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Ring-Opening Oligomerization of Propylene Carbonate Initiated by the Bisphenol A/$KHCO_3$ System: A Matrix-Assisted Laser Desorption/Ionization Mass Spectrometric Study of the Oligomers Formed

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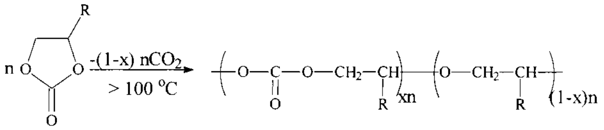
ABSTRACT: The decarboxylation upon oligomerization of propylene carbonate in the presence of the bisphenol A/$KHCO_3$ initiating system was studied by means of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Five different series of peaks appeared in the MALDI-TOF MS spectra of the oligomerization mixture. In addition to the chain-extension reaction with the propylene oxide units, the oligomers of all of the propylene oxide units and oligomers containing carbonate end groups condensed. The product of the oligomerization reaction was hydrolyzed under alkaline conditions. It was found that hydrolyzed oligomers do not carry carbonate groups. The results of the MS studies agreed well with those obtained by ^1H and ^{13}C NMR spectroscopies and size-exclusion chromatography (SEC). On the basis of the results of the present investigation, a mechanism for the oligomerization is also proposed.

Introduction

The ring-opening polymerization of the five-membered cyclic carbonates (e.g., ethylene and propylene carbonate) occurs in the presence of Lewis acids or bases or transesterification catalysts at elevated temperatures (>100 °C), and the process is always accompained by decarboxylation to yield poly(ether carbonates)[1−8] (R = H or CH_3), as shown below



where x is the mole fraction of carbonate units. For initiation by Lewis acids or transesterification catalysts,[1−6] $x = 0.4-0.5$, and for initiation by base, $x = 0.1-0.3$.[7,8]

The oligomerization of ethylene (EC) and propylene carbonates (PCs) in the presence of bisphenol A (BPA) to yield oligo(ethers) is of great industrial importance.[9] This is because ethylene and propylene oxides can be replaced with their carbonates, thereby ensuring a more convenient synthesis of the corresponding oligo(ethers). However, our previous SEC studies on the oligomerization of PC in the presence of the BPA/base system showed that dimeric and trimeric products of the oligomers also formed.[10] This inspired us to perform a detailed matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)[11−14] study on the mixtures formed in the oligomerization reaction of PC in the presence of the BPA/$KHCO_3$ system. Identification and establishment of the microstructure of the oligomers formed should elucidate the mechanism of the oligomerization.

Results and Discussion

The reaction mixture was warmed continuously up to 160 °C within 2 h. Intense CO_2 evolution was observed. To obtain information on the CO_2 evolution during the reaction, the reaction volume was reduced to 100 mL. Figure 1 shows a typical amount of CO_2 evolved versus time curve, together with a reaction temperature versus time plot.

The amount of CO_2 evolved versus time plot demonstrates that the intense CO_2 evolution starts when the reaction temperature reaches 140 °C. The total amount of CO_2 evolved level off at the final value of 100% conversion.

A typical MALDI-TOF MS spectrum of the reaction mixture obtained after a 24-h reaction time is shown in Figure 2. Five different series of peaks can be identified.

The legend and possible chemical structures of the series identified are summarized in Scheme 1.

The first series of peaks (a) corresponds to the oligomers containing propylene oxide units with the BPA moiety. The mass numbers for series a can be expressed by

$$M_a = 228 + 39 + 58n, \quad \text{i.e.,} \quad M_a = 267 + 58n \qquad (1)$$

where 228, 39, and 58 Da are the mass of the BPA, potassium (potassium cationized peaks), and propylene oxide units, respectively, and n is the number of the propylene oxide units.

Series b corresponds to the oligomers containing BPA and propylene oxide units in which only one propylene carbonate unit is incorporated. The masses of series b components can be written as

$$M_b = 228 + 39 + 102 + 58n, \quad \text{i.e.,} \quad M_b = 369 + 58n \qquad (2)$$

where 102 Da is the mass of a propylene carbonate unit.

Series c is assigned as the peaks of the oligomers formed in the reaction of oligomers a with oligomers b via condensation by loss of H_2O. The masses of series c components can be expressed by eq 3.

$$M_c = M_a + M_b - 39 - 18, \quad \text{i.e.,} \quad M_c = 579 + 58n \qquad (3)$$

Series d originates from the product of condensation of two b oligomers with each other. The masses of series

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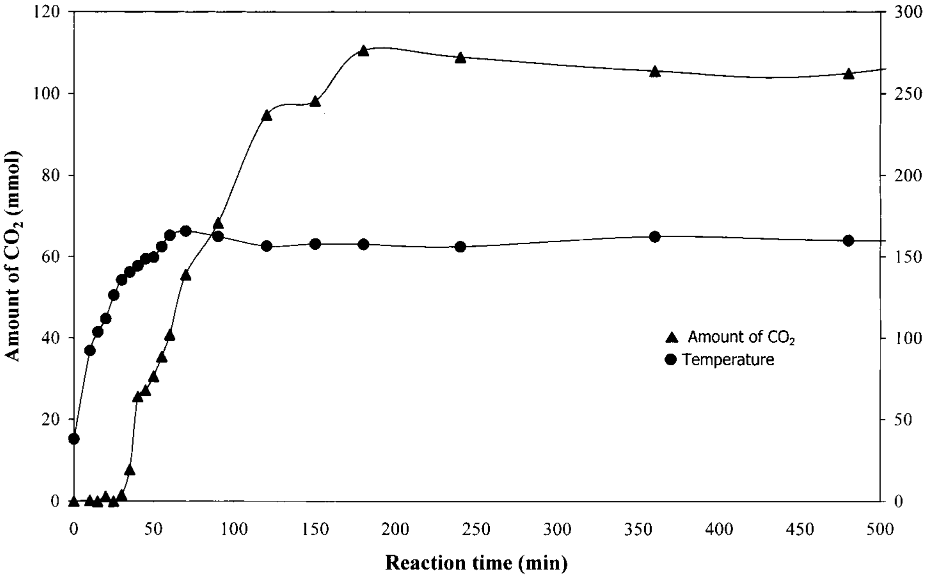


Figure 1. Amount of CO_2 evolved and reaction temperature versus time curves for the oligomerization of propylene carbonate (PC) initiated by BPA/$KHCO_3$. Experimental conditions: 15.6 mmol BPA, 112.5 mmol PC, 0.5 mmol $KHCO_3$.

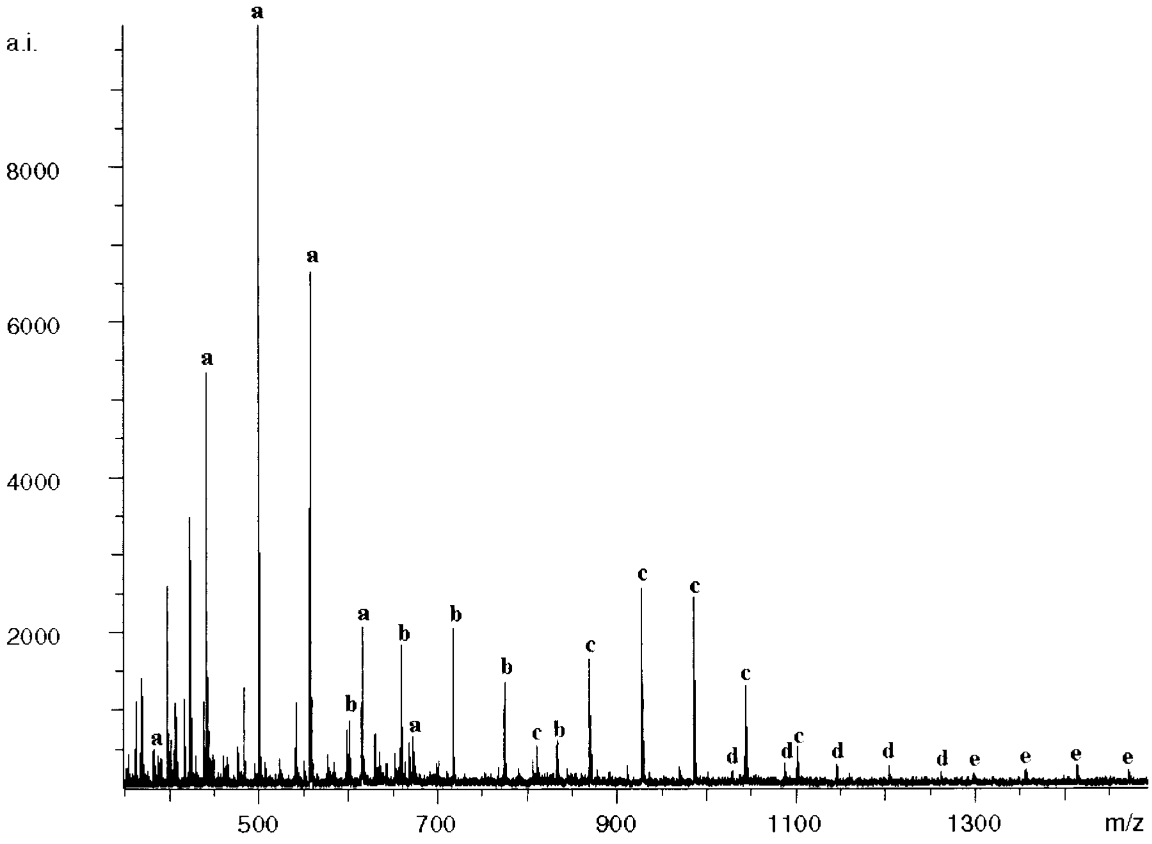


Figure 2. MALDI-TOF MS spectrum of the oligomer mixture of **S1** (for experimental conditions, see Table 1).

d components obey eq 4.

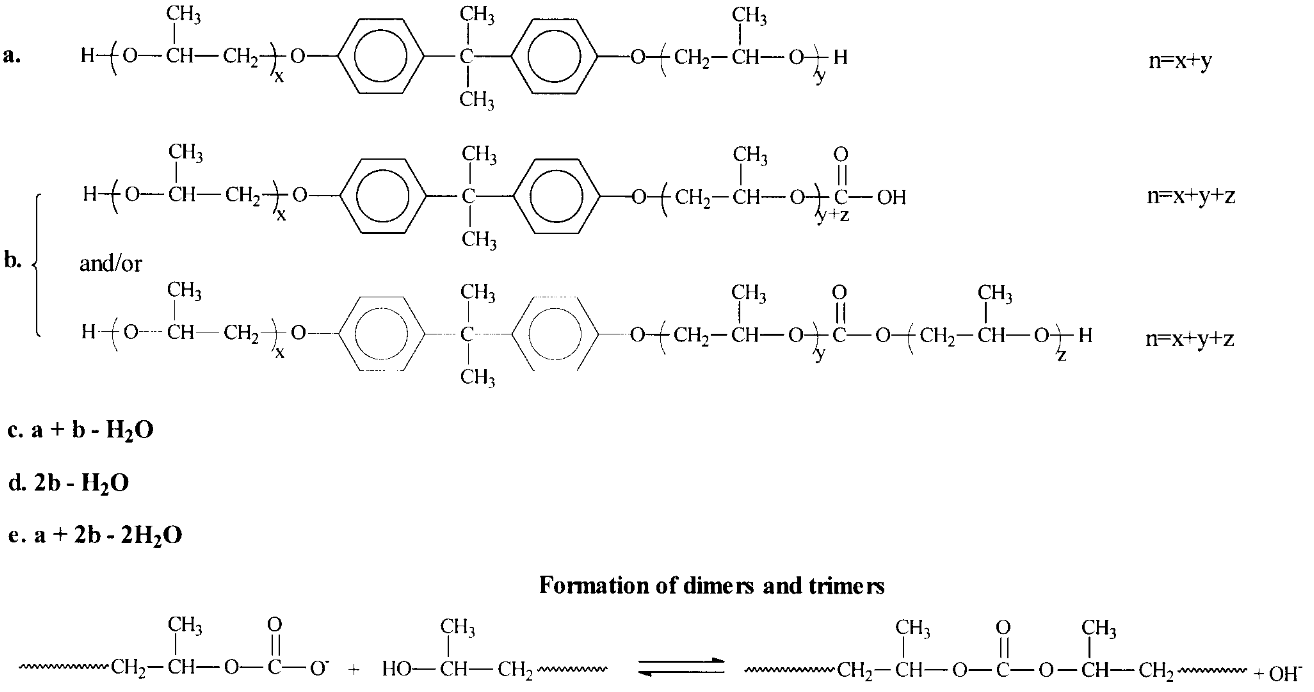
$$M_d = 2M_b - 39 - 18, \quad \text{i.e.,} \quad M_d = 681 + 58n \qquad (4)$$

Series e is derived from the product of reaction of an a oligomer with two b oligomers via condensation with loss of two H_2Os. The masses of series e components are given by

$$M_e = 2M_b + M_a - 2 \times 39 - 2 \times 18, \quad \text{i.e.,} \quad M_e = 891 + 58n \qquad (5)$$

The MALDI-TOF MS spectrum of the sample does not show any oligomers with two propylene carbonate units per BPA unit or dimers and/or trimers of series a. The first observation indicates that the frequency of formation of carbonate linkages in the oligomers is very low at 160 °C. In the case of ethylene carbonate polymerization under basic conditions, there was a maximum of 32 mol % ethylene carbonate content.[8] The second finding reveals that the oligomer should contain carbonate groups at the chain end for dimerization (series c and d) and trimerization (series e) to take place. These

Scheme 1. Assigment of the Series of Peaks Observed in the MALDI-TOF MS Spectra



findings also indicate that an alkoxide anion chain end is not able to activate dimerization and/or trimerization.

Increasing the initial concentration of monomer with respect to the BPA concentration results in some oligomers containing two propylene carbonate units. This is because the average chain length also increases at higher monomer concentration, so that the probability of finding two propylene carbonate units within the chain increases. To support assigments of MALDI-TOF MS results, a model reaction was designed, and the product of the reaction was investigated by SEC.

Figure 3 shows a multimodal molar mass distribution. The ratio of the UV/RI signals does not vary significantly in the elution volume range of 39−42 mL, indicating that the aromatic initiator moiety is evenly distributed independently of the chain lengths. Based on the calibration, the relations $M_n(1) = 2M_n(2) = 3M_n(3)$ are obtained. This result indicates that dimerization and trimerization take place.

The ^{1}H NMR spectrum of the oligomer mixture obtained after a 24-h reaction time is shown in Figure 4.

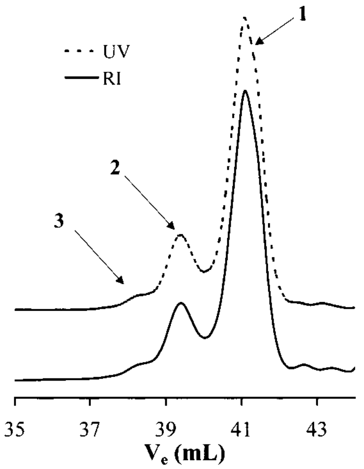


Figure 3. SEC trace of **S1** (for experimental conditions, see Table 1).

The number-average degree of oligomerization (DP$_n$) can be calculated by comparing the area of the signal at 1.63 ppm, assigned to the methyl protons of BPA (e), with that of the signals at 0.82−1.36 ppm, asssigned to the methyl protons of propylene oxide (a)

$$\mathrm{DP_n} = \frac{I_a N_e}{I_e N_a} \tag{6}$$

where I_a and I_e are the intensities and N_a and N_e are the numbers of the a and e protons, respectively.

Figure 5 shows the quantitative ^{13}C NMR spectrum of the oligomer mixture obtained at [PC]/[BPA] = 14. DP$_n$ can also be calculated by eq 7

$$\mathrm{DP_n} = 2I_{a,b}/I_h \tag{7}$$

where $I_{a,b}$ and I_h are the peak areas of the methyl carbon signals of propylene oxide (carbonate) and of BPA, respectively. As shown in Figure 5, a signal at 153.9 ppm appears in the spectrum, which is apparently due to carbonyl carbons and which supports the MALDI-TOF MS results indicating that the oligomers contain carbonate links.

The average number of propylene carbonate units (X_{pc}) in the chain of the oligomers can be calculated from the ^{13}C NMR and MALDI-TOF MS spectra with the aid of eqs 8 and 9, respectively

$$X_{pc} = 2I_g/I_j \tag{8}$$

where I_g and I_j are the intensities of the carbonyl (g) and quaternary carbons of the aromatic rings (j)

$$X_{pc} = \sum_i n_{pc,i} I_i / \sum_i n_{bpa,i} I_i \tag{9}$$

where I_i is the intensity of ith peak and $n_{pc,i}$ and $n_{bpa,i}$ are the numbers of propylene carbonate and BPA units of the ith peak, respectively.

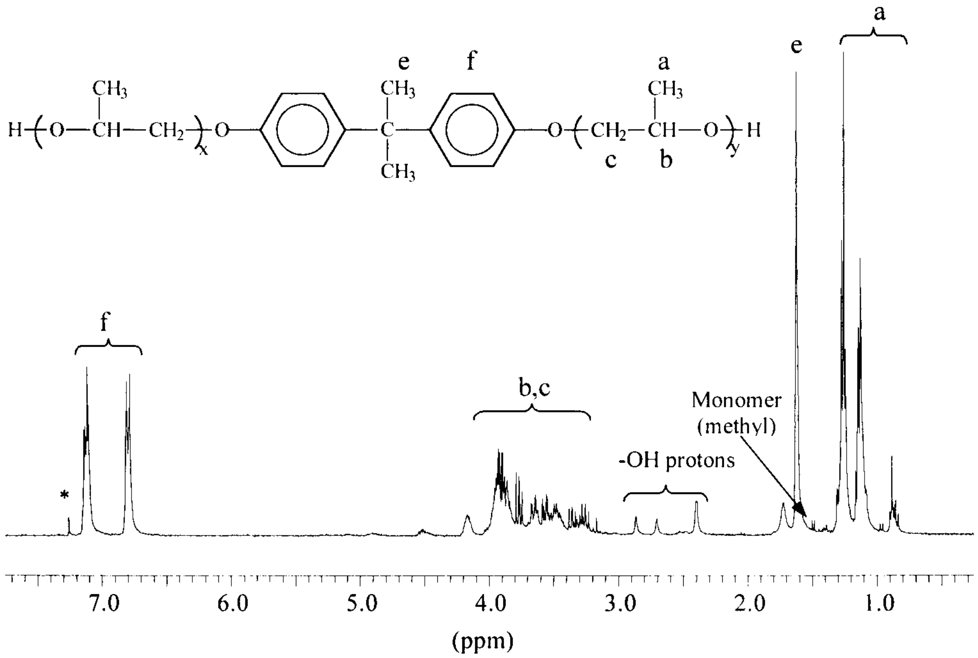


Figure 4. ^{1}H NMR spectrum of the oligomer mixture of **S1** (for experimental conditions, see Table 1).

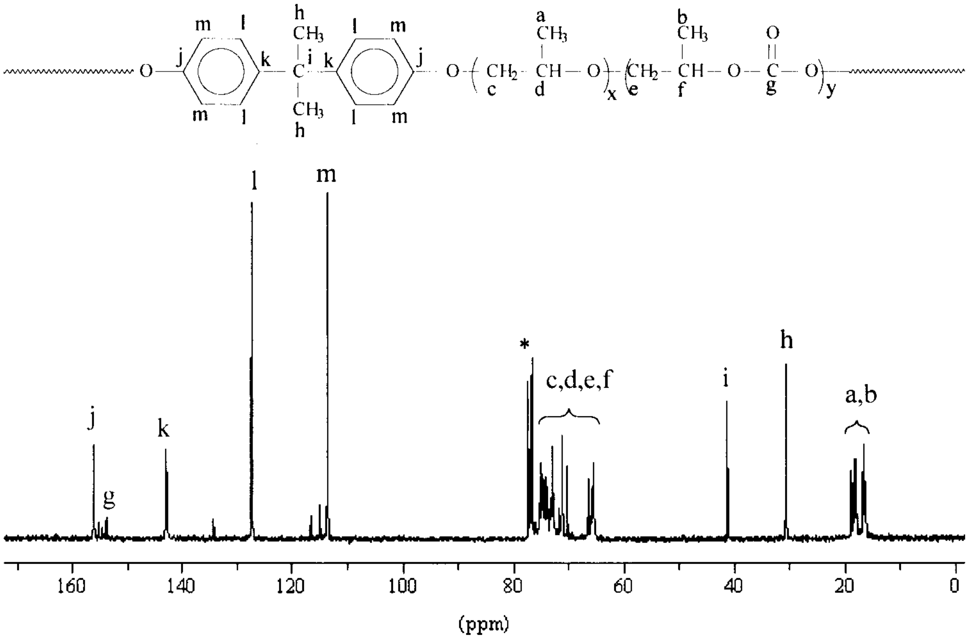


Figure 5. Quantitative ^{13}C NMR spectrum of the oligomer mixture of **S2** (for experimental conditions, see Table 1).

The value calculated from the ^{13}C NMR spectrum of the sample presented in Figure 5 is $X_{\mathrm{pc}} = 0.58$, and that from the MALDI spectrum $X_{\mathrm{pc}} = 0.48$.

Judging from the MALDI results, DP$_\mathrm{n}$, and the number- and weight-average molecular weights (M_n and M_w, respectively) can be directly obtained using eqs 10−12

$$\mathrm{DP_n} = \sum_i n_{\mathrm{p},i} I_i / \sum_i n_{\mathrm{bpa},i} I_i \tag{10}$$

$$M_\mathrm{n} = \sum_i M_i I_i / \sum_i I_i \tag{11}$$

$$M_\mathrm{w} = \sum_i M_i^2 I_i / \sum_i M_i I_i \tag{12}$$

where I_i is the intensity and M_i is the mass of the ith peak and $n_{\mathrm{p},i}$ is the number of the propylene oxide and carbonate units and $n_{\mathrm{bpa},i}$ is the number of the BPA units of the ith peak. The ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and GPC results are summarized in Table 1.

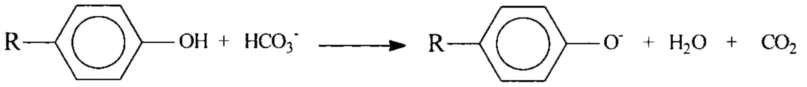
The results obtained by the different methods agree well.

Table 1. DP$_\mathrm{n}$, M_n, and $M_\mathrm{w}/M_\mathrm{n}$ Values Obtained by Different Methods with Samples S1 and S2[a]

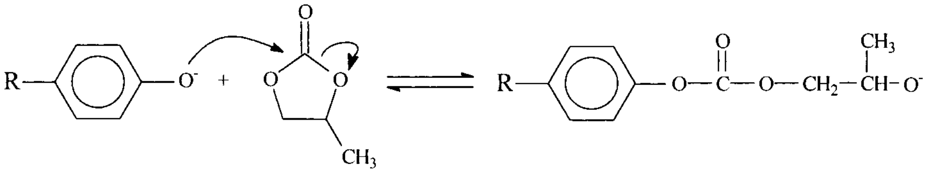
	^{1}H NMR		^{13}C NMR		GPC		MALDI	
	S1	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
DP$_\mathrm{n}$	4.7	7.1	4.8	7.3	–	–	4.4	6.3
M_n	–	–	–	–	560	750	640	760
$M_\mathrm{w}/M_\mathrm{n}$	–	–	–	–	1.32	1.31	1.15	1.08

[a] Experimental conditions: 0.25 mol of BPA, 0.0075 mol of KHCO$_3$, after 24 H, at 160 °C; 1.8 mol of PC (**S1**) and 3.6 mol of PC (**S2**).

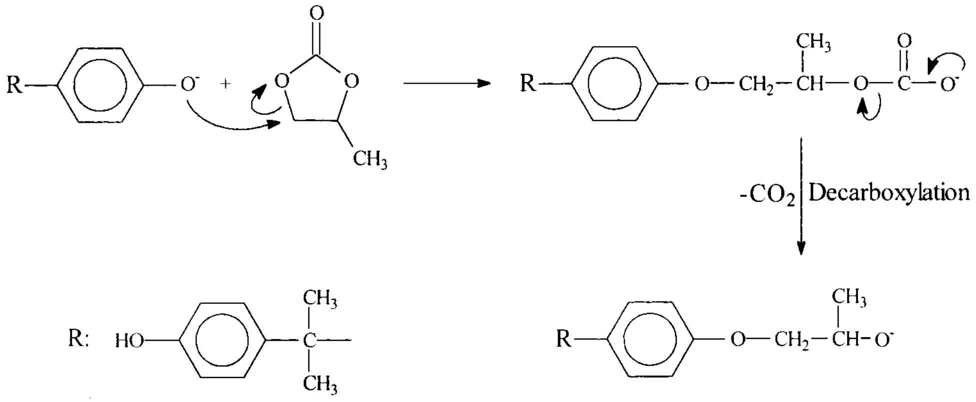
Scheme 2. Proposed Reaction Mechanism for the Initiation of the Oligomerization of Propylene Carbonate (PC) by BPA/$KHCO_3$



a. Initiation by Carbonyl Carbon Attack Mechanism

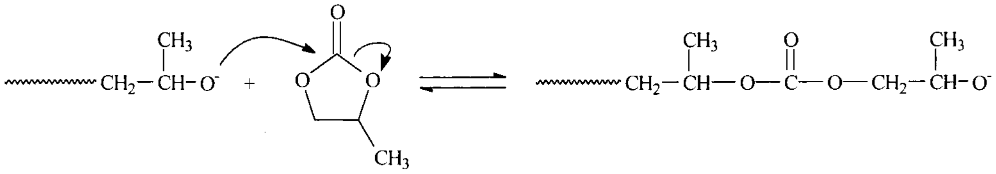


b. Initiation by Alkylene Carbon Attack Mechanism

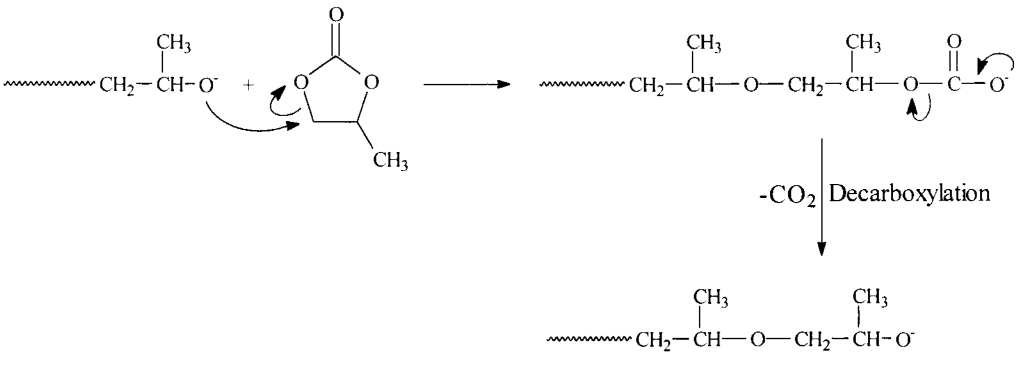


Scheme 3. Proposed Reaction Mechanism for the Oligomerization of Propylene Carbonate (PC) Initiated by BPA/$KHCO_3$

a. Oligomerization by Carbonyl Carbon Attack Mechanism



b. Oligomerization by Alkylene Carbon Attack Mechanism



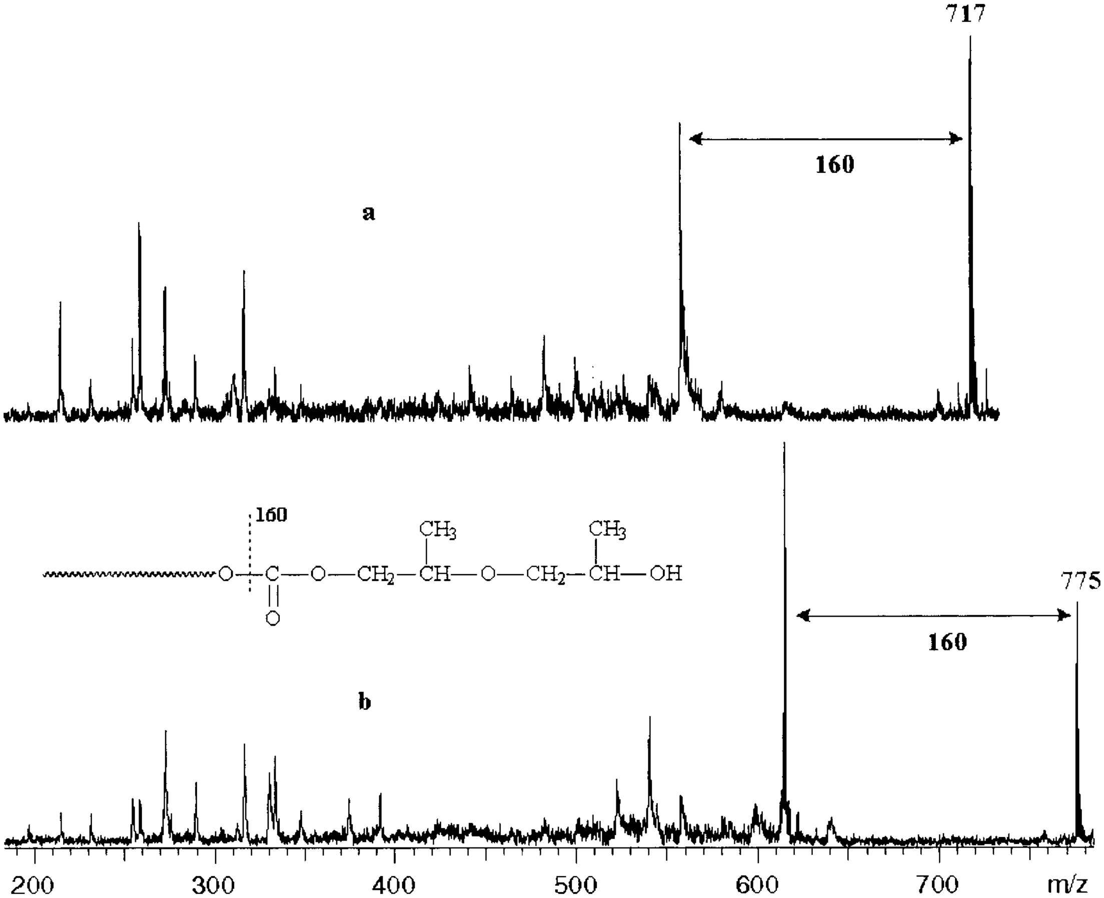


Figure 6. MALDI-TOF MS/PSD spectra of the oligomers with parent masses (a) 717 Da and (b) 775 Da from mixture **S2**.

Mechanistic Considerations

The proposed mechanisms for the initiation and the oligomerization of propylene carbonate are depicted in Schemes 2 and 3, respectively.

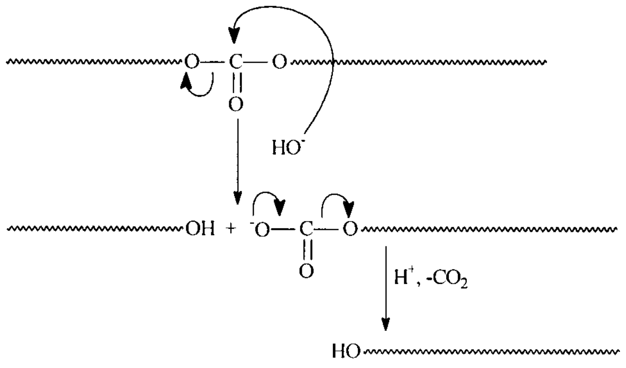
There are two possible routes for the alkoxide anion to react with PC.[8] One is attack at the carbonyl carbon of PC. In this case, the attack is reversible and results in the formation of an oligocarbonate. The second route involves an irreversible attack at the alkylene carbon of PC, which is accompanied by decarboxylation. If only the former mechanism operated, the resulting oligomers would contain all propylene oxide units. On the other hand, if the oligomerization proceeded by the alkylene attack mechanism, carbonate and alkoxide anion chain ends would coexist in the mixture. However, because the carbonate anion is a much weaker nucleophile than the alkoxide anion, it cannot open the ring of PC and would rather react with the alcohol group (series c–e).

Although the oligomers evidently contained carbonate links, we must determine the position of the carbonate group in the oligomers of series b in order to determine which of the above two mechanisms operates under the applied experimental conditions.

MALDI-TOF MS can be combined with the so-called "post-source" decay technique (PSD)[13,14] to obtain structural information on the oligomers in question. Several peaks belonging to series b were selected for PSD, which should fragment the carbonate linkages. Figure 6 shows two PSD spectra of series b components with parent masses of 717 and 775 Da.

As shown in Figure 6, intensive fragmentation of a 160-Da unit occurs in both cases, which we attribute to loss of the propylene carbonate and propylene oxide units. If the carbonate group in the oligomers of series b were at the end of the chain, the mass would decrease by 44 Da (CO_2) in the PSD spectra. However, as this is not the case, the oligomers of series b contain mostly propylene carbonate and propylene oxide units at the chain end, as indicated in Figure 6.

Scheme 4. Mechanism of the Hydrolysis of Polycarbonates



To support the presence of carbonate linkages in oligomer series b–e, the product of the oligomerization reaction was hydrolyzed[8] under alkaline conditions, as shown in Scheme 4.

Figure 7 shows the MALDI-TOF MS spectra of the oligomer mixture before and after hydrolysis.

The spectra demonstrate that the series b–e oligomers contain carbonate linkages. The hydrolyzed oligomers do not carry carbonate groups, as do all of the resulting oligomers belonging to series a, i.e., they consist of propylene oxide units and BPA. These results

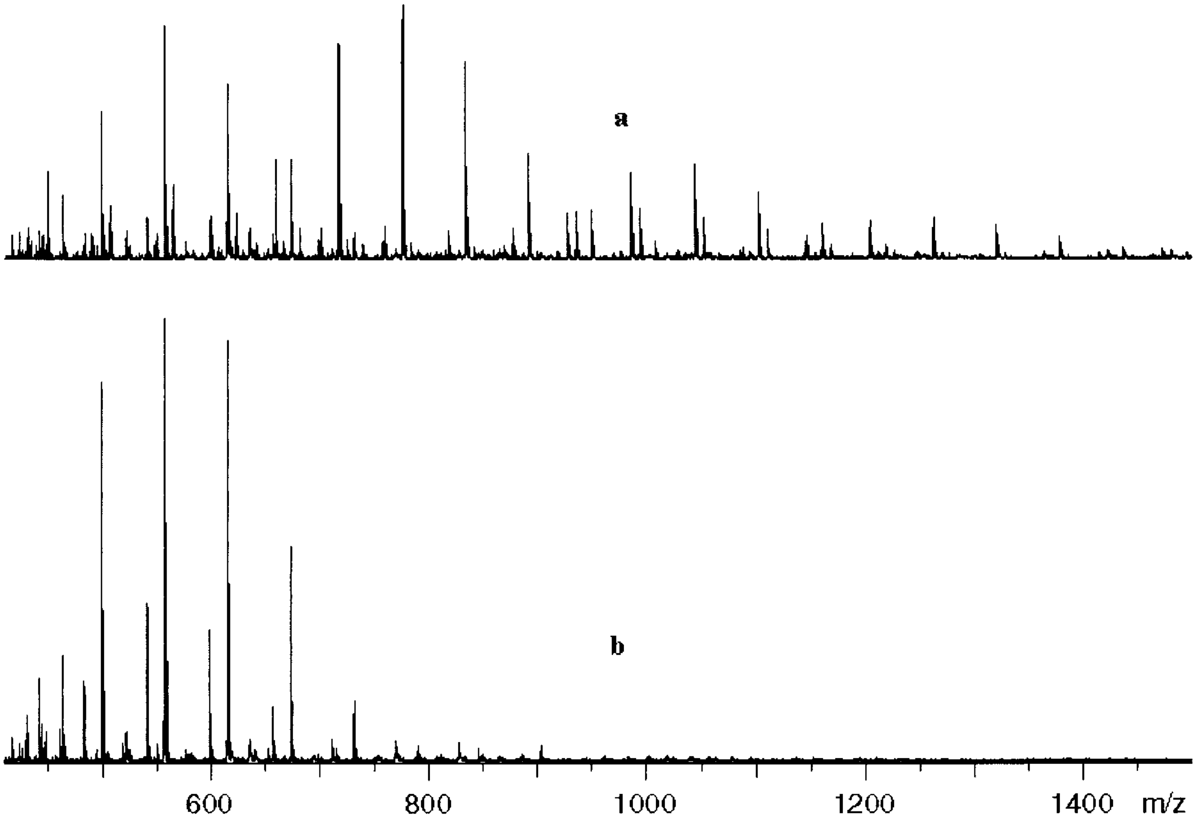


Figure 7. MALDI-TOF MS spectra of the oligomer mixture (a) before and (b) after hydrolysis from mixture **S2**.

indicate that the mechanisms presented in Schemes 2 and 3 operate under the applied experimental conditions.

Conclusions

At least five different series of peaks were identified by MALDI-TOF MS. Our investigation showed that in, addition to the chain-extension reaction with propylene oxide units, the oligomers that contain carbonate end groups also react by condensation. According to the present studies, the alkoxide anion also attacks at both the carbonyl carbon and the alkylene carbon in the oligomerization reaction investigated.

Experimental Section

Materials. Propylene carbonate (analytical grade, Merck, Germany), bisphenol A (polycarbonate grade, Zaklady Chemiczene Blachovnia, Poland), NaOH, KOH, $KHCO_3$, HCl (analytical grade, Reanal, Hungary), and ethanol (analytical grade, Aldrich, Germany) were used as received.

General Procedure of Oligomerization. A 1-L resin kettle equipped with a mechanical stirrer, thermometer, and nitrogen inlet/outlet in an oil bath was charged with BPA (57.0 g, 0.25 mol), propylene carbonate [183.6 g, 1.8 mol (sample **S1**); 367.2 g, 3.6 mol (sample **S2**)], and $KHCO_3$ (0.75 g, 0.0075 mol) under nitrogen atmosphere. The reaction mixture was continuously heated to 160 °C in about 2 h, and it was kept at 160 °C for an additional 22 h. Yields: 110.3 g (**S1**); 202.5 g (**S2**).

Determination of the Amount of CO_2 Evolved. A 100-mL three-necked flask equipped with a magnetic stirrer, thermometer, condenser, and nitrogen inlet/outlet in an oil bath was charged with BPA (3.56 g, 15.6 mmol), propylene carbonate (11.48 g, 112.5 mmol), and $KHCO_3$ (0.05 g, 0.5 mmol) under nitrogen atmosphere. The temperature of the reaction mixture was continuously increased up to 160 °C in about 1 h, and it was kept at 160 °C for additional 23 h. Yield: 9.25 g. The evolved CO_2 was absorbed in NaOH solution (300 mL, 1 mol/dm^3). From the NaOH solution, 1-mL samples were taken at predetermined times. The CO_2 contents of the samples were determined by acidic−alkalimetric titration as follows: A 0.900 mL sample was diluted with distilled water to 15.00 mL. The samples were titrated with HCl (0.1 mol/dm^3), and the pH was monitored. The amounts of CO_2 were calculated by means of the Gran function.[15]

Hydrolysis of the Oligomers. KOH (3.5 g, 0.0625 mol) was dissolved in ethanol (100 mL); then, 2 g of the oligomer mixture was added to the solution, and the mixture was stirred at room temperature for 2 h. The reaction mixture was neutralized with concentrated hydrochloric acid and filtered, and then the solvent from the filtrate was evaporated using a rotary evaporator. Yield: 1.31 g.

Characterization. *MALDI-TOF MS.* The MALDI-TOF measurements were performed with a Bruker BIFLEX III mass spectrometer. In all cases, 19-kV acceleration voltage was used with pulsed ion extraction (PIE). The positive ions were detected in the reflectron mode (20 kV). A nitrogen laser (337 nm, 3-ns pulse width, 10^6−10^7 W/cm^2) operating at 4 Hz was used to induce laser desorption, and 100−120 shots were summed. The spectra were externally calibrated with poly(ethylene glycol) PEG ($M_n = 1450$ g/mol, MWD = 1.02) with linear calibration. Samples were prepared with a DHB (2,5-dihydroxybenzoic acid) matrix (20 mg/mL). In some cases, KCl (5 mg/mL) was added to the matrix/analyte solution to enhance cationization. The analyte solution (5 mg/mL) was mixed in 10:1:1 v/v ratio (matrix:analyte:KCl). The solvent was methanol. A volume of 0.5−1 μL of these solutions was deposited onto the sample plate (stainless steel) and allowed to air dry. The differences between the measured and calculated masses were within 0.1 Da in each case.

MALDI-TOF MS/PSD. All of the PSD spectra were recorded by selection of the ion to be studied, using the pulser to allow an approximately 20-Da window for selection. In each segment, the reflectron voltage was decreased in 14−16 steps with 100−120 laser shots. The segments were pasted and calibrated using XMASS 5.0 software from Bruker. The PSD was calibrated using the fragmentation pattern of adrenocorticotropic hormone (ACTH).

Size-Exclusion Chromatography (SEC). The M_n and molecular mass distribution (MMD) of the oligomers were measured by SEC in THF at 35 °C with a Waters chromatograph equipped with four gel columns (7-μm Ultrastyrolgel columns: 500, 10^3, 10^4, and 10^5 Å), a Waters 501 HPLC pump, and Waters 490E UV and Waters 410 refractive index detectors. The M_n and M_w/M_n values of the oligomers were calculated relative to polystyrene.

NMR Spectroscopy. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AM 360 spectrometer with tetramethylsilane as the internal standard.

Titration. Titrations were performed with a 716 DMS Titrino, Metrohm 6.0202.000 glass electrode.

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