Z + H + N \quad (1)$$

where: M—the molar mass of the adduct of the macrodiol with a sodium ion;

Q—the molar mass of the $HO(CH_2)_6O$ unit (117 Da);

X—the molar mass of the hexamethylene carbonate repeating unit (144 Da);

n—a number of the repeating units;

Y—the molar mass of an oxyethylene unit (44 Da);

Z—the molar mass of an ethylene carbonate unit (88 Da);

H—the atomic mass of hydrogen atom;

N—the atomic mass of sodium atom.

In the ^1H and ^{13}C NMR spectra of the product there are no signals characteristic for protons and carbon atoms originated from oxyethylene units (Fig. 2b). In the IR spectrum there also were no absorption bands characteristic for ether linkages.

The reaction temperature was easy to control by the addition of an appropriate amount of xylene as an azeotropic solvent. It was found that when the reaction was carried out at above 145 °C some oxyethylene fragments appeared in the product (Table 1, run 7) (Fig. 2a). The amount of oxyethylene fragments in the oligomer increased for a higher temperature (Table 1, runs 6 and 7). The reaction progress was monitored by the measurement of the amount of ethylene glycol collected as a condensate in the azeotropic mixture and by the intensity analysis of the absorption band at 1745 cm^{-1} in the IR spectra characteristic for the linear carbonate linkages carbonyl group.

In the MALDI-TOF mass spectrum of the product obtained in the presence of NaCl at 165 °C (Fig. 3), there are additional series of signals corresponding to oligocarbonates containing one oxyethylene unit. Signals correspond-

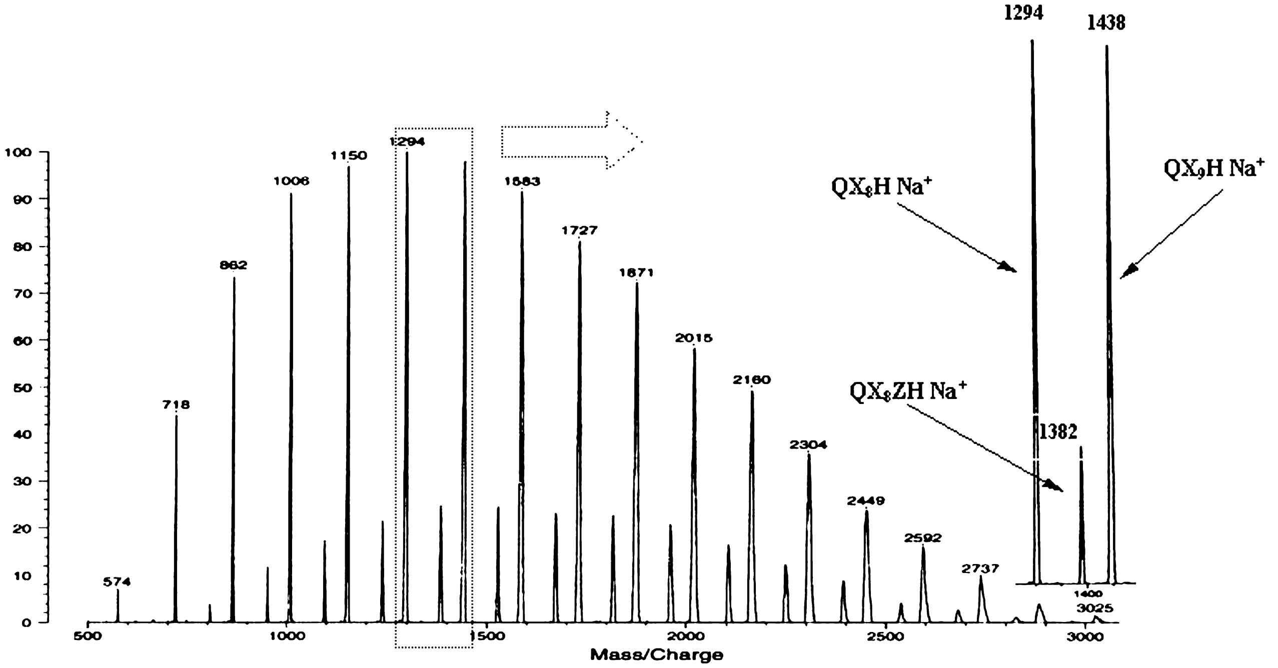


Fig. 1. MALDI-TOF mass spectrum of the oligocarbonate diol obtained from hexane-1,6-diol and ethylene carbonate (1:1.5 mol/mol) in the presence of NaCl at 142–145 °C, where X = $C(O)O(CH_2)_6O$, Q = $HO(CH_2)_6O$, Z = $C(O)O(CH_2)_2O$.

ing to oligomers with two and more oxyethylene units are overlapped by signals which can be assigned to oligomers containing ethylene carbonate unit. No series of signals which can be assigned to oligomers obtained only from ethylene carbonate can be observed.

It was found that when the reaction was carried out without catalyst at 145 °C, no reaction progress was observed. No ethylene glycol was collected for 12 h of xylene recirculation (Table 1, run 26).

At below 145 °C an attack of the alkoxy group on the carbonyl group of cyclic carbonate (pathway a in Scheme 4) takes place and linear carbonate molecules terminated with an OH group are formed. At higher temperature (>145 °C), the reaction proceeds according to the both pathways, a and b to produce macrodiols with a significant amount of the oxyethylene fragments (Table 1, run 7). In the IR spectrum of the reaction product, an intensive band at 1100 cm^{-1} characteristic for ether linkages was present besides the absorption band at 1740 cm^{-1} characteristic for carbonyl group of carbonate (Fig. 4).

It was found that solubility of alkali metal salts in the reaction mixture has no significant influence on the course of the reaction. For similar solubility of NaCl and NaF no reaction was observed for sodium fluoride used as a catalyst (Tables 1 and 2). In the case of NaBr of much higher solubility, the reaction proceeded similarly to that when NaCl was used as a catalyst.

Table 2
Alkali metal salts solubility in the reaction mixture of hexane-1,6-diol, ethylene carbonate and xylene at 145 °C

Salt	NaF	NaCl	NaBr	NaI	KCl	K_2CO_3
Solubility (μg/g)	8	13	410	1030	25	5300

For more details see Section 2.

In the case of using propylene carbonate instead of ethylene carbonate, alkali metal salts are inactive catalysts under such reaction conditions. Polycarbonates from propylene carbonate can be obtained using Bu_2SnO as a catalyst at higher temperature (170 °C) as was reported in our previous paper [18].

3.1. Influence of an excess of ethylene carbonate on the synthesis of the oligocarbonate diols

A stoichiometric amount of monomers should be usually used to obtain a high molecular weight polymer using step growth polymerization method. However, in the case of the transesterification reaction of ethylene carbonate with an appropriate diol, similarly to the synthesis of poly(ethylene terephthalate) from dimethyl terephthalate and ethylene glycol [19], the molar excess of ethylene carbonate to diol was not critical for the polycarbonate molecular weight. Moreover, some excess of cyclic carbonate is needed, because ethylene carbonate is lost during azeotropic distillation of ethylene glycol. Additionally, due to the relatively small reaction equilibrium (Scheme 4) an excess of ethylene carbonate is also required to achieve adequate concentration of 2-hydroxyethyl carbonate groups in the reaction system.

Our investigations revealed that the optimal molar ratio of ethylene carbonate to diol is equal to ca. 1.5:1. For this molar ratio after 5 h, 73% of the theoretical amount of ethylene glycol was distilled off from the reaction system,

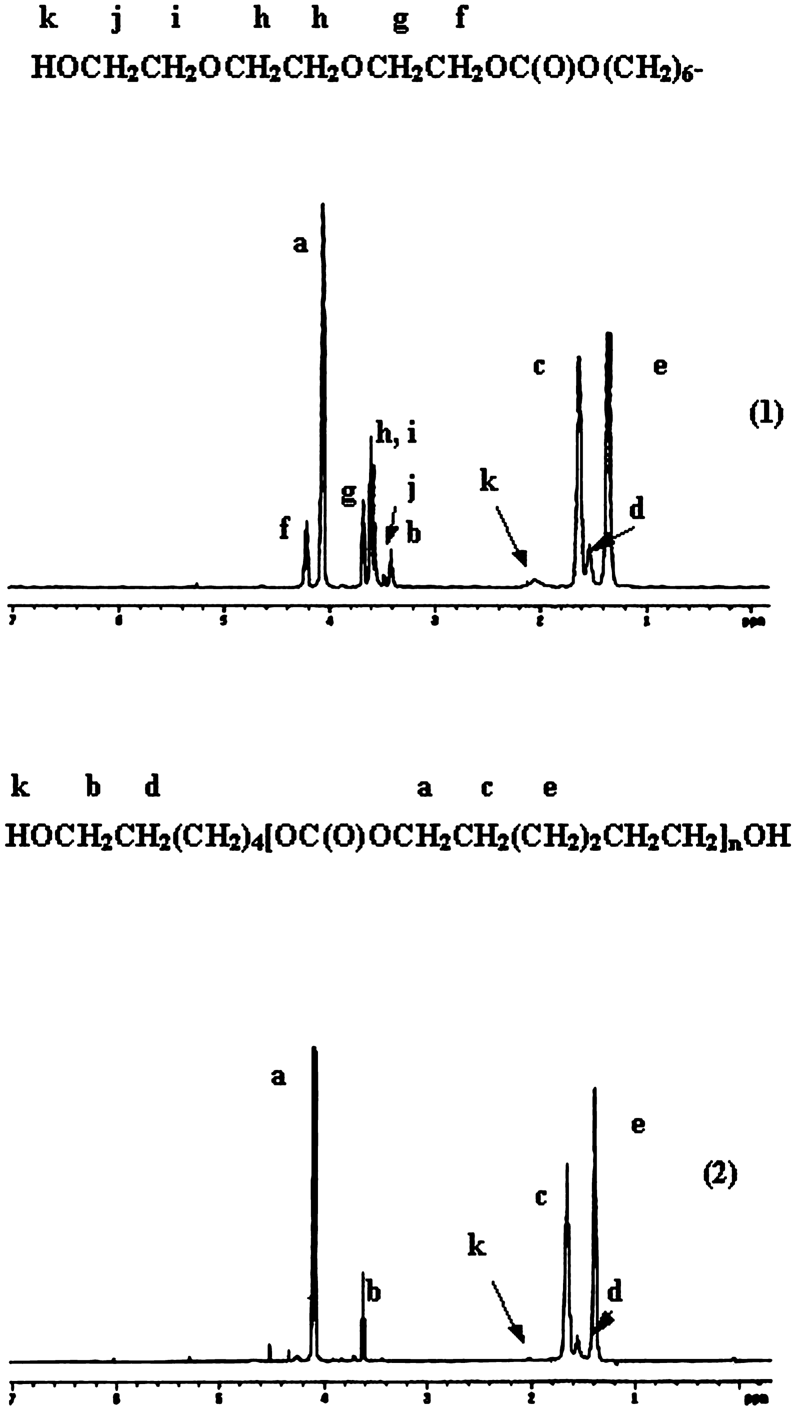


Fig. 2. ^{1}H NMR spectrum of the oligocarbonate diols obtained from hexane-1,6-diol and ethylene carbonate (1:1.5 mol/mol) in the presence of NaCl at 170–173 °C (a) and 142–145 °C (b) using xylene as azeotropic solvent.

and oligocarbonate diol of 1150 number average molecular weight was obtained (Table 3, run 2). When a larger excess of cyclic carbonate was used, the reaction rate was lower and a smaller amount of ethylene glycol was distilled off at the same time. In the case of the transesterification reaction carried out with a 10-fold excess of ethylene carbonate, after 10 h only 7% of the theoretical amount of ethylene glycol was removed from the reaction system as the azeotrope with xylene.

A similar effect was observed for the polycondensation carried out maintaining an excess of hexane-1,6-diol in the system at the first stage of the process. After 10 h only 25% of the theoretical amount of glycol was distilled off, when the reaction was carried out with the starting molar ratio of ethylene carbonate to diol equal ca. 1:1.5. To maintain a constant molar ratio of hydroxyl groups to cyclic carbonate, the cyclic carbonate was added dropwise.

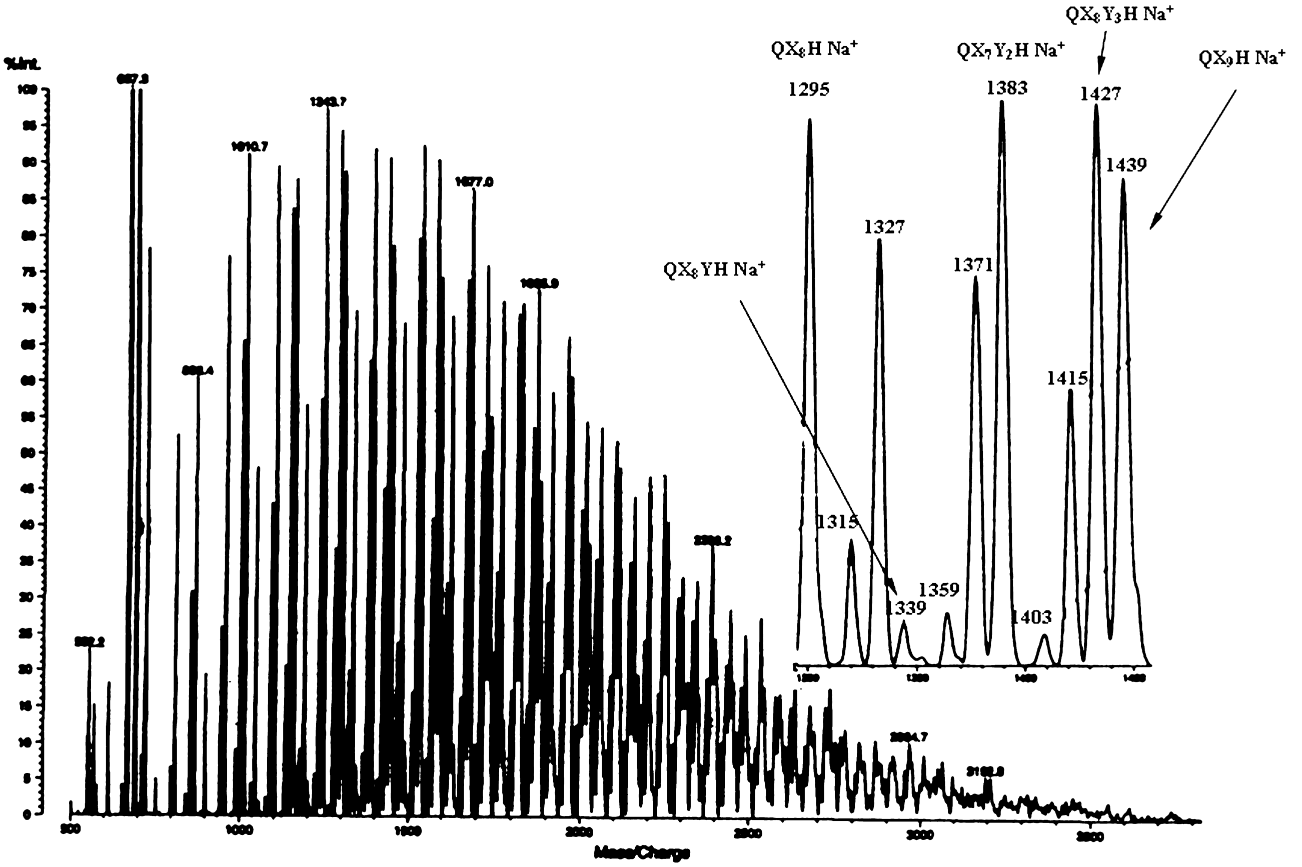
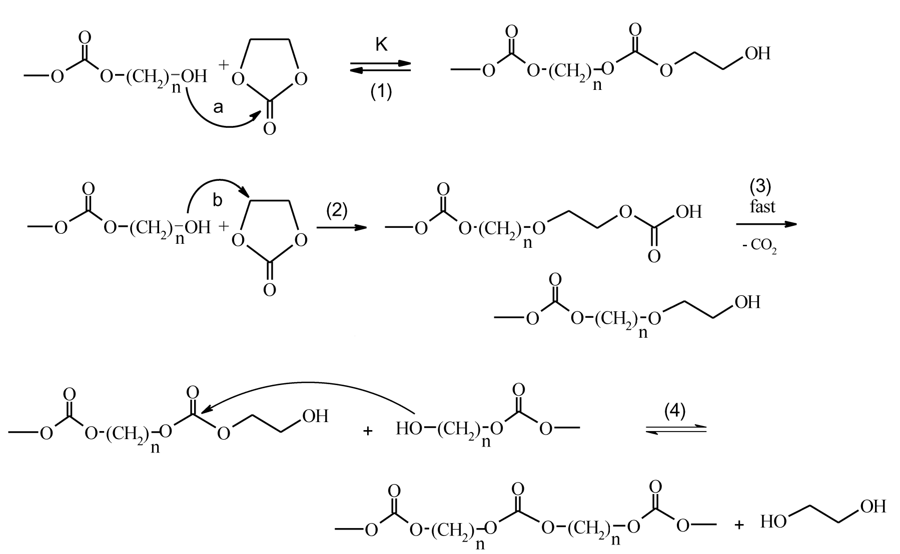


Fig. 3. MALDI-TOF mass spectrum of the macrodiols obtained from hexane-1,6-diol and ethylene carbonate (1:1.5 mol/mol) in the presence of NaCl at 165 °C, where X = $C(O)O(CH_2)_6O$, Q = $HO(CH_2)_6O$, Y = $(CH_2)_2O$, Z = $C(O)O(CH_2)_2O$.

In the MALDI-TOF mass spectrum of the reaction products obtained for a higher excess of ethylene carbonate (2.2:1), there were three series of signals (Fig. 5). The less intensive series can be assigned to macromolecules of oligocarbonates with two ethylene carbonate units. It is characteristic that more intensive signals corresponding to macromolecules with two ethylene carbonate units were present in the mass spectra when a higher excess amount of ethylene carbonate was used. In the ^1H NMR spectrum of the reaction products,



Scheme 4.

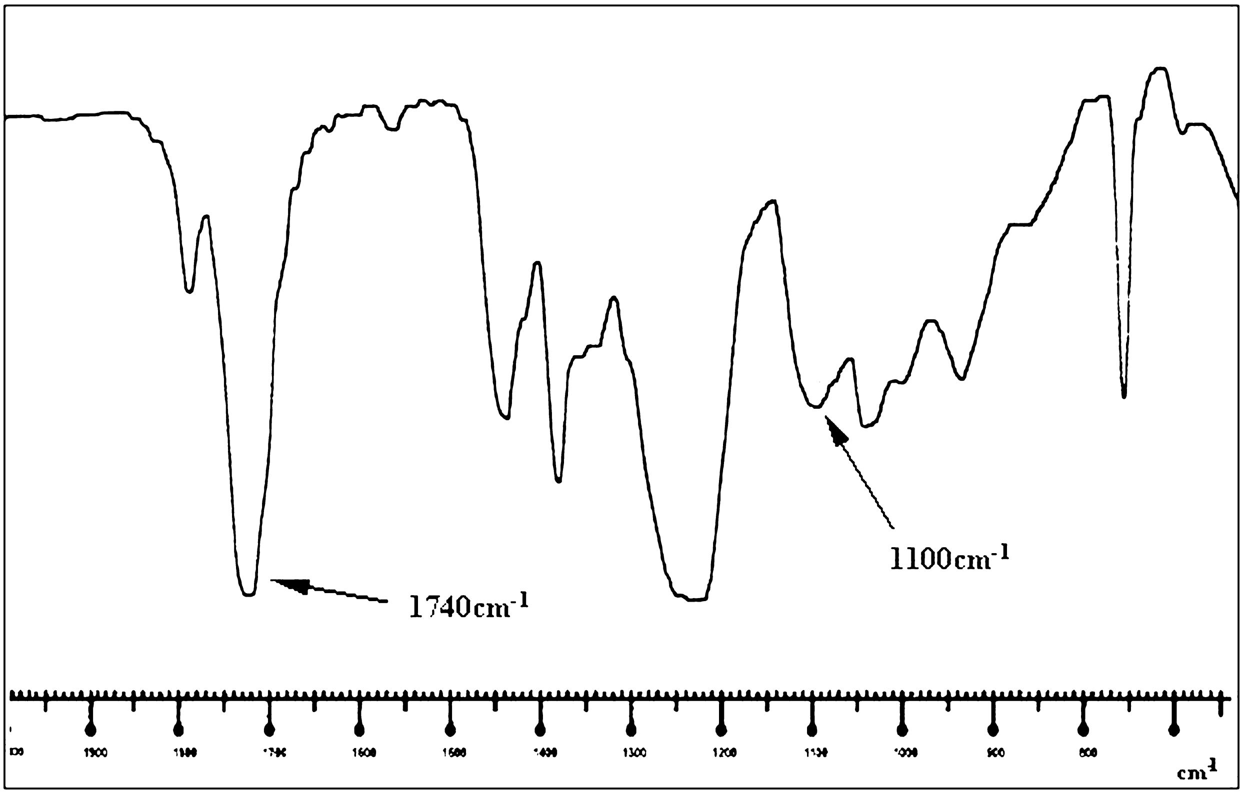


Fig. 4. IR spectrum of the macrodiols with ca. 45% of the oxyethylene units obtained from hexane-1,6-diol and ethylene carbonate in the presence of NaCl at 170 °C (Table 1, run 7).

there are signals corresponding to methylene groups adjacent to the carbonate linkage (4.11 ppm), and OH group (3.64 ppm) additionally indicating the presence of the ethylene carbonate unit in the polymer chain.

It is significant that no signals corresponding to macromolecules with three ethylene carbonate units can be observed in the MALDI-TOF mass spectrum of the reaction products obtained, even for a much higher excess of cyclic carbonate used (molar ratio = 10:1). From these observations, one can draw the conclusion that ethylene carbonate units are present as the 2-hydroxyethyl carbonate terminal groups of macromolecules.

For a larger excess of ethylene carbonate, the concentration of 2-hydroxyethyl carbonate groups is higher, and mainly a homofunctional condensation reaction should proceed leading to the incorporation of oxycarbonyloxyethylene units between two hexamethylene groups (Scheme 5, Eq. (2)). However, as was earlier shown, the rate of the polycondensation reaction decreases with a larger excess of cyclic carbonate, and a small amount of ethylene glycol was distilled off at the same time.

This means that the homofunctional condensation of two 2-hydroxyethyl carbonate groups do not proceed under the above mentioned conditions. The ‘back-biting’ reaction leading to the thermodynamically stable cyclic carbonate is much more plausible (Scheme 5, Eq. (1)).

As was earlier indicated by Harris [16] and Storey [17], there were no sequences with oxycarbonyloxyethylene units between ethylenoxyethyl groups in the products obtained via polymerization of ethylene carbonate at above 180 °C using various diols as ‘starters’ (Scheme 6). This observation additionally confirms that such oxycarbonyloxyethyl carbonate fragments (**1**) cannot be formed under the earlier mentioned reaction conditions.

The reaction of ethylene carbonate with the molecules terminated with a 2-hydroxyethyl carbonate group (Scheme

Table 3
The influence of the molar ratio of ethylene carbonate to diol for the conversion of hexane-1,6-diol

Run no	Hexane-1,6-diol/EC (mol/mol)	Reaction time (h)	Conversion (%)	MALDI TOF (M_n)	Yield (%)
1	1.5:1	10	25	–	–
2	1:1.5	5	73	1150	87
3	1:2.2	5	26	1000	79
4	1:10	10	7	–	–

for more details see Section 2.

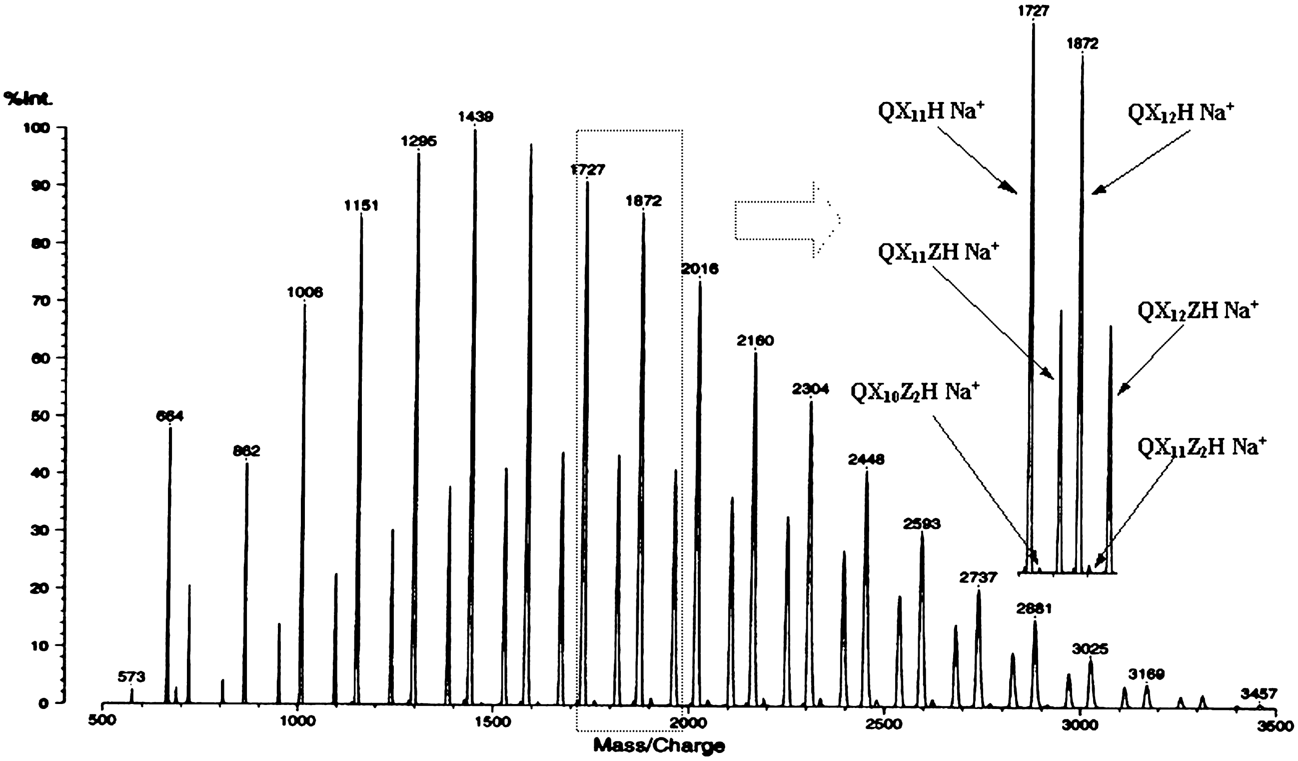


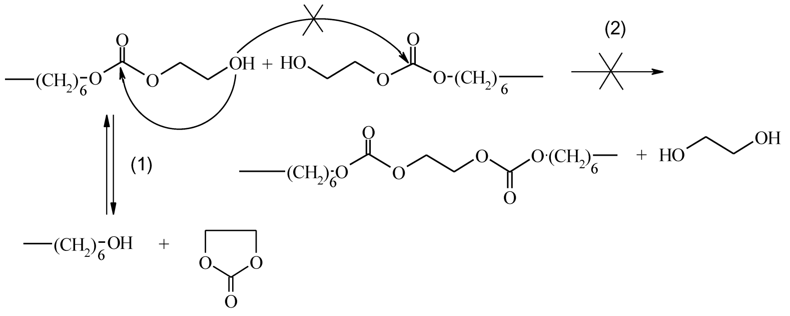
Fig. 5. MALDI-TOF mass spectrum of the oligocarbonate diol obtained from hexane-1,6-diol and ethylene carbonate (1:2.2 mol/mol) in the presence of NaCl at 145 °C, where X = $C(O)O(CH_2)_6O$, Q = $HO(CH_2)_6O$, Z = $C(O)O(CH_2)_2O$.

7, Eq. (2)), is also forbidden due to the thermodynamic reasons [14], thus, again no signals corresponding to macromolecules with poly(ethylene carbonate) units were present in the MALDI-TOF mass spectrum of the reaction products (Fig. 5).

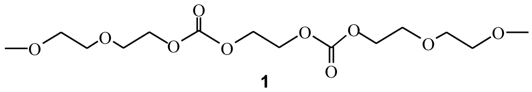
When the reaction was carried out at 165 °C, oxyethylene fragments were formed connected to hydroxyhexamethylene groups by a carbonate linkage (Scheme 7, Eq. (1)) (Fig. 3).

3.2. Influence of the diol structure on the oxyethylene units formation

The central feature of the ring-opening process is that the carbonyl group attack is favored kinetically (Scheme 4, Eq. (1)), over the methylene group attack (Scheme 4, Eq. (2)); however, the carbonyl group attack is reversible, whereas the methylene group attack is not, due to rapid decarboxylation of the terminal hydrocarbonate groups. It should be emphasized that the position of the equilibrium is dependent on the number of methylene groups (n) in the diol molecules used in the polycondensation reaction. If $n = 3$ or 4, the equilibrium is shifted to the left, effectively decreasing the formation of oligocarbonate. When butane-1,4-diol was used ($n = 4$), significant amounts of oxyethylene units were present in the oligocarbonate chains (Table 4, run 1). Moreover, some amount of the butane-1,4-diol was lost due to its distillation together with the azeotropic solvent. For pentane-1,5-diol the amount of ether linkages in the product was reduced to 15 mol% (Table 4, run 2). In contrast, for $n = 6$, as was earlier shown, when the reaction was carried out at below 145 °C, practically no etherification was observed and almost regular oligocarbonate diol can be obtained (Table 4, run 3). Also when decane-1,10-diol was



Scheme 5.



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Scheme 6.

used, no ether formation was observed even for the reaction carried out at a higher temperature (150–155 °C) (Table 4, run 4). It was also found that the presence of an oxygen atom at the β-position in the diol molecule additionally enhances the alkylene group attack (Scheme 8). Thus, when triethylene glycol was used in the transesterification reaction with ethylene carbonate, a larger amount of oligomers with ether linkages was produced (Table 4, run 5).

3.3. Methods of increasing the oligocarbonate molecular weight

It is characteristic for this method that the molecular weight of polycarbonate is limited by the solubility of ethylene glycol in xylene at the temperature of distillation. A small amount of glycol generated at the end of the process cannot be removed from the system due to its solubility in hot xylene. To overcome this problem, we used a Soxhlet apparatus filled with molecular sieves A5 to trap small amounts of ethylene glycol from xylene at the final stage of the process. After 5 h of distillation using a Soxhlet apparatus with molecular sieves, the molecular weight of oligocarbonate increased from 1150 to 1540.

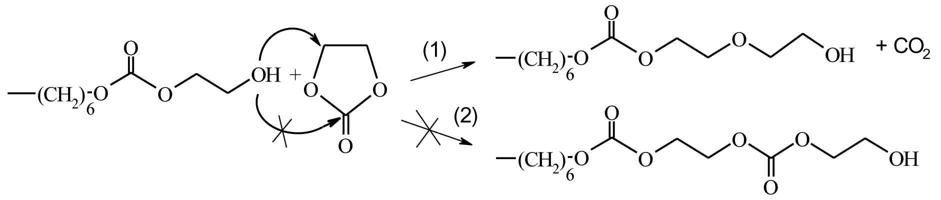
The heating of the post-reaction mixture, containing unreacted ethylene carbonate, under reduced pressure was another method of increasing the oligocarbonate molecular weight. It was found that during heating at 132–135 °C/2 mmHg of the post-reaction mixture ethylene glycol and a small amount of hexane-1,6-diol were distilled off besides cyclic carbonate. During distillation, the transesterification reaction proceeds according to Scheme 4 (Eq. (4)), leading to an increase in the poly(hexamethylene carbonate) molecular weight.

The residual amount of alkali metal salts as well as ethylene carbonate can be easily removed from the reaction product by washing its methylene chloride solution with deionized water. The washing was repeated until the resultant water conductivity was lower than 30 μS.

It is characteristic that for monomers concentration of 1.85 mol/l, no formation of oligocarbonate macrocycles was observed when the reaction was carried out in xylene at 145 °C in the presence of NaCl as a catalyst. The cyclic carbonate oligomers were formed during heating of oligocarbonate diols ($M_n = 3900$) in an *o*-dichlorobenzene solution (0.14 mol/l concentration of the polymer repeated units) under reflux at 178 °C for 96 h in the presence of Bu_2SnO. In the MALDI-TOF mass spectrum of the products, three series of signals corresponding to linear oligocarbonates terminated with hexamethylene units (a), macrocyclic oligocarbonates (b) and macrocyclic oligocarbonates with the oxyethylene unit (c) can be found (Fig. 6). However, in the reaction of ethylene carbonate with hexane-1,6-diol (1.5:1) carried out using a similar concentration of monomers (0.136 mol/l), no reaction progress was observed for 20 h. Under such conditions, the equilibrium concentration of ethylene glycol was too small to form a second phase in the condensate.

3.4. Influence of the presence of alkali metal salts on the transesterification reaction

The cyclic carbonate five-membered ring can be opened at elevated temperature by alcohols. In the ^{13}C NMR spectrum of the reaction product of ethylene carbonate with hexane-1,6-diol at 110 °C, characteristic signals (59 and 70 ppm) corresponding to carbon atoms of 2-hydroxyethyl-



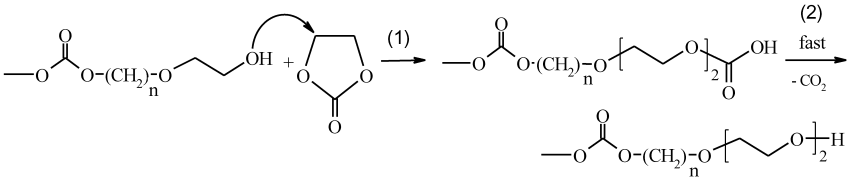
Scheme 7.

Table 4
The influence of diole structure on the oxyethylene units formation in the reaction with ethylene carbonate catalyzed with NaCl

Run no	Diol	Reaction temperature (°C)	Contents of oxyethylene units[a] (mol%)
1	Butane-1,4-diol	140–145	40
2	Pentane-1,5-diol	143–145	15
3	Hexane-1,6-diol	143–145	<2
4	Decane-1,10-diol	150–155	<2
5	Triethylene glycol	143–145	78

For more details see Section 2.

[a] After 5 h.



Scheme 8.

carbonate groups were present. Additionally, in the IR spectrum, two absorption bands 1800 and 1745 cm^{-1} corresponding to carbonyl groups of cyclic and linear carbonates were also identified. To obtain polycarbonate macromolecules, the transesterification reaction of the 2-hydroxyethyl carbonate groups with diol should be carried out at below 145 °C in the presence of a catalyst and the side product—ethylene glycol should be removed continuously from the system. This means that the crucial problem is the selection of a catalyst, able to catalyze the transesterification reaction (Scheme 4, Eq. (4)), but not the methylene group attack in the ethylene carbonate (Scheme 4, Eq. (2)).

It should be emphasized that, in the case of using alkali metal salts, there is no insertion of cyclic carbonate between oxygen and metal atoms, as was observed for the polymerization of cyclic carbonate catalyzed by tin-based catalysts (Scheme 2), but alkoxy groups are generated to enhance the transesterification reaction.

Alkoxy groups are generated in the reaction of NaCl with ethylene carbonate similarly to the reaction reported by Bergmann et al. [20]. At high temperature the halide anion attacks the methylene group and sodium 2-halogenoethyl carbonate is formed and then decarboxylation takes place (Scheme 9). The highest yield of halogenohydrin was obtained for fluorides, lower for bromides, and the lowest for iodides.

In the case of the reaction carried out in the presence of hexane-1,6-diol, the exchange of the alkali metal cation can proceed leading to ionization of hexane-1,6-diol.

No reaction progress of ethylene carbonate with hexane-1,6-diol was observed, when alkali metal fluorides were used as catalysts at 145 °C. At a higher temperature (175 °C), in the presence of CsF the reaction proceeds, but the resultant product contained oxyethylene units in a significant amount (Table 1, run 20).

In contrast, when alkali metal iodides were used, no oxyethylene units were present in the product, for the reaction carried out at 145 °C. However, the yield of oligocarbonate, as well as the oligomer molecular weight were rather small (Table 1, runs 15, 16 and 17). Unstable iodohydrins are formed which easily forms volatile ethylene oxide (due to the presence of a good leaving group), and rapidly evaporates from the reaction system (Scheme 10).

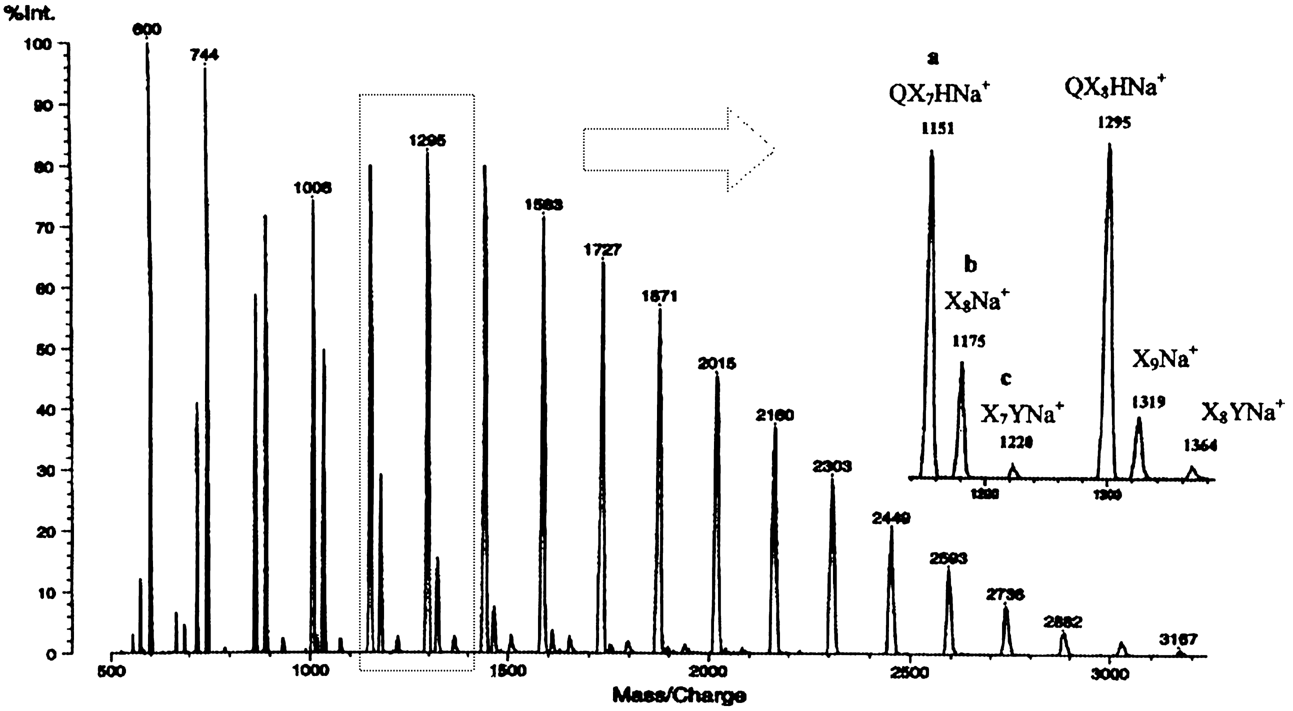
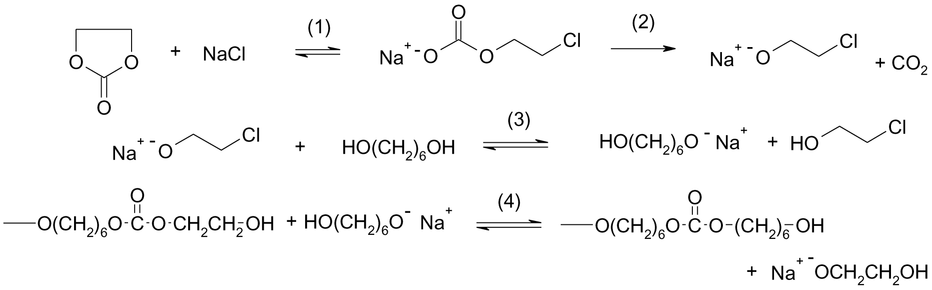


Fig. 6. MALDI-TOF mass spectrum of the products obtained after heating oligocarbonate diol (M_n = 3900) in the presence of Bu_2SnO (4.2 mmol/dm^3) in o-dichlorobenzene at 178 °C for 96 h, where X = $C(O)O(CH_2)_6O$, Q = $HO(CH_2)_6O$, Y = $(CH_2)_2O$.



Scheme 9.

Ethylene chlorohydrin and bromohydrin can be generated from ethylene carbonate at 145 °C, and due to the relatively higher stability, they are able to exchange an alkali metal cation with diol (Scheme 9), and formation of oxyethylene units was suppressed when chlorides and bromides were used as the catalyst. The differences in the reactivity of halogenides are due to the bonds energies ($E_{\mathrm{C-H}} = 415$ kJ/mol, $E_{\mathrm{C-I}} = 220$ kJ/mol, $E_{\mathrm{C-Br}} = 275$ kJ/mol, $E_{\mathrm{C-Cl}} = 330$ kJ/mol, $E_{\mathrm{C-F}} = 495$ kJ/mol).

The nucleophilicity of halides in S_N2-type reactions is known to be $Cl^- > Br^- > I^-$ [21–23]. Thus, the order of activity of halide anions is consistent with the order of nucleophilicity. The low activity of the fluoride ion can be explained by its low leaving ability [24]. Furthermore, the role of the catalyst cation is notable. In the experiments with bromide and iodide, the order of the activity is lithium salt > sodium salt > potassium salt. This order is in accord with the order of Lewis acidity of the indicating the cation [25], acted as Lewis acid to activate the 1,3-dioxolan-2-one ring similarly to oxirane activation [26,27].

When catalysts such as Na_2CO_3 and K_2CO_3 were used, at 145 °C a small amount of ethylene glycol was collected, and in the IR spectrum of the products, the absorption band characteristic for cyclic carbonate decreased, and a strong absorption band corresponding to ether groups increased indicating the presence of poly(oxyethylene) fragments in the product. Sodium and potassium carbonates, good catalysts of the transesterification reactions, exhibit a better catalytic effect of the etherification reaction, than that of the ester exchange when a five-membered cyclic carbonate was used as a monomer. The shares of oxyethylene fragments in the products obtained in the presence of these carbonates were 72 and 73%, respectively (Table 1, runs 2 and 3). In contrast, when Li_2CO_3 was used, no oxyethylene fragments formation was observed in the reaction carried out under the same conditions (Table 1, run 1). Lithium salts are better soluble in organic media, so their catalytic effect of the transesterification process can be attained without additional reaction with ethylene carbonate.

Other alkali metal salts such as NaH_2PO_4 and Na_2SO_4 exhibited relatively low activity in the ester exchange catalysis, and thus the polycondensation reaction should be carried out at higher temperature (>165 °C), and the contribution of oxyethylene fragments in the oligomer structure was 65 and 58 mol%, respectively (Table 1, runs 21–23). In the case of CH_3COONa in the reaction carried out at 145 °C, the methylene group attack is also significant (77 mol%) (Table 1, run 24). Although anions with higher nucleophilicity react with 1,3-dioxolan-2-one more rapidly, acetate anions show low catalytic activity because of their low leaving ability in the S_N2-type reaction on sp3 carbon atoms.

4. Conclusion

Oligo(hexamethylene carbonate) diols, valuable material for elastomeric polyurethane production, can be obtained from hexane-1,6-diol and ethylene carbonate in the presence of NaCl or NaBr catalyst at 142–145 °C using xylene as a azeotropic solvent, removing ethylene glycol from the reaction system. Higher reaction temperature leads to the formation oligomers containing oxyethylene units. For 'shorter' diols, such as butane-1,4-diol also, significant amounts of oxyethylene units are also formed even at 145 °C.

Acknowledgements

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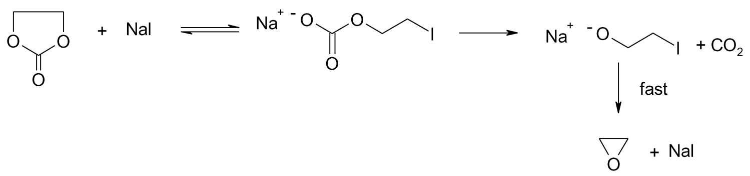

Scheme 10.

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