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Synthesis of oligocarbonate diols and their characterization by MALDI-TOF spectrometry

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Abstract

A method of the synthesis of oligocarbonate diols from five-membered cyclic carbonates and aliphatic diols using azeotropic solvents is presented. The influence of a catalyst and reaction conditions on the alkylene oxide and alkylene carbonate insertion into macrodiol molecules were studied and the reaction mechanism is discussed. The oligomeric products were analyzed by means of MALDI-TOF mass spectrometry. The transesterification reaction between propylene carbonate and diols containing six or more carbon atoms in a molecule carried out in the presence of the coordination catalysts such as tin or zinc carboxylate leads to almost pure oligocarbonate diols. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oligocarbonate diols; Alkylene carbonate; Azeotropic solvents

1. Introduction

In conventional polyurethane elastomers soft segments usually originate from polyether or polyester macrodiols [1]. However, polyurethanes based on polyester are susceptible to hydrolysis and those based on polyether are unstable under oxidative conditions. In contrast, polyurethanes based on aliphatic polycarbonates are resistant both to hydrolysis and oxidation. Additionally, polyurethanes containing oligocarbonate soft segments exhibit high tensile strength and modulus [2,3]. Poly(carbonate–urethane)s are among the most extensively tested biomaterials that have been developed. They are the first biomedical polyurethanes to be promoted for their biostability. The carbonate linkages make these polymers attractive in applications in which oxidation is a potential mode of degradation, such as in pacemaker leads, ventricular assist devices, catheters, stents, and many other biomedical devices [4].

Aliphatic polycarbonates derived from diols have also attracted interest as biodegradable and biocompatible materials, alone or as copolymers with other heterocyclic monomers such as lactones and lactides.

Oligocarbonates can be prepared by various methods:

- in the reaction of diols with phosgene or phosgene derivatives [1];

- by the copolymerization of oxiranes with carbon dioxide in the presence of organozinc catalysts [5,6];
- by the polymerization of six- and seven-membered cyclic carbonates [7];
- by the transesterification of dimethyl- or diethylcarbonate [8] as well as alkylene carbonate [9] with diols.

The latter method seems to be the most convenient one since no hazardous materials are used nor produced as by-products. However, in the case of dialkyl carbonate the resultant polycarbonate molecules may be terminated to some extent by methyl- or ethyl-carbonate groups [8], that excludes them as starting materials in the production of high molecular weight polymers, e.g. polyurethanes.

In contrast, when alkylene carbonate such as ethylene carbonate is used instead of dialkyl carbonic acid esters the resultant polymer is exclusively terminated by hydroxyl groups. A ring-opening of the alkylene carbonates shows an equilibrium character [10], similar to that of common heterocyclic compounds [11], and according to Daiton's equilibrium equation some amount of monomer is present in the post-reaction mixture. It is especially true for five-membered heterocycles. The equilibrium concentration of 2-hydroxyethyl carbonate moieties is rather small and to obtain high molecular weight polycarbonate even small amount of glycol produced as a side transesterification product should be removed from the reaction system. To remove glycol, reduced pressure and distillation column are used [9,12,13]. In the reaction of diols with alkylene

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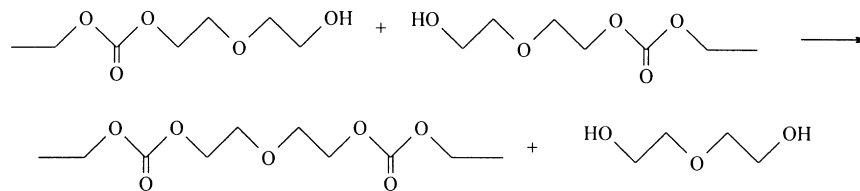
Scheme 1.

carbonate carried out at high temperature (>180°C) in the presence of catalyst, especially those containing alkali metal salt, polycarbonates with considerable amounts of poly(oxyethylene) fragments are formed.

In the method reported by Harris et al. [9] in the first stage ethylene carbonate was subjected to reaction with diol consisting of four or more carbon atoms in the molecule used as a "starter" to produce oligomers with 2-hydroxyethyl ether and 2-hydroxyethyl carbonate end-groups. Heating these poly(ethylene ether carbonate) diols at temperatures >180°C under reduced pressure with the removal of diethylene glycol (DEG) as a distillate, enables one to build molecular weight in a controllable manner. This is suggested to be a transesterification process in which $-OC(O)OCH_2CH_2OCH_2CH_2OH$ end-groups on one molecule react with carbonate moieties on a second molecule with loss of DEG (Scheme 1).

It was also shown that at high temperatures, in the presence of tin catalyst, the decomposition of poly(ethylene ether carbonate) macrodiols takes place. The hydroxyl end group intramolecularly attacks the proximal carbonate moiety to form 1,4-dioxane and CO_2 as by-products (Scheme 2).

The aim of our work was the investigations on oligocarbonate diol synthesis by the transesterification of propylene and ethylene carbonates with aliphatic diols carried out in the presence of various catalyst using azeotropic solvents to remove 1,2-propylene or ethylene glycol formed as a by-product. It seemed interesting to study how the reaction conditions, i.e. a catalyst and temperature, affect the reaction pathway to curb polyether formation.

The oligomeric products were analyzed by means of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) and NMR spectroscopy.

MALDI-TOF mass spectrometry was introduced by Karas and Hillenkamp [14] in 1988 and has been successfully used to determine the molecular weight of bio-

molecules as well as synthetic polymers. The analysis of commodity polymers has been reviewed in a number of papers [15,16]. MALDI-TOF is known to give reliable results for narrow molecular weight distribution, though in the case of polydisperse polymers the values obtained are not in agreement with those from conventional methods (GPC). High molecular weight (MW) polymers require higher laser power for the desorption/ionization process than do low MW polymers. This causes smaller peak areas for the high mass component and can also be responsible for fragmentation of the low MW part of a mixture, if the molecular weights of the polymers are widely distributed. Furthermore, doubly charged molecular peaks and molecular clusters peaks appear in the spectra and influence the experimentally measured distribution [17,18]. However, for the lower MW species studied the MS data were closer to theoretical values than the GPC data. Hagelin et al. [19] have found that determination of molecular weight of a series of low MW surfactants with narrow MW distribution (MW ranging from 860 to 5310 Da) by MALDI-TOF mass spectrometry offered a far more convenient method of characterization of these polymers than GPC. The major advantages were lack of requirement for a chromatographic separation system, short time for sample preparation, speed of analysis, and structure information (repeating unit) of the polymers.

2. Experimental

2.1. Materials

Hexane-1,6-diol (HD), decane-1,10-diol (DD) and propylene carbonate (Fluka), ethylene carbonate (Aldrich), were used as received. The solvents: xylene, toluene, hexane and neptane (Polish Chemical Reagents, Gliwice) were distilled and the middle fraction was used for polycondensation as the azeotropic medium.
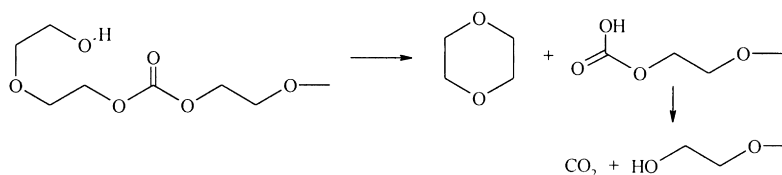
Scheme 2.

Table 1
The characteristics of oligocarbonate diols obtained from propylene carbonate using azeotropic solvents

Run	Catalyst (mol%)	Temperature (°C)	Time (h)	Diol	Azeotropic solvent	MALDI-TOF			Yield (%)
						M_n[a]	M_w	M_w/M_n	
1	–	180	15	DD	Heptane	–	–	–	10
2	Bu$_2$SnO (5)	180	9	DD	Heptane	2920 (3050)	3200	1.10	80
3	Bu$_2$SnO (5)	180	9	DD	Octane	2760 (2740)	3090	1.12	78
4	Bu$_2$SnO (2)	175	10	DD	Heptane	2580 (2670)	2860	1.11	75
5	Bu$_2$SnO (5)	175	8	HD	Hexane	2630	2880	1.09	40
6	Sn(stearate)$_2$ (2)	175	10	DD	Heptane	2660	2980	1.12	70

[a] Molecular weight calculated from a hydroxyl number is shown in parentheses.

K$_2$CO$_3$ (Polish Chemical Reagents, Gliwice), CsF (Fluka), LiBr (BDH), were used as catalysts after drying under reduced pressure at 120°C. Bu$_2$SnO (Aldrich) was used without additional purification and SnOct$_2$ (Laboratory of Technological Processes, Warsaw) after distillation under vacuum. Sn- and Zn-stearate were prepared in the reaction of stearic acid (Reachim) with Sn-octoate and Zn-acetate (Aldrich), respectively [20].

2.2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer. Deuterated solvents were used and tetramethylsilane served as the internal standard.

IR spectra were recorded on 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.

2.3. Macrodiols synthesis

The synthesis of the macrodiols was carried out using a monomer mixture consisting of diol and alkylene carbonate in the molar ratio 1:2.2. A typical procedure is as follows.

In a 250 ml three-necked flask, equipped with a mechanical stirrer, reflux condenser, thermometer and Barrett type receiver, propylene carbonate (56.2 g, 0.55 mol), decane-1,10-diol (43.6 g, 0.25 mol), 20 ml of heptane as the azeotropic solvent, and Bu$_2$SnO (5 mol%, 12.5 mmol, 3.1 g) were placed. The transesterification was carried out at

170–175°C under reflux collecting 1,2-propylene glycol in a Barret receiver. The progress of the polycondensation reaction was monitored by analyzing samples of the reaction mixture by IR spectroscopy and measuring the absorption band characteristic for OH and C͟O groups using the calibration curve and the amount of glycol distilled off. After 8 h the azeotropic solvent was evaporated under vacuum from the post-reaction mixture and the oligocarbonate diol was precipitated in cold methanol. The yield of the crude oligocarbonate diol was 39 g.

^{1}H NMR (CDCl$_3$): δ(ppm) = 1.28 (s, CH$_2$), 1.54–1.71 (m, C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 3.6 (m, HOCH$_2$), 4.09 (t, C(O)OCH$_2$).

^{13}C NMR (CDCl$_3$): δ(ppm) = 25.61, 28.61, 29.12, 29.30 C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$, 32.72 HOCH$_2$CH$_2$, 62.91 HOCH$_2$, 67.92 C(O)OCH$_2$, 155.37 C͟O.

FTIR (KBr): 3400, 2930, 1745, 1470, 1400, 1260, 1020, 930, 770 cm^{-1}.

In the case of using ethylene carbonate a residual amount of cyclic carbonate was removed by washing the post-reaction mixture three times with 100 ml of hot water and then the solvent was distilled off under vacuum.

The yield of the macrodiol obtained from ethylene carbonate (19.5 g, 0.22 mol) and decane-1,10-diol (17.5 g, 0.1 mol) in the reaction catalyzed by Bu$_2$SnO (1.25 g, 5 mmol) was 11.1 g.

^{1}H NMR (CDCl$_3$): δ(ppm) = 1.27 (s, C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 1.54–1.71 (m, C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 3.4 (m, CH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$CH$_2$), 3.60 (m, HOCH$_2$), 3.71 (m, OCH$_2$CH$_2$O), 4.09 (t, C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$), 4.24 (m, CH$_2$OCH$_2$CH$_2$OC(O)O and OC(O)OCH$_2$CH$_2$O-C(O)O).

^{13}C NMR (CDCl$_3$): δ(ppm) = 25.61, 28.61, 29.11, 29.30 C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$, 29.40 C(O)OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$, 32.71 HOCH$_2$CH$_2$CH$_2$, 61.65 HOCH$_2$CH$_2$OCH$_2$, 62.92 HOCH$_2$CH$_2$CH$_2$, 66.61 C(O)OCH$_2$CH$_2$OC(O), 67.93 CH$_2$CH$_2$CH$_2$OC(O)OCH$_2$CH$_2$CH$_2$, 68.21 OCH$_2$CH$_2$OC(O)OCH$_2$CH$_2$CH$_2$, 68.88 CH$_2$OCH$_2$CH$_2$OC(O)OCH$_2$CH$_2$CH$_2$, 70.55 CH$_2$CH$_2$CH$_2$OCH$_2$CH$_2$CH$_2$, 72.35 HOCH$_2$CH$_2$OCH$_2$ 155.17 CH$_2$CH$_2$CH$_2$OC(O)OCH$_2$CH$_2$O, 155.37 CH$_2$CH$_2$CH$_2$OC(O)OCH$_2$CH$_2$CH$_2$.

FTIR (KBr): 3510, 2970, 1745, 1510, 1400, 1300, 1120, 1110, 775 cm^{-1}.
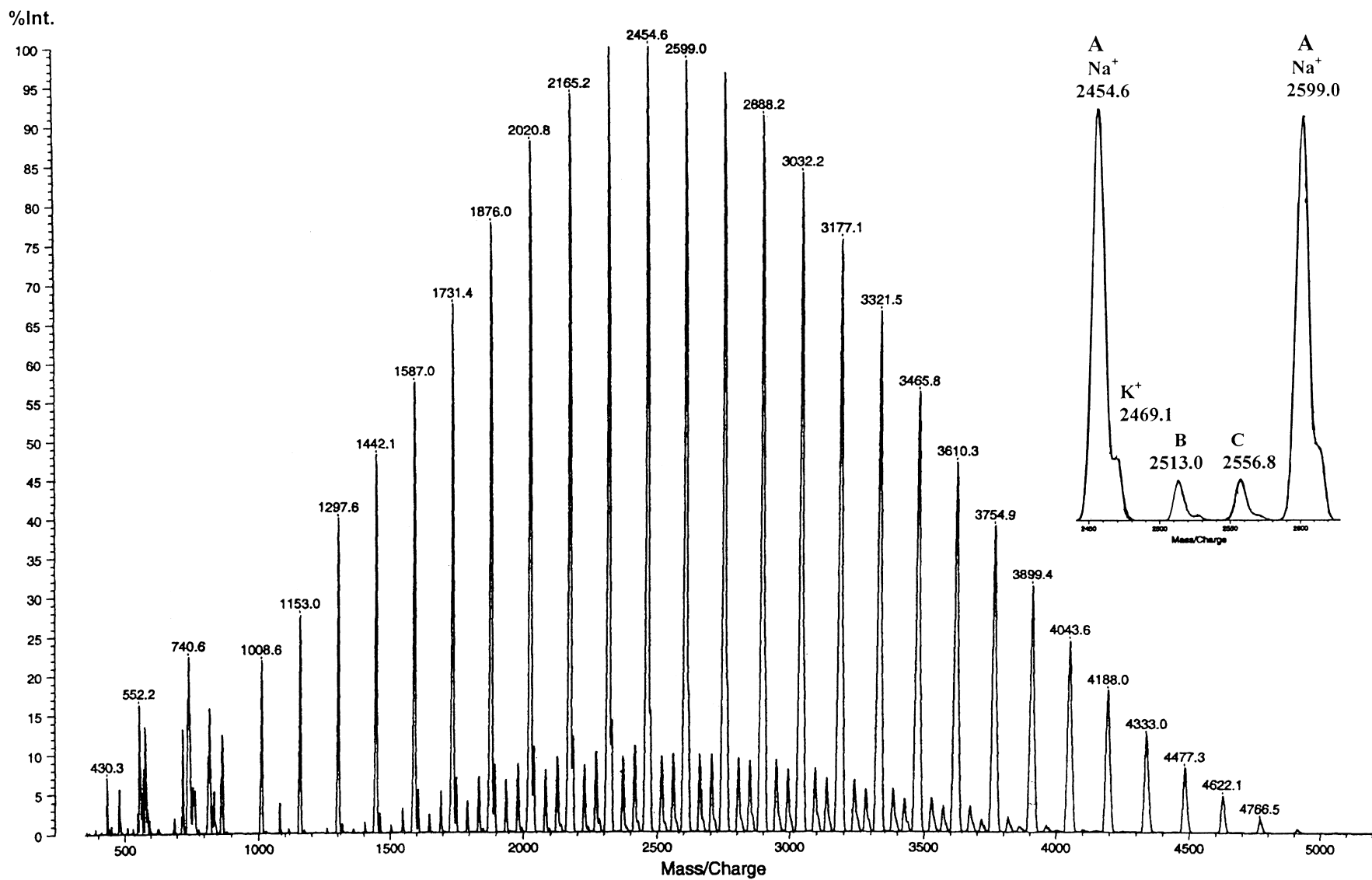
Fig. 1. The MALDI-TOF mass spectrum of the oligo(hexamethylene carbonate) diol obtained from propylene carbonate and hexane-1,6-diol (molar ratio 2.2:1) in the presence of Bu_2SnO (5 mol%) using heptane as an azeotropic solvent.
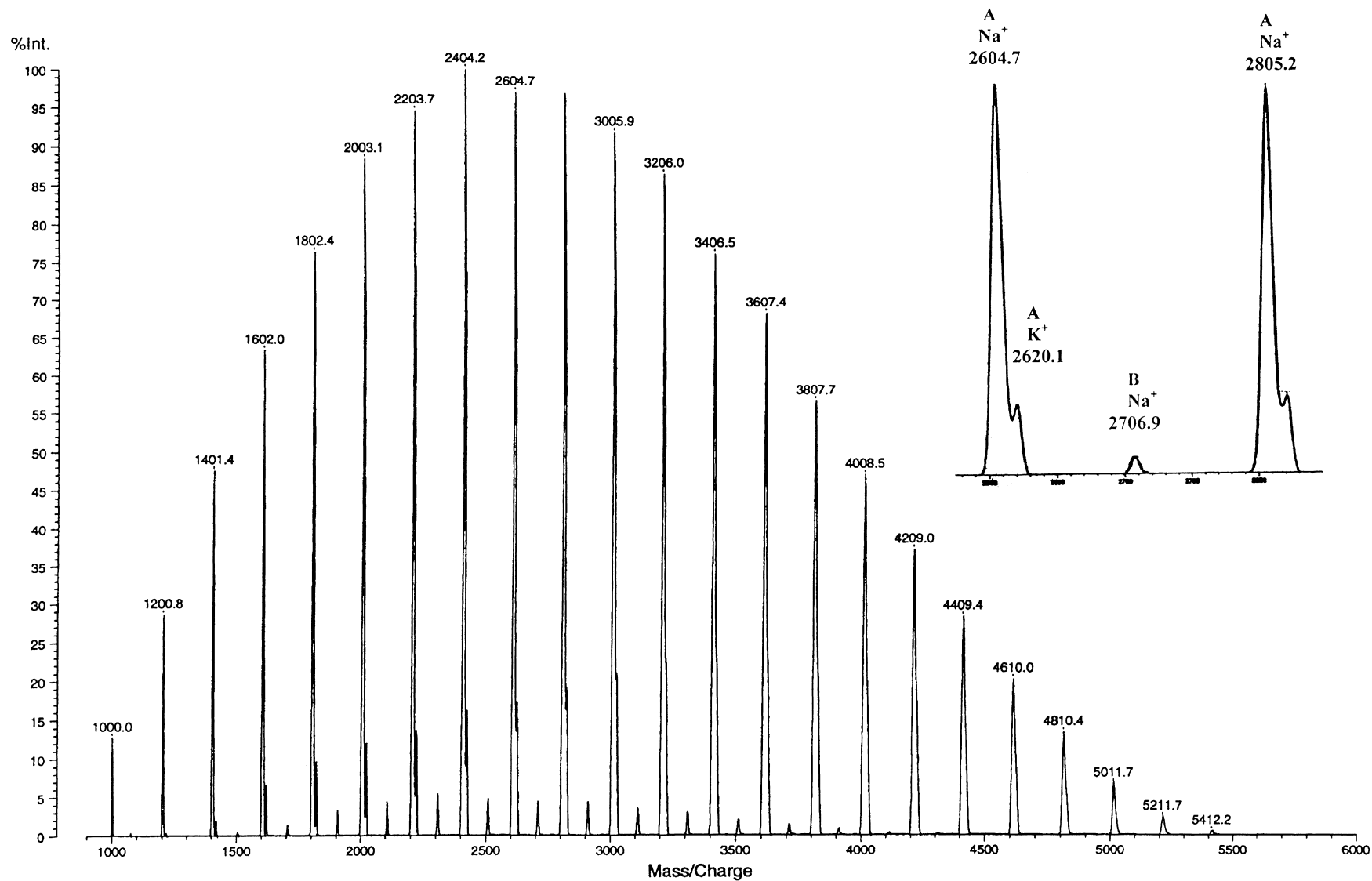
Fig. 2. The MALDI-TOF mass spectrum of the oligo(decamethylene carbonate) diol obtained from propylene carbonate and decane-1,10-diol in the presence of Bu$_2$SnO (5 mol%) using heptane as an azeotropic solvent.
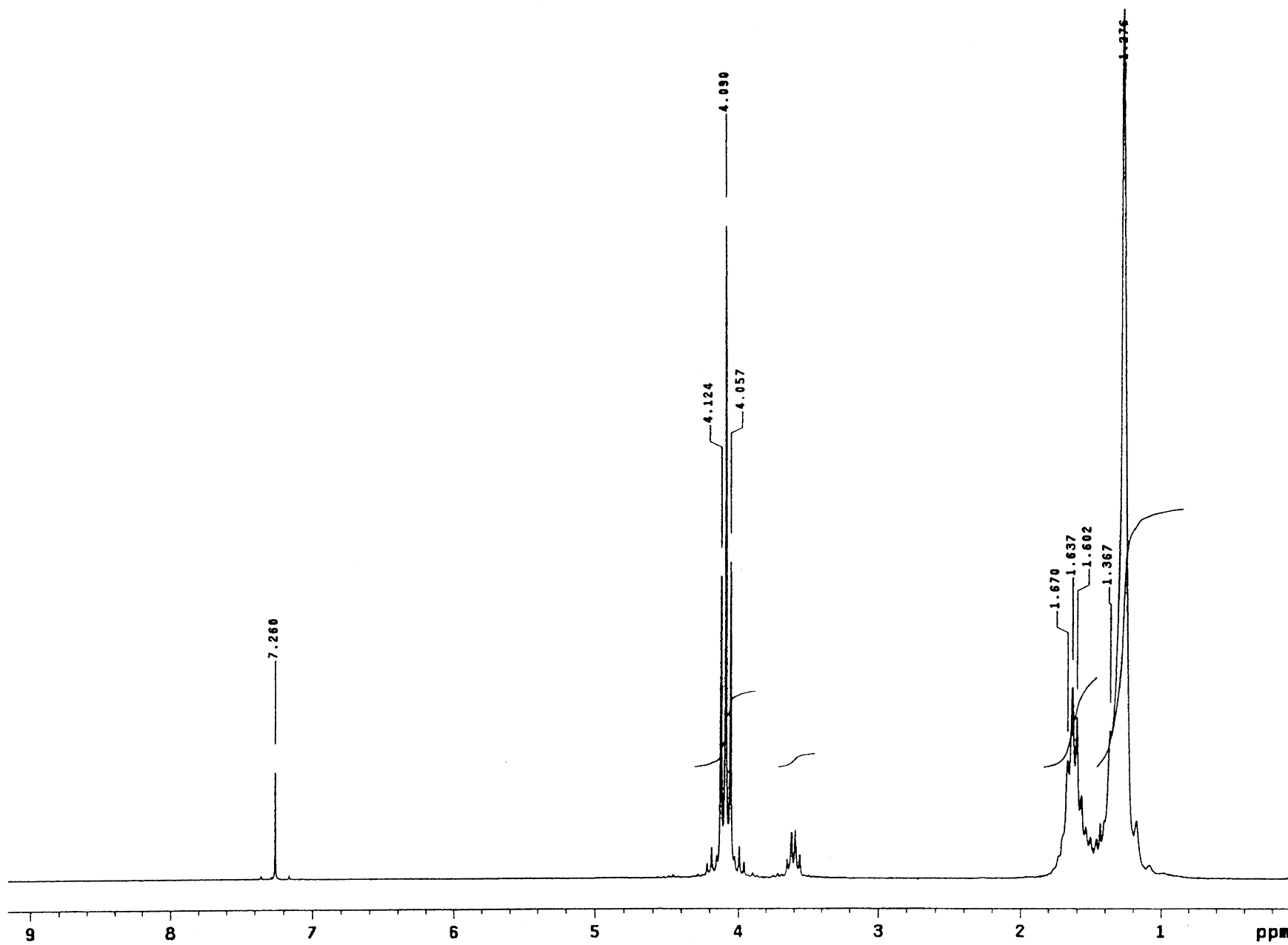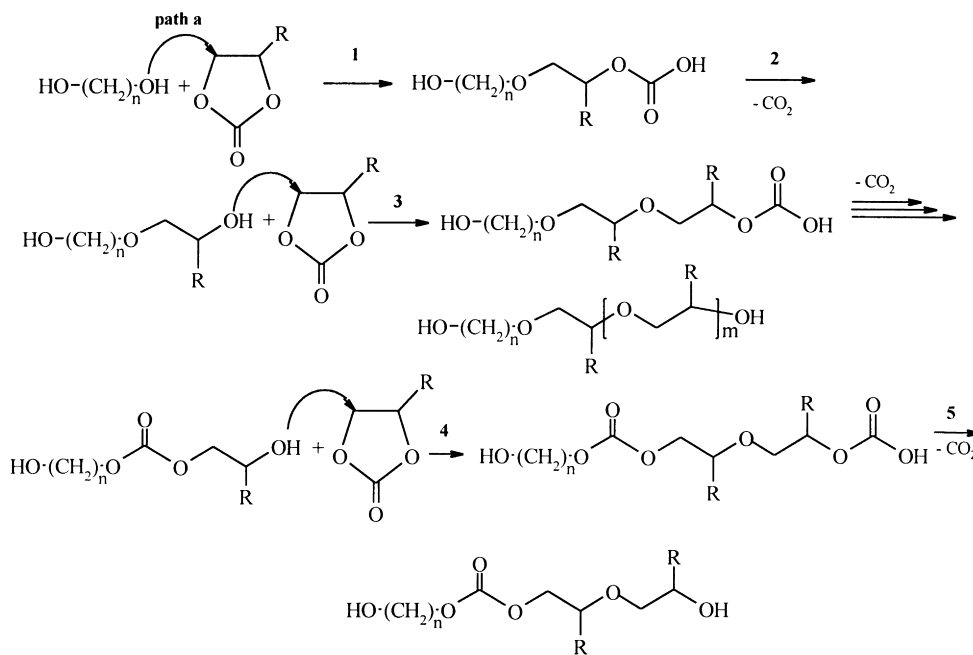
Fig. 3. The ¹H NMR spectrum of the oligo(decamethylene carbonate) diol obtained from propylene carbonate and decane-1,10-diol in the presence of Bu₂SnO (5 mol%) using heptane as an azeotropic solvent.

Scheme 3.

3. Results and discussion

3.1. Transesterification with propylene carbonate

It was found that the reaction of propylene carbonate with hexane-1,6-diol and decane-1,10-diol carried out at 170–175°C under atmospheric pressure in the presence of Bu_2SnO as a transesterification catalyst with heptane as an azeotropic solvent removing 1,2-propylene glycol from the reaction system, afforded almost pure poly(hexamethylene carbonate) and poly(decamethylene carbonate), respectively (Table 1, runs 1–4) (Figs. 1–3). In the ^1H and ^{13}C NMR spectra of the polycarbonate diols there were no signals characteristic of protons and carbon atoms originating from propylene carbonate. Also, in the IR spectrum there were no absorption bands characteristic for ether linkages.

Apart from heptane and octane, other solvents, effective in removing ethylene carbonate, appeared to be ineffective in the transesterification with propylene carbonate because the composition of the distillate was very similar to that of the reaction mixture.

In the case of using hexane-1,6-diol, due to its lower boiling point and a possible distillation together with heptane, the yield of poly(hexamethylene carbonate) was lower than that of poly(decamethylene carbonate) (Table 1, run 1).

It is characteristic that no 1,2-propylene glycol was collected in a Barret receiver after 12 h of heptane re-circulation. Consequently no macrodiol was formed when the reaction was carried out without catalyst at temperature up to 175–185°C (Table 1, run 1).

As was shown in the MALDI-TOF mass spectra (Figs. 1 and 2) (Table 1, runs 1 and 2) only a very small part of poly(hexamethylene carbonate) and poly(decamethylene carbonate) chains were terminated by the 1,2-propylene glycol moiety when Bu_2SnO was used as a catalyst. In the case of poly(hexamethylene carbonate) the main series of high-intensity peaks are present together with two series of peaks of much lower intensity (Fig. 1). The most abundant peaks are characterized by a mass increment of 144 Da from one peak to the next. This mass increment equals the mass of the repeating unit in the poly(hexamethylene carbonate). The above mentioned series of peaks ($M_n = 2630$ Da) corresponds to polycarbonates terminated with hexane-1,6-diol molecule (residual mass: 118 Da) (A). The second and third series of peaks correspond to poly(hexamethylene carbonate) molecules containing additionally one propylene oxide (residual mass: 34 Da) (B) and one propylene carbonate unit (residual mass: 78 Da) (C), respectively.

Taking into consideration that a series peak area is equivalent to concentration, the relative amounts of three fractions are calculated to be 14.2:1.4:1.4. From these results it can be stated that less than 0.6% of propylene carbonate and 0.6% of propylene oxide were inserted into the oligocarbonate molecules.

Very similar MALDI-TOF mass spectrum was obtained for the macrodiols obtained in the transesterification of decane-1,10-diol with propylene carbonate carried out under the same reaction conditions (Fig. 2). The main series of peaks are characterized by the mass increment of 200 Da. This series of peaks ($M_n = 2251$ Da) corresponds to poly-(decamethylene carbonate) molecules terminated by

R = H or CH₃; n > 4
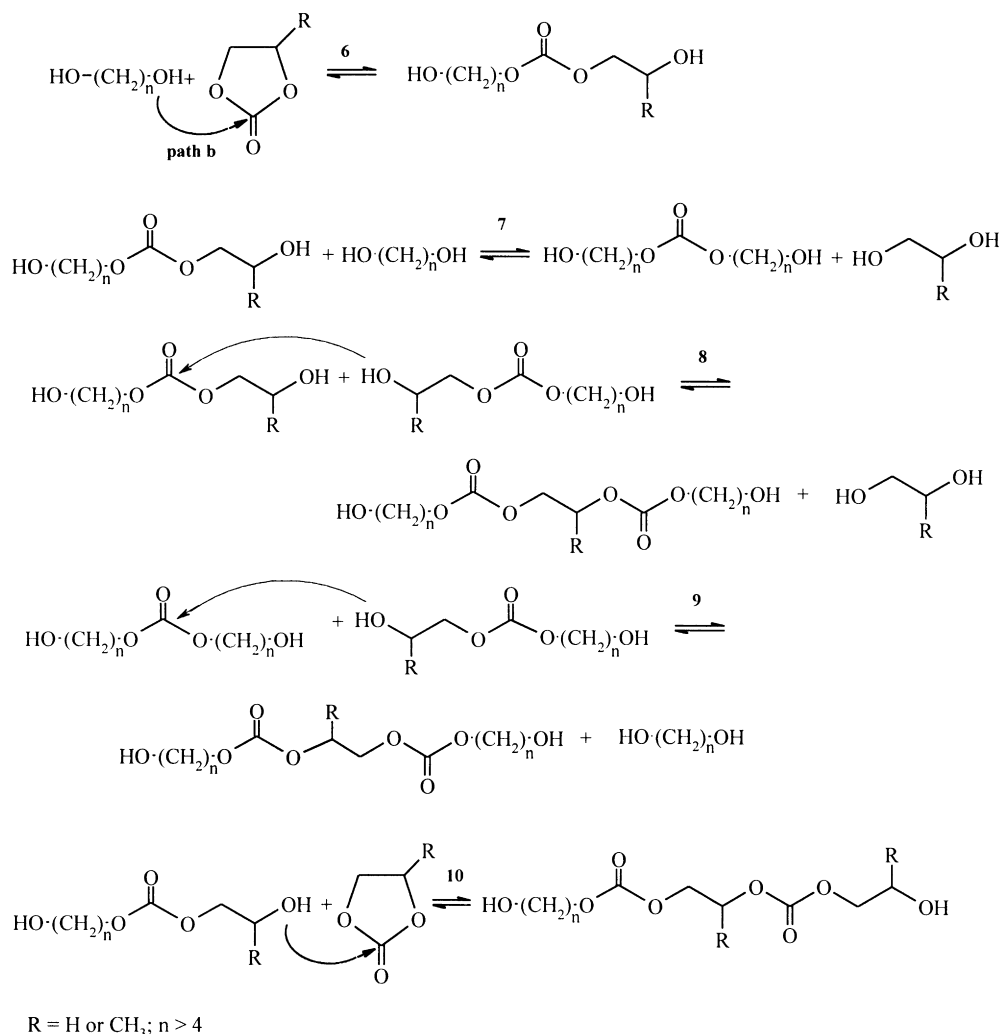
Scheme 4.

decane-1,10-diol (residual mass: 174 Da) (A). The mass spectrum additionally contains the low intensity series of peaks corresponding to the molecules with one propylene carbonate unit (residual mass: 78 Da) (B).

Taking into consideration that in the reaction of the aliphatic diols with ethylene carbonate usually the molecules with oxyethylene fragments are formed [21], the suppression of the propylene oxide and propylene carbonate insertion into the polycarbonate molecules is thought to be due to the presence of methyl substituent in the 1,3-dioxolan-2-one ring. The electron-donating methyl group reduces the possibility of the nucleophilic attack at the methylene group in the 1,3-dioxolan-2-one ring (pathway **a** in Scheme 3 and Eq. (12) in Scheme 6).

On the other hand, the attack of the alkoxy group at the carbonyl group of cyclic carbonate (pathway **b** in Scheme 4 and Eq. (11) in Scheme 6) leads to the linear carbonate molecules mainly terminated with secondary alcohol group. Less reactive secondary alcohol groups cause a decrease in the transesterification extent between two

2-hydroxypropyl carbonate moieties (Eq. (8) in Scheme 4) as well as the 2-hydroxypropyl carbonate moiety with poly-(hexamethylene carbonate) (Eq. (9) in Scheme 4). Thus, a very small amount of propylene carbonate is inserted into the polycarbonate molecules even for a relatively high excess of propylene carbonate (2.2:1).

3.2. Transesterification with ethylene carbonate

In contrast to the transesterification with propylene carbonate, when ethylene carbonate was used in the reaction with diols the oligocarbonate diols containing oxyethylene fragments were obtained. The reaction was carried out using different azeotropic solvents to remove ethylene glycol from the reaction system. It was shown that the amount of the oxyethylene fragments in the product depends on a catalyst employed and reaction temperature.

In the MALDI-TOF mass spectrum of the oligocarbonate diol obtained from decane-1,10-diol and ethylene carbonate under similar reaction conditions to that in which propylene
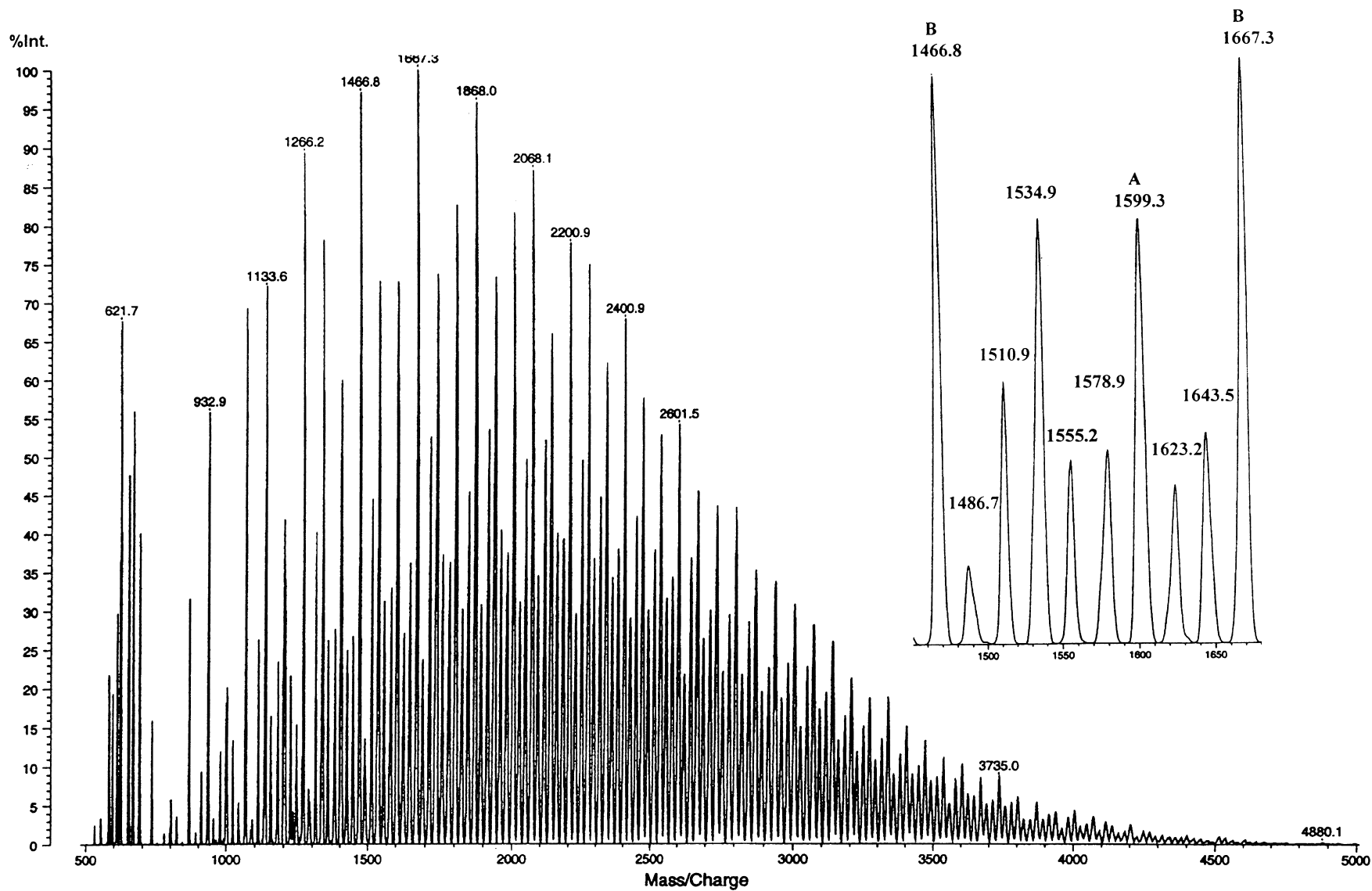
Fig. 4. The MALDI-TOF mass spectrum of the macrodiol obtained from ethylene carbonate and decane-1,10-diol in the presence of Bu$_2$SnO (2 mol%) using xylene as an azeotropic solvent.

Table 2
The characteristics of macrodiols obtained in the transesterification of ethylene carbonate with hexane-1,6-diol in the presence of different catalysts (11.8 g (0.1 mol) of hexane-1,6-diol and 19.5 g (0.22 mol) of ethylene carbonate were used in the transesterification; xylene was used as an azeotropic solvent)

Run	Temperature (°C)	Catalyst (mol%)	Time (h)	EO inserted (wt%)	EC inserted (wt%)	MALDI-TOF			Yield (g)
						M_n	M_w	M_n/M_w[a]	
1	175[b]	Bu$_2$SnO (2)	5.5	13	12	1960	2240	1.14	11.1
2	150	Bu$_2$SnO (2)	10	9	8	1530	1710	1.12	9.5
3	120	K$_2$CO$_3$ (1)	10	30	12	2300	2430	1.06	11.1
4	180	K$_2$CO$_3$ (1)	4	50	5	2020	2260	1.12	11.4
5	175	CsF (1)	4.5	25	7	1200	1470	1.23	11.8
6	190	LiBr (5)	4.5	3	1	1570	1770	1.13	10.0
7	150	Sn(stearate)$_2$ (1)	8	3	7	2230	2500	1.12	10.5
8	150	Zn(stearate)$_2$ (1)	10	2	5	1510	1810	1.20	10.4
9	175[c]	Zn(stearate)$_2$ (1)	5	3	6	1710	1810	1.15	10.2
10	150	Zn(Ac)$_2$ (1)	10	1.5	4	1510	1860	1.23	9.8
11	170	–	20	11	16	2010	2330	1.16	11.2

[a] Characterized by MALDI-TOF mass spectrometry.
[b] Decane-1,10-diol was used as the diol reagent.
[c] Heptane was used as the azeotropic solvent.

carbonate was used (Fig. 4) (Table 2, run 1) three series of high-intensity peaks together with six series of peaks of lower intensity are present (Fig. 4). The main series of peaks (A) ($M_n = 1800$ Da) corresponds to oligocarbonate molecules terminated with decane-1,10-diol (residual mass: 176 Da). The second main series of peaks (B) corresponds to molecules with two ethylene oxide and two ethylene carbonate inserted units or with other combinations of ethylene oxide and ethylene carbonate units giving the residual mass 43 Da (molecular weight similar to that of ethylene oxide or carbon dioxide). The other series corresponds to macrodiol molecules with different combinations of ethylene oxide, ethylene carbonate and decamethylene carbonate units. From the intensity of proton signals characteristic for ethylene carbonate (4.24 ppm) and ethylene oxide (3.71 ppm) in the ¹H NMR spectrum (Fig. 5) it can be estimated that about 22 mol% of ethylene carbonate and a similar amount of ethylene oxide units were inserted in the poly(decamethylene carbonate) molecules. The molecular weights of oligocarbonatediols calculated from hydroxyl numbers was very similar to that obtained from MALDI TOF mass spectrometry (Table 1) and calculated from ¹H NMR spectra.

The most useful azeotropic solvents for this reaction system, among those tested, were aromatic hydrocarbons such as xylene, ethylbenzene and cumene besides heptane and octane. They form azeotropes relatively easily with ethylene glycol, and at room temperature these solvents are immiscible with ethylene glycol (Table 3). It was shown that the higher the boiling point of the solvent, the higher is the content of ethylene carbonate in the azeotropic mixture. The transesterification can also be carried out under "pseudo-azeotropic conditions", at temperature higher than the boiling point of the azeotrope. Ethylene glycol was continuously removed at temperature above 140°C even when solvents with low boiling point such as *n*-heptane or xylene were used (Table 2). The analysis of the

glycol fraction of the distillate revealed the presence, besides that of ethylene glycol and some amount of diethylene glycol additionally, up to 6 wt% of ethylene carbonate.

When alkaline catalysts, such as potassium carbonate are used at high temperature (>180°C) the process proceeds according to both pathways **a** and **b** to produce macrodiols with a relatively large amount of the oxyethylene fragments (Table 2, run 4). In the IR spectrum of the reaction product a weak absorption band at 1745 cm^{-1} characteristic of the carbonyl group of linear carbonate and an intense band at 1100 cm^{-1} characteristic of ether linkages were present. It is suggested that poly(oxyethylene) moieties are produced in the subsequent reaction of an oxyethylene alkoxide group with the next alkylene carbonate molecules (Scheme 3; Eq. (3)). Under such conditions the reaction direction is similar to that with phenolate ion [22,23]. Oxyethylene units may also be formed in the reaction of the 2-hydroxyethyl carbonate groups with ethylene carbonate according to Eq. (4) of Scheme 3. Due to positive enthalpy of polymerization of five-membered cyclic carbonates [24] the reaction course according to Eq. (10) in Scheme 4 is not possible and no linear poly(ethylene carbonate) segments were present in the resultant macrodiols.

In the case of using alkaline catalysts (e.g. K$_2$CO$_3$), a comparable molecular weight of macrodiol (ca. 2000 Da) was obtained for much higher conversion of ethylene carbonate. At temperatures >180°C the reaction proceeds almost exclusively according pathway **a** (Scheme 3) and a large amount (even up to 50%, depending on a reaction temperature) of hexane-1,6-diol was left unreacted (Table 2, run 4). It suggests that mainly alkoxy groups of the increasing poly(oxyethylene) chains react with alkylene carbonate (Eq. (3) in Scheme 3). The presence of ether group separated from an alkoxy group by two carbon atoms enhances the alcoholate anion basicity. Also less basic catalyst such as CsF leads to oxyethylene fragments formation (Table 2, run
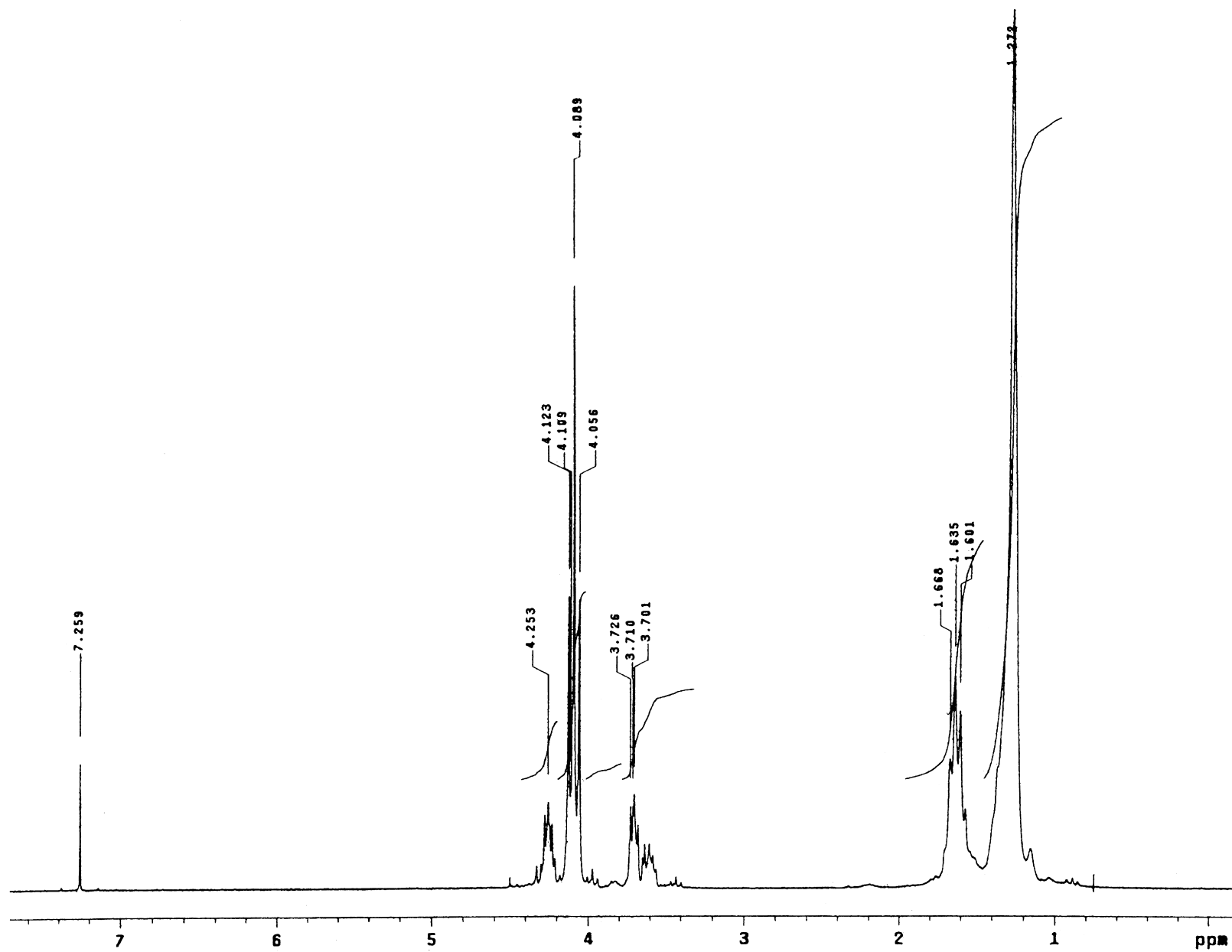
Fig. 5. The ^{1}H NMR spectrum of the oligo(decamethylene carbonate) diol obtained from ethylene carbonate and decane-1,10-diol in the presence of Bu$_2$SnO (2 mol%) using xylene as an azeotropic solvent.

Table 3
The ethylene glycol content in an azeotrope with different solvents

Solvent	Boiling point (°C)	Azeotrope b.p. (°C)	Ethylene glycol content (wt%)
Ethylene glycol	197.4	–	–
Toluene	110.6	110.2	2.3
Xylene[a]	~140.0	~135.0	~15.0
Ethylbenzene	136.1	133.2	13.5
Cumene	158.8	152.1	20.0
Heptane	98.5	97.9	3.0
Octane	125.6	123.5	11.5

[a] Mixture of isomers.

5). However, when LiBr was used as a transesterification catalyst the oligocarbonate diols containing much less oxyethylene fragments were formed (Table 2, run 6).

The MALDI-TOF mass spectrum of macrodiols obtained in the presence of potassium carbonate consists of two main series of peaks corresponding to polycarbonate with high amounts of poly(oxyethylene) fragments (Fig. 6). These peaks are characterized by the mass increment of 44 Da from one peak to the next, and is equal to the mass of the ethylene oxide repeating unit. The series of peaks ($M_n = 2304$ Da) corresponds to poly(ethylene ether carbonate) molecules containing 2–4 hexamethylene carbonate units. The most abundant series of peaks corresponds to the K^+ adducts (originated from catalyst) and less abundant counterpart series corresponds to the Na^+ adducts. The mass increment between these two series of peaks is 16 Da. The MALDI-TOF mass spectrum with a similar pattern was obtained when CsF was used as catalyst ($M_n = 1350$ Da). The most abundant series of peaks corresponds to Cs^+ adducts (Fig. 7).

On the other hand, a quite different mass spectrum was obtained for the macrodiol synthesized in the presence of LiBr. The most abundant series of peaks are originated from the poly(hexamethylene carbonate) molecules terminated by hexane-1,6-diol (Li^+ adduct, residual mass: 119 Da) (A). As one can predict, in this case also the signals from the Na^+ adducts are less abundant. The second (B) and third (C) series of peaks correspond to poly(hexamethylene carbonate) molecules with one ether (residual mass: 78 Da) and two ether linkages (residual mass: 34 Da), respectively. The other series, but much less abundant, corresponds to the poly(hexamethylene carbonate) molecules containing combinations of ethylene oxide and ethylene carbonate units (Fig. 8). The presence of ether linkages between hexamethylene moieties was confirmed by NMR spectral analysis. In the ^1H and ^{13}C NMR spectra there are signals from protons and carbon atoms of methylene groups neighboring ether linkages at 3.4 and 70.90 ppm, respectively.

Such type of decarboxylation can be explained by complexing properties of ethylene carbonate with lithium cations. The resultant active "naked" bromide anion can attack the carbon atom neighboring carbonate linkage and the resultant alkyl carbonate anion decarboxylates at high temperature to form the ether linkage (Scheme 5).

The decarboxylation reaction catalyzed by LiBr proceeds simultaneously with ethylene carbonate leading to gaseous ethylene oxide. Thus, even after 4 h no cyclic carbonate was present in the reaction mixture. A similar catalytic effect was observed for KI and crown ether in the reaction of oxirane and CO_2 (reverse to the above mentioned) leading to cyclic carbonate [25].

In contrast to alkaline catalysts, in the presence of coordination catalysts such as Zn- or Sn(II)-carboxylates (Table 2, runs 7–10) the transesterification with ethylene carbonate proceeds mainly according to pathway **b** (Eq. (8) in Scheme 4 and Eq. (11) in Scheme 6) and polycarbonates with a small amount of oxyethylene fragments are formed. The ring opening of ethylene carbonate in the presence of tin catalyst is through tin alcoholate formation similarly to mechanism proposed by Kricheldorf et al. [26] for six-membered cyclic carbonates (Eq. (11) in Scheme 6). The reaction course according to Eq. (12) in Scheme 6 leads to the formation of oxyethylene fragments.

When Zn-stearate was used as a catalyst in the transesterification of ethylene carbonate with hexane-1,6-diol (mole ratio = 2.2:1) carried out at a temperature of 150°C for the same amount of ethylene glycol liberated, a higher amount (ca. 40%) of ethylene carbonate was removed (left unreacted in the post-reaction mixture) than when alkaline catalyst was used. It means that oxyethylene units formation (Eq. (3) in Scheme 3 and Eq. (12) in Scheme 6) in the transesterification reaction with the 2-hydroxyethyl carbonate moieties proceeding according to Eq. (8) and (9) in Scheme 4 were, to a large extent, confined. In the ^1H NMR spectrum no signals characteristic of methylene protons neighboring the ether linkages (3.7 ppm) neither signals characteristic for methylene protons of ethylene carbonate (4.3 ppm) were present.

In the MALDI-TOF mass spectrum of the oligocarbonate obtained in the presence of zinc stearate as a catalyst (Table 2, run 8) (Fig. 9) the highest intensity series of peaks (A) ($M_n = 1510$ Da) are observed for poly(hexamethylene carbonate) molecules terminated by hexane-1,6-diol (residual mass: 119 Da). The second (B) and third (C) peaks series ($M_n = 2010$ and 2250 Da, respectively) correspond to the molecules containing one ethylene carbonate (residual mass: 63 Da) and both ethylene oxide and ethylene carbonate units (residual mass: 107 Da), respectively. It is characteristic that in the mass spectrum there were only very small intensity series of peaks (D) corresponding to poly(hexamethylene carbonate) molecules containing one ethylene oxide unit (residual mass: 19 Da). It suggests that the reaction catalyzed by Zn-stearate proceeds mainly according to pathway **b** (Eq. (11) in Scheme 6) and the oxyethylene units can be formed mainly according to Eqs. (4) and (5) of Scheme 3. The other, much less intensive, series of peaks (E–G) correspond to the molecules
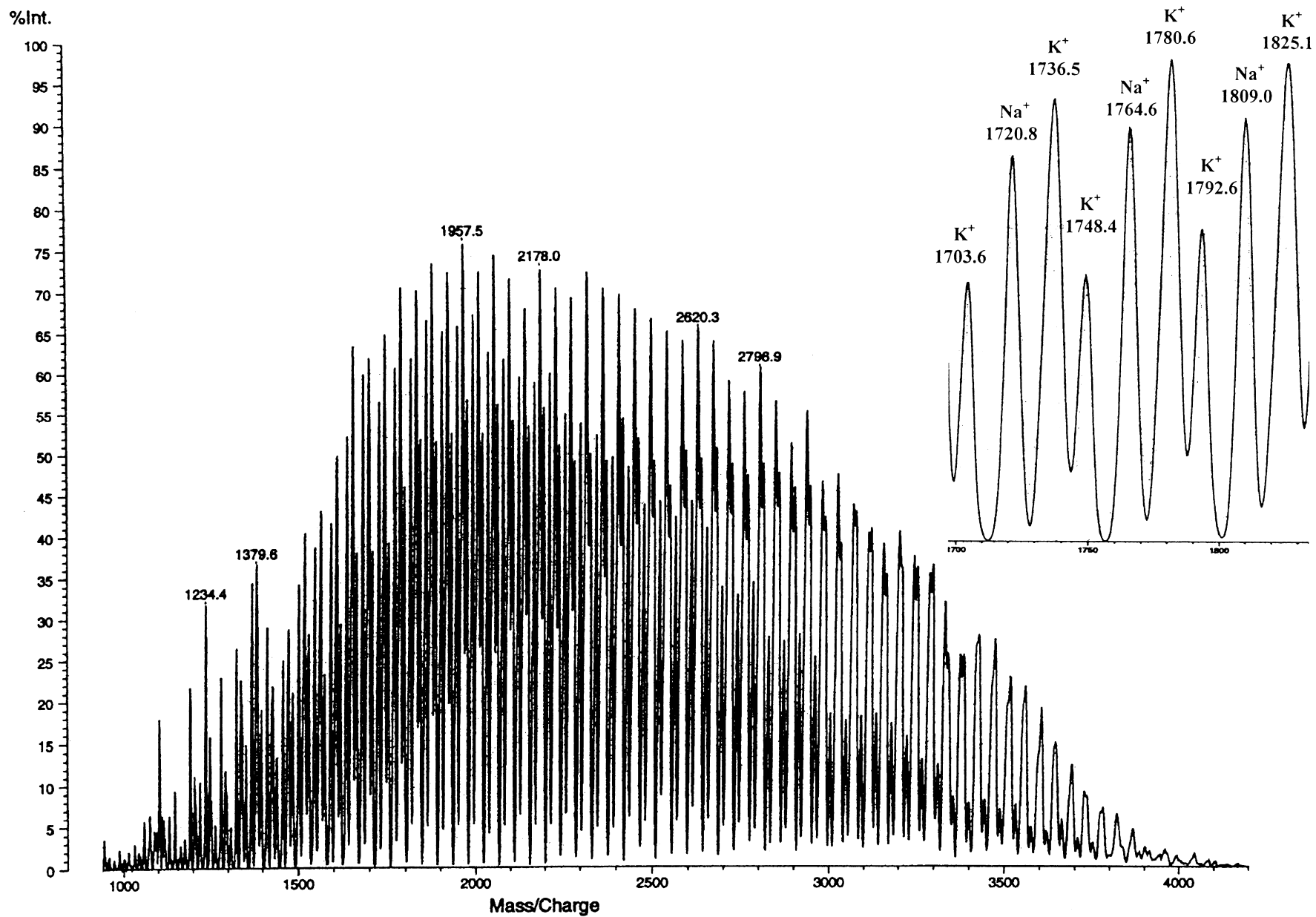
Fig. 6. The MALDI-TOF mass spectrum of the macrodiol obtained from ethylene carbonate and hexane-1,6-diol in the presence of K_2CO_3 (2 mol%) using xylene as an azeotropic solvent.
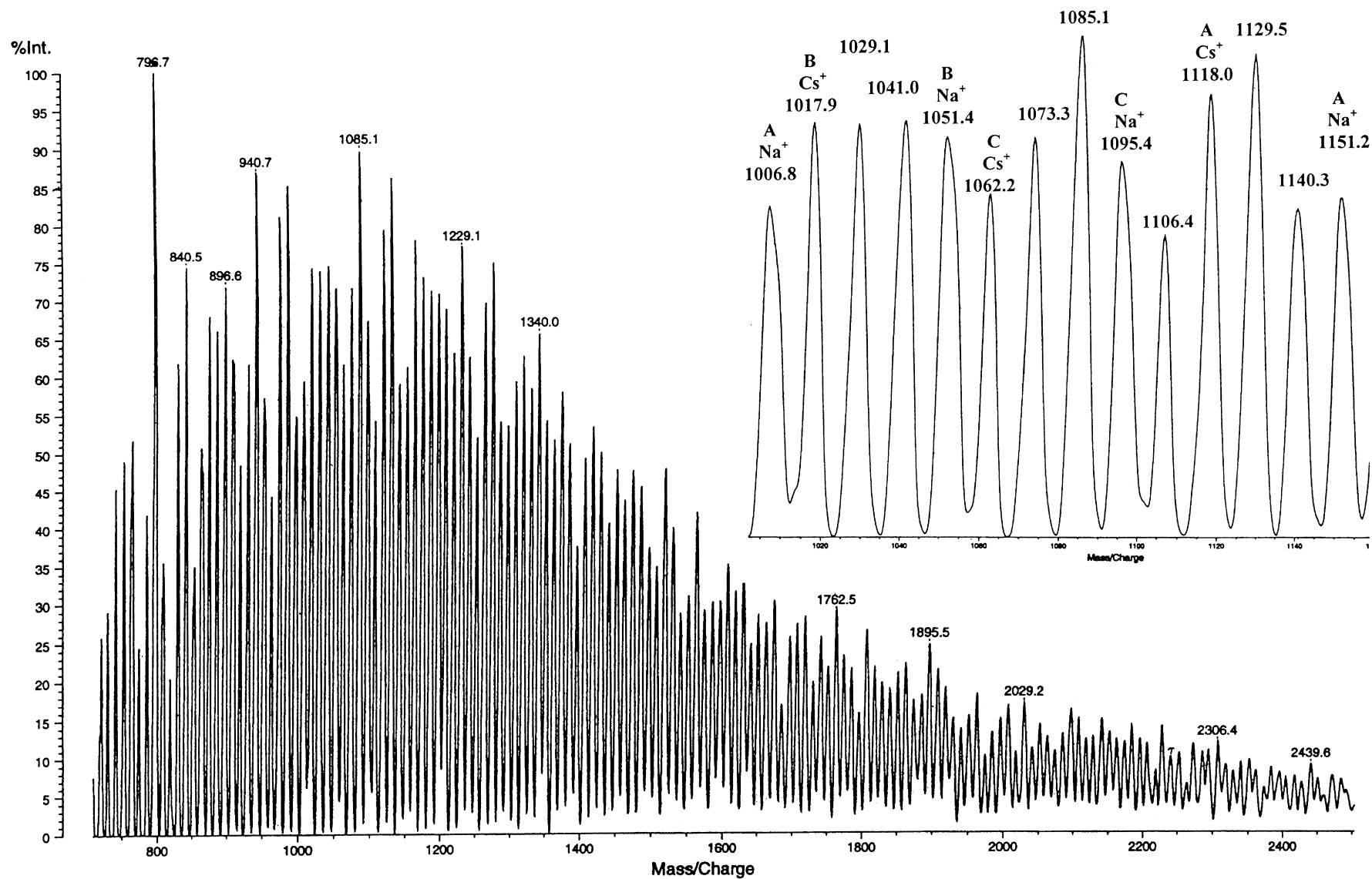
Fig. 7. The MALDI-TOF mass spectrum of the macrodiol obtained from ethylene carbonate and hexane-1,6-diol in the presence of CsF (1 mol%) using xylene as an azeotropic solvent.
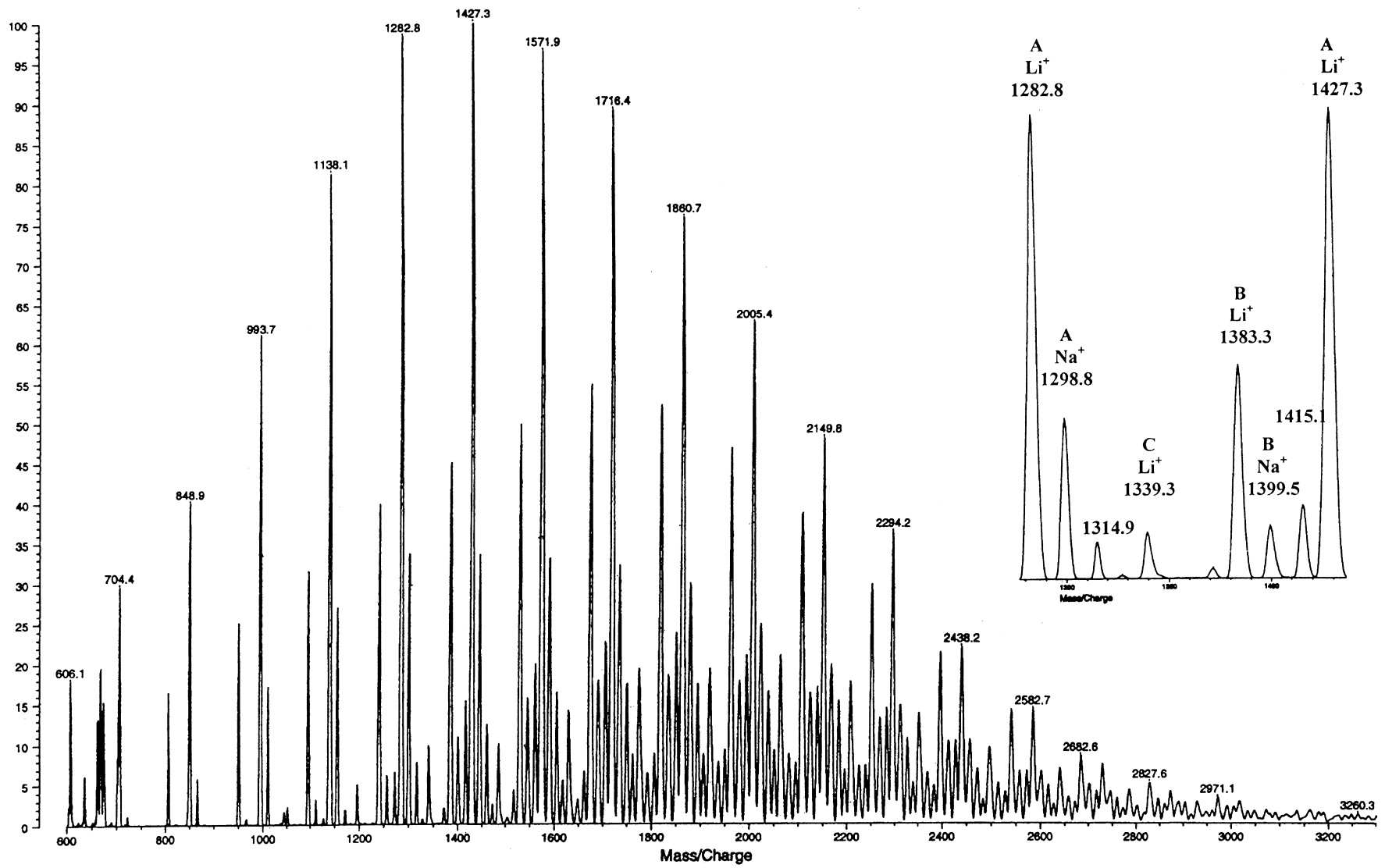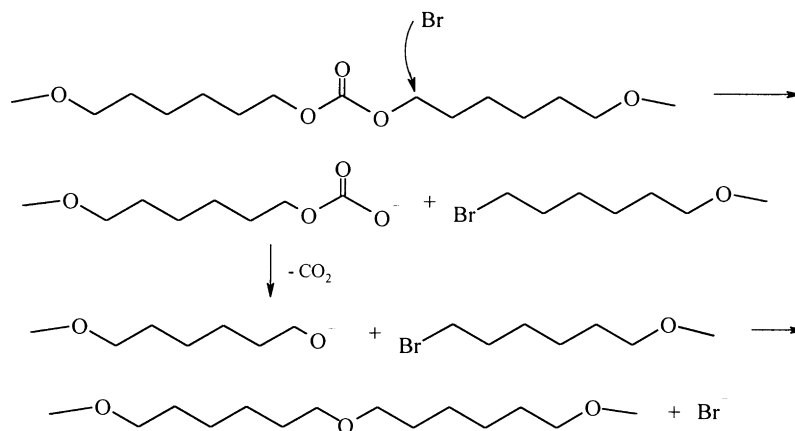
Fig. 8. The MALDI-TOF mass spectrum of the macrodiol obtained from ethylene carbonate and hexane-1,6-diol in the presence of LiBr (5 mol%) using xylene as an azeotropic solvent.

Scheme 5.

containing two and more inserted ethylene carbonate as well as ethylene oxide units. The relative amounts of these fractions are calculated to be: 14.7 (A), 10.6 (B), 11.3 (C), 16.2 (D–G). From these results it can be stated that about 5 wt% of ethylene carbonate and 2 wt% of ethylene oxide were introduced into oligocarbonate.

When Sn(stearate)$_2$ was used as a catalyst the MALDI-TOF mass spectrum of the resultant polycarbonate was similar to that in which the zinc stearate catalyst was applied but the intensity of peak series corresponding to molecules containing ethylene oxide and ethylene carbonate were a little bit higher (Table 2, run 7).

It was found that the transesterification between ethylene carbonate and diols also proceeds without catalyst (Table 2, run 10). However, the reaction rate is slower and longer time (20 h at 170–175°C) is necessary to achieve a molecular weight of ca. 2000 Da. The resultant oligomer contained, besides ethylene carbonate units, some amount of oxyethylene fragments.

The macrodiols based on hexane-1,6-diol as well as decane-1,10-diol exhibit similar glass transition temperatures, from −59.3 (Table 2, run 7) to −64.7°C (Table 2,

run 10) for oligo(hexamethylene carbonate) diol and −57.7°C (Table 2, run 1) for oligo(decamethylene carbonate) diol. The macrodiol obtained without catalyst (Table 2, run 10) showed a characteristic cold crystallization exotherm at −32.7°C and melting endotherm at 15°C (Fig. 10).

4. Conclusions

The transesterification reaction between propylene carbonate and diols containing six or more carbon atoms in a molecule carried out under atmospheric pressure using azeotropic solvents in the presence of the coordination catalysts leads to almost pure oligocarbonate diols. In the case of using ethylene carbonate the resultant macrodiols contained the ethylene carbonate and ethylene oxide units. The transesterification with ethylene carbonate carried out in the presence of alkaline catalysts, especially those containing alkali metal ions (K$_2$CO$_3$, CsF) leads to macrodiols with high amount of oxyethylene fragments. At higher temperature the attack at the methylene carbon atom in alkylene
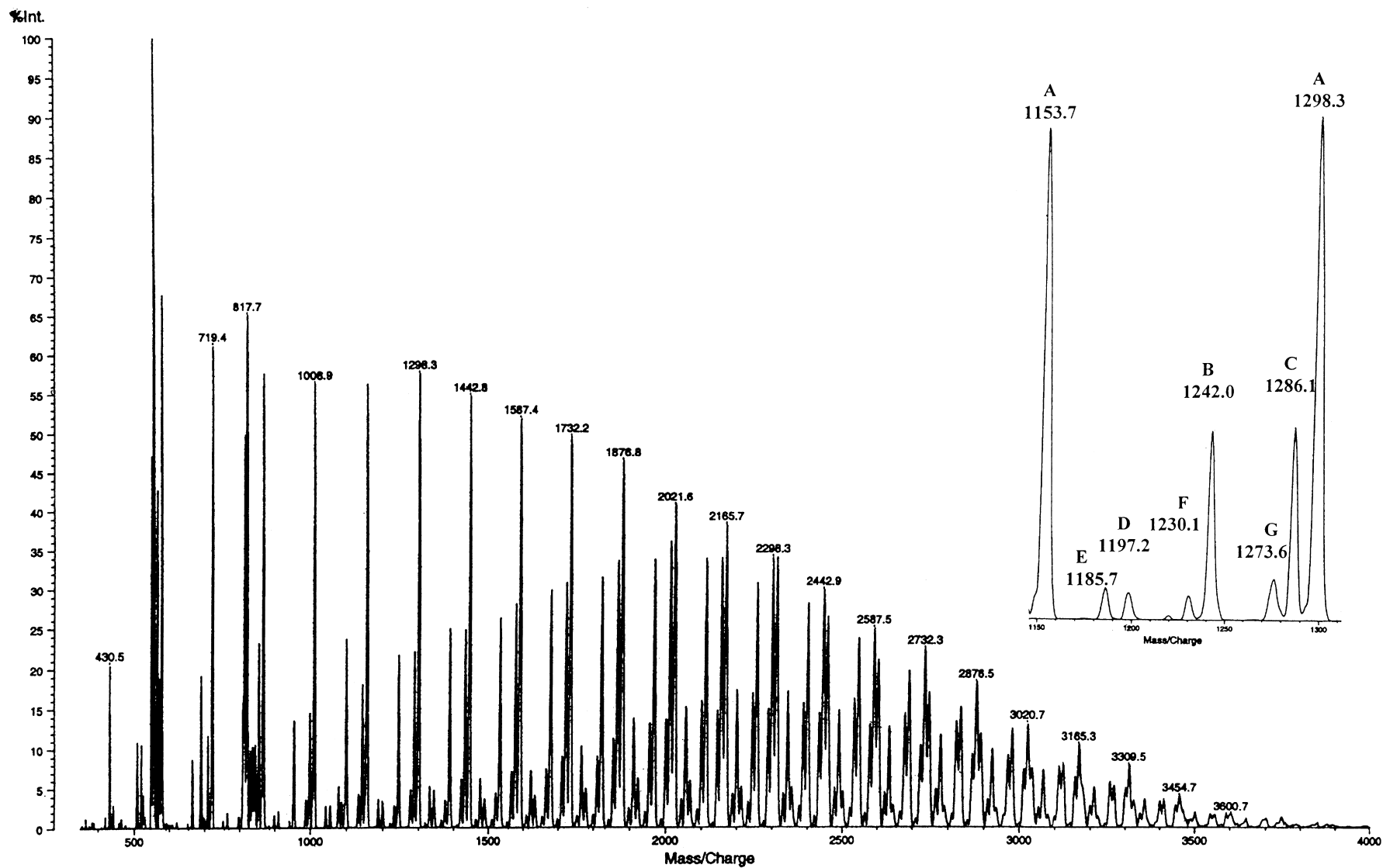

R = H or CH$_3$
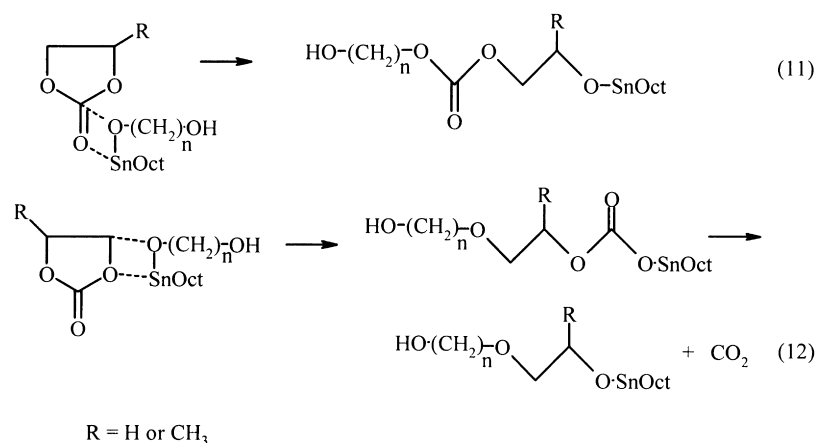
Scheme 6.

Fig. 9. The MALDI-TOF mass spectrum of the macrodiol obtained from ethylene carbonate and hexane-1,6-diol in the presence of Zn stearate (1 mol%) using xylene as an azeotropic solvent.
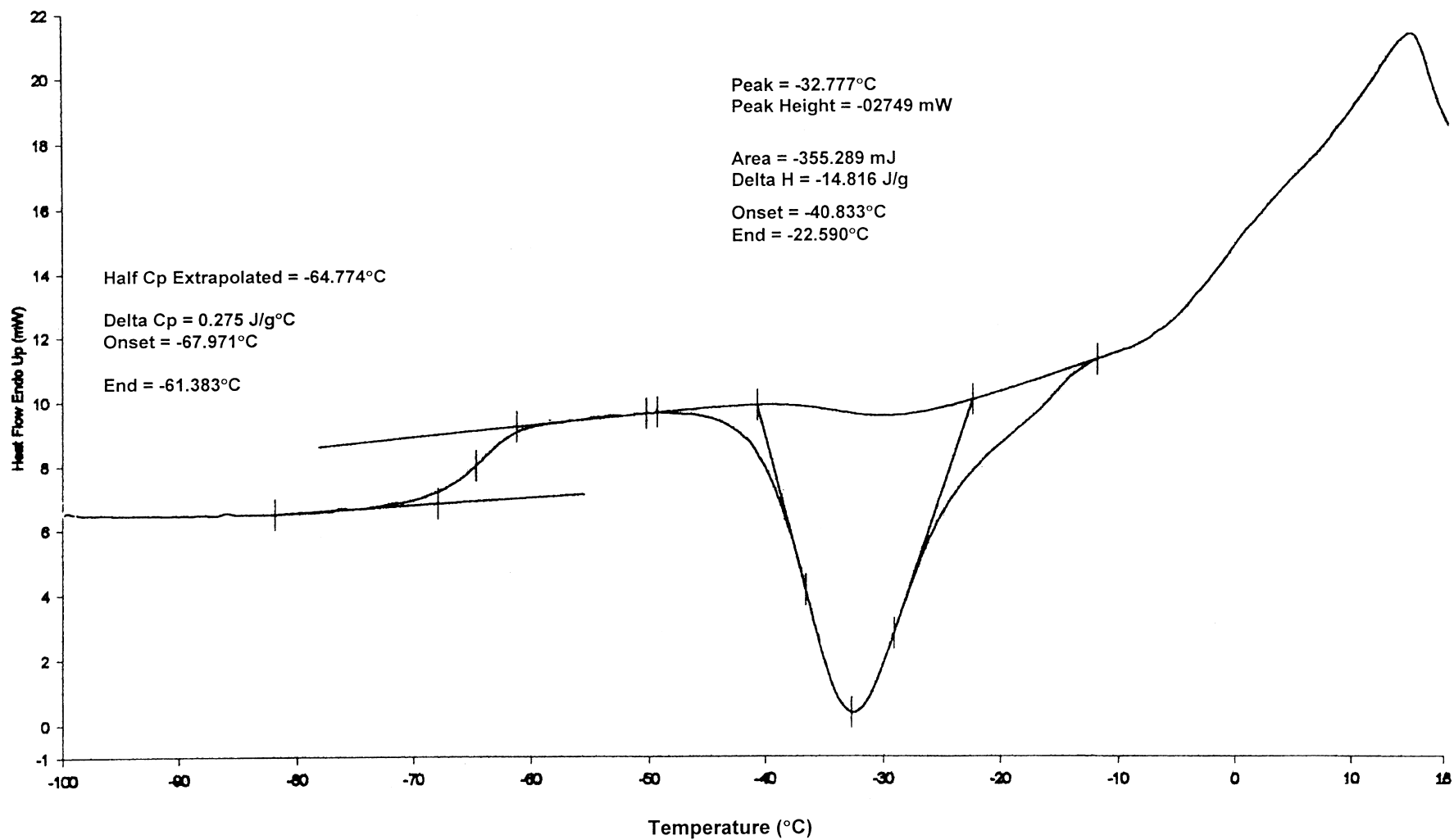
Fig. 10. The DSC thermogram of the macrodiol obtained from ethylene carbonate and hexane-1,6-diol without catalyst using xylene as an azeotropic solvent. The measurements were carried out at a heating rate of 20°C/min.

carbonate is favored and the macrodiols with larger amount of oxyethylene fragments are produced. However, in the case of using coordination catalysts such as zinc or tin carboxylates relatively small amount of oxyethylene fragments were inserted in the macrodiols.

The molecular weight, polydispersity, the structure of macrodiols and their end groups can be determined by a MALDI-TOF mass spectrometry. In comparison with the structure analysis of the reaction products reported by Harris [21], in which oligo(ether-carbonate)s were degraded in alkaline conditions to the poly(oxyethylene) diols and then subjected to gas chromatographic analysis, the oligomer analysis by means of MALDI-TOF in combination with NMR spectroscopy seems to be very effective. As was shown by Martin et al. [18] MALDI-TOF mass spectrometry cannot be considered as an absolute method in the measurement of polymers with high polydispersity, whereas it has been shown that MALDI-TOF is a reliable method in the analysis of narrowly distributed oligomeric samples.

Acknowledgements

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