Mechanism of the Anionic Ring-Opening Oligomerization of Propylene Carbonate Initiated by the tert-Butylphenol/ $KHCO_3$ System

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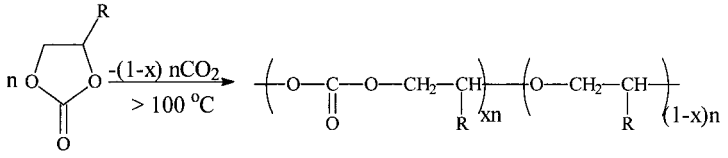
Summary: The ring-opening oligomerization reaction of propylene carbonate in the presence of the tert-butylphenol/$KHCO_3$ initiating system was studied by means of Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF MS) and Electrospray Ionization Time of Flight Mass Spectrometry (ESI-TOF MS). According to the MS spectra obtained, different series of peaks were identified. The MS spectra clearly showed that besides the chain-extension reaction yielding oligomers with all propylene oxide units, the formation of oligomers containing carbonate linkages in the chain, and condensation reaction between the latter two also took place. The structure of the oligomers carrying carbonate linkages was determined by the post-source decay (PSD) MALDI-TOF MS/MS method. Based on the MS results, a mechanism for the oligomerization reaction is proposed.

Keywords: MALDI; oligomers; polyethers; ring-opening polymerization; separation of polymers

Introduction

Cyclic carbonates (e.g. ethylene- and propylene carbonate) undergo ring-opening polymerization at elevated temperatures (> 100 °C) in the presence of appropriate initiators such as Lewis acids, bases, or transesterification catalysts. The oligomerization of EC and PC yields poly(ether carbonates)[1-8] (R= H or CH_3) with the structure shown below:



where x is the mol fraction of the carbonate units. It was shown that the carbonate content of the resulting polymer is dependent upon the initiator applied. Initiation with Lewis acids or

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transesterification catalysts[1-6] yielded polymers with x=0.4-0.5 carbonate content, and in the presence of base x=0.1-0.3 carbonate was observed[7,8].

The ring opening oligomerization of ethylene- and propylene carbonate in the presence of the bisphenol-A/base initiating system yielding oligomers with all ethylene- and propylene oxide units is of great industrial importance[9]. Previous studies[10,11] have shown that the oligomerization of PC-initiated by the bisphenol-A/base system (in addition to the formation of oligomers with all propylene oxide units), resulted in the formation of oligomers containing carbonate linkages. It was also experienced that the carbonate linkages could be hydrolyzed in an ethanolic solution of potassium hydroxide to yield the desired oligomers (all propylene oxide chain) were obtained[11].

As a continuation of our work, in the present article we have investigated the reaction mechanism of the oligomerization of PC in the presence of a monofunctional phenol derivative using the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF)[12,13] electrospray time-of-flight (ESI-TOF)[14,15], and the post-source decay (PSD MALDI-TOF MS/MS)[16,17] mass spectrometric methods.

Experimental

Materials. Methanol, acetonitrile (HPLC grade), ethanol, 2,5-dihydroxybenzoic acid (DHB), sodium trifluoroacetate (NaTFA), potassium trifluoroacetate (KTFA) and tert-butylphenol were received from Aldrich (Germany) and were used without further purification.

Propylene carbonate (analytical grade, Merck, Germany), KOH, $KHCO_3$, and HCl (analytical grade, Reanal, Hungary) were used as received.

Oligomerization. A 50 ml three-necked flask equipped with a magnetic stirrer, thermometer, and nitrogen inlet/outlet in an oil bath was charged with the tert-butylphenol (9.93 g; 0.066 mol), propylene carbonate (27 g; 0.265 mol) and $KHCO_3$ (0.11 g, 0.0011 mol) under nitrogen atmosphere. The reaction mixture was continuously heated to 160 °C in about 1 hour, and it was kept at 160 °C for an additional 23 hours. (Yield: 23.3 g; 91 %).

Hydrolysis of the Oligomers. 2.5 g of the oligomer mixture was added to the solution of KOH in ethanol (1 mol/L) and stirred at room temperature for 2 hours. The reaction mixture was neutralized with concentrated hydrochloric acid, filtered and then the solvent from the filtrate was evaporated using a rotary evaporator. (Yield: 2.13 g; 85 %)

Characterization. *MALDI-TOF MS.* The MALDI MS measurements were performed with a Bruker BIFLEX III^{TM} mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a TOF analyzer. In all cases 19 kV total acceleration voltage was used with pulsed ion extraction (PIE^{TM}). The positive ions were detected both in the linear and in the reflectron mode. A nitrogen laser (337 nm, 3 ns pulse width, 10^6-10^7 W/cm^2) operating at 4 Hz was used to produce laser desorption, and 200-250 shots were summed. Samples were prepared with DHB matrix dissolved in methanol (20 mg/ml). Bulk solutions of the oligomer mixture in methanol were made at a concentration of 5 mg/mL. To enhance the cationization, NaTFA or KTFA in methanol (5 mg/mL) was added to the corresponding matrix/analyte solutions. The solutions were mixed in 10:2:1 v/v ratio (matrix:analyte:cationization agent). A volume of 0.5-1.0 μl of these solutions was deposited onto the sample plate (stainless steel), and allowed to air-dry.

MALDI-TOF MS/PSD. All of the PSD spectra were recorded by selection of the ion to be studied, using a pulser allowing an approximately 20 Da window for selection. In each segment the reflectron voltage was decreased. The segments were pasted and calibrated using XMASS 5.0 software from Bruker. The PSD was calibrated using the fragmentation pattern of the Adrenocorticotropic Hormone (ACTH).

The electrospray ionization Time-of-Flight Mass Spectrometry (ESI-TOF MS). ESI-TOF MS measurements were performed on a BioTOF II instrument (Bruker Daltonics, Billerica, MA). Sample solutions were prepared in methanol at 0.01 mg/mL concentration. To enhance the cationization, solutions of NaTFA or KTFA in a concentration of 0.1 mmol/L in methanol were added to the analyte solutions. The solutions were introduced directly into the ESI source by a syringe pump (Cole-Parmer Ins. Co.) at a flow rate of 2 μL/min. The temperature of drying gas (N_2) was maintained at 100 °C. The voltages applied on the ESI source were the following: 2000

V capillary, 4000 V cylinder, 4500 V endplate and 120 V capillary exit voltages. The spectra were accumulated and recorded by a digitizer at a sampling rate of 2 GHz.

Liquid Chromatography (HPLC). Samples for HPLC were prepared in acetonitrile (ACN) at a concentration of 1 mg/mL. The measurement were preformed on a Waters 2695 HPLC system equipped with a Waters 2996 photodiode array detector. Separations were made on a C-18 reverse phase column (Waters) thermosted at 35 °C.

30 μL of the analyte solutions were injected and eluted with ACN at a flow rate of 0.7 mL/min.

Results and Discussion

The oligomerization of propylene carbonate was achieved in the presence of the tert-butylphenol/$KHCO_3$ initiating sytem. The reaction mixture was continuously heated to 160 °C within one hour. The evolution of CO_2 started at elevated temperature (110 °C) indicating the onset of the reaction. The MALDI-TOF and ESI-TOF MS of the oligomerization reaction mixture obtained after 24 hours reaction time are shown in Fig. 1. The assignments of the peaks appearing in the MS spectra are listed in Table 1.

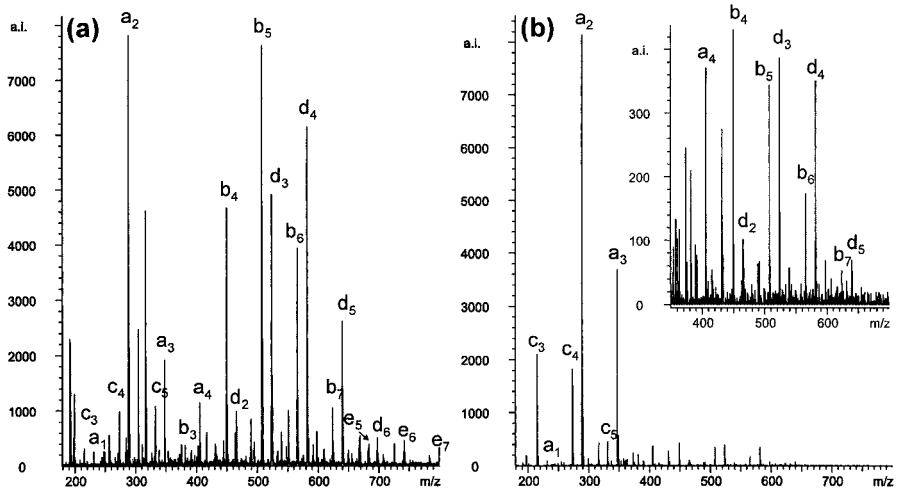


Figure.1. MALDI-TOF MS and ESI-TOF MS spectra obtained on the product of the oligomerization reaction of propylene carbonate initiated by the tert-butylphenol/$KHCO_3$ system. Experimental conditions: 0.25 mol PC, 0.0625 mol tert-butylphenol, 1.8 x 10^{-3} mol $KHCO_3$; Reaction time=24 hours, temperature=160 °C. The subscripts reflect the number of the propylene-oxide units in the given oligomer.

Fig. 1. shows that different series of peaks appeared (**a**,**b**,**c**,**d** and **e** series) in both the MALDI-TOF and the ESI-TOF MS spectra obtained on the resulting reaction mixture. Although there are some differences in the intensity of the oligomer series in the two types of MS spectra, both spectra exhibit practically the same oligomer series. These intensity differences are due to the different sensitivities of the two ionization methods to the oligomer adduct ions.

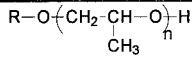
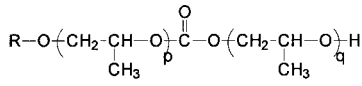
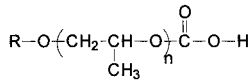
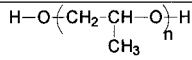
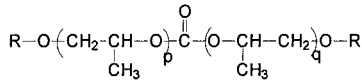
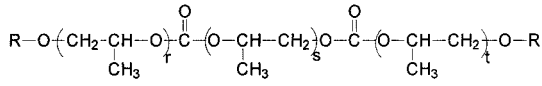
The mass series of an oligomer mixture in both the MALDI-MS and the ESI-MS (for single charged ions) can be formulated as shown below:

$$M=M_I+M_{endgroups}+n_xM_r+M_{Cat} \qquad (1)$$

where M_I, $M_{endgroups}$, M_r and M_{Cat} are the mass of the initiator moiety, the endgroups, repeating unit, and the cation attached to the oligomer, respectively, and n stands for the number of the repeating units (degree of polymerization).

Applying Eq. 1 for the mass series observed in the MS spectra, the types of oligomers formed can be rationalized (Table 1).

Table 1. Assignments of the sodium cationized ($[M+Na]^+$) oligomer series formed in the oligomerization reaction of propylene carbonate initiated by the tert-butylphenol/$KHCO_3$ system.

Series	Structure	Mass of Series
a		173+nx58
b	 or 	217+(p+q)x58, i.e., 217+nx58
c		41+nx58
d		349+(p+q)x58, i.e., 349+nx58
e		393+(r+s+t)x58, i.e., 393+nx58

According to these findings, series **a** corresponds to oligomers containing the initiator moiety with all propylene oxide chains. Series **b** comes from oligomers containing the initiator moiety, propylene oxide repeating units, and one of the propylene carbonate units. The position of the carbonate linkage in series **b** may be in the chain or at the end of the chain. The position of this linkage cannot be judged from simple MS measurements. Series **c** is assigned as propylene glycol oligomers bearing with bearing hydroxyl termini. Series **d** and **e** can be derived from series **a** and **b** as **d** = **a**+**b**-H_2O and **e** = 2**b**-H_2O.

The presence of the carbonate linkages and their position in the chain in series **b** and **d** were further supported and determined by using the PSD MALDI-TOF MS/MS method. The corresponding $[oligomer+Na]^+$ adduct peaks were selected for PSD and the fragment ions formed under these conditions were recorded. The fragmentations are expected to occur at the carbonates linkages, therefore, by recording the mass of the fragment ions formed from the precursor adduct ions, the position of the carbonate linkages can be determined. Several peaks belonging to the **b** series were selected for PSD, and no fragment ions formed by the loss of a single CO_2 molecule was observed. This implies that carbonate linkages in series **b** are not located at the end of the chain. A representative PSD MALDI-TOF MS/MS spectrum of the precursor ion mass of 507 Da is shown in Fig. 2., which shows that no fragment ions were formed by a loss of a single CO_2 molecule. However, the fragment ions appearing at m/z 197, 215, 259 and 289 derive from structure **1** as depicted in Fig. 2, and peaks at m/z 255, 273 and 317 originate from structure **2** (Fig. 2.). These observations indicate that the precursor ions (at m/z 507) are the mix of three oligomers as shown in Fig. 2; structure **3** is most likely because of the presence of the fragment ions at m/z 347 and 157, and similar fragmentations were observed for the other members of series **b**. It was found in the PSD MALDI-TOF MS/MS spectra of this series that all oligomers carried at least one propylene oxide and one propylene carbonate unit at the chain-end (i.e., $q \geq 2$ in Table 1, row 2).

The presence of carbonate linkages in series **d** was also supported by the PSD MALDI-TOF MS/MS method. For example, we have found that the $[oligomer+Na]^+$ adduct ions appearing at m/z 581 are composed of oligomers with p=2; q=2 and p=1; q=3 (see Table 1, row 4).

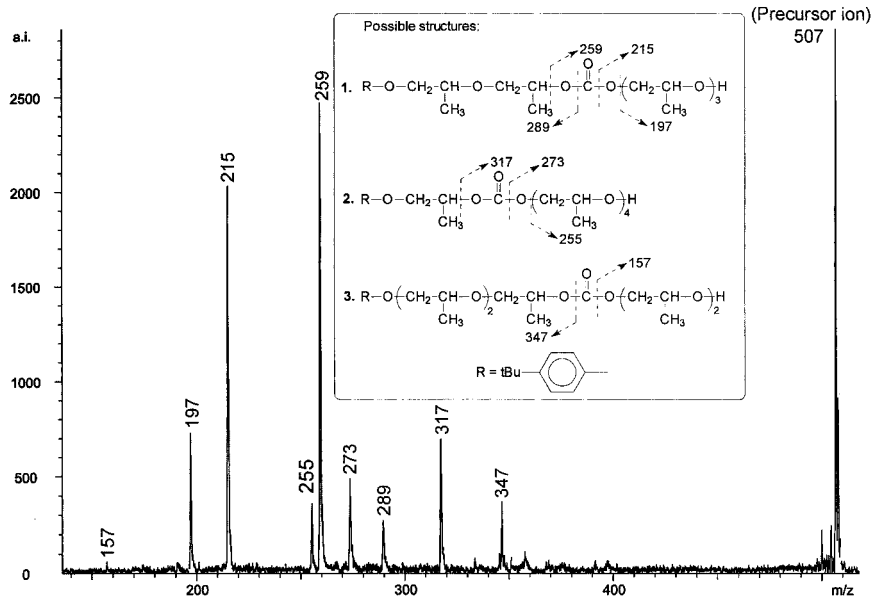
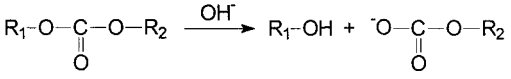
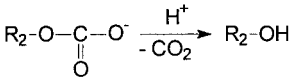


Figure 2. PSD MALDI-TOF MS/MS spectrum obtained on the sodiated oligomer with a precursor ion mass of 507 Da. The inset shows the possible structure and the fragmentation of the oligomer investigated.

To support chemically the presence of the carbonate linkages in the series **b**, **d**, and **e**, the reaction mixtures were treated with an ethanolic solution of KOH. If these oligomers contain carbonate linkages, cleavage at these linkages would occur by hydrolysis according to Eq. 2 and Eq. 3.



(2)



(3)

Indeed, the MALDI-TOF MS and ESI-TOF MS spectra of the reaction mixtures obtained after hydrolysis showed no presence of **b**, **d** and **e** series., i.e., only series **a** and **c** appeared in the MS spectra.

Fig. 3 shows the HPLC UV traces recorded at 273 nm of the reaction mixture obtained before and after hydrolysis. Fig. 3 a shows that most of the oligomers are separated by liquid chromatography. The inset in Fig. 3 shows very similar UV spectra indicating that the length of the chain practically does not influence the electronic properties of the aromatic moiety. The assignments of the peaks on the chromatogram presented in Fig. 3 were made by the off-line MALDI-TOF and ESI-TOF MS methods. Fig. 3 b clearly demonstrates that after hydrolysis, the peaks at higher retention time assigned to series b and d completely disappeared.

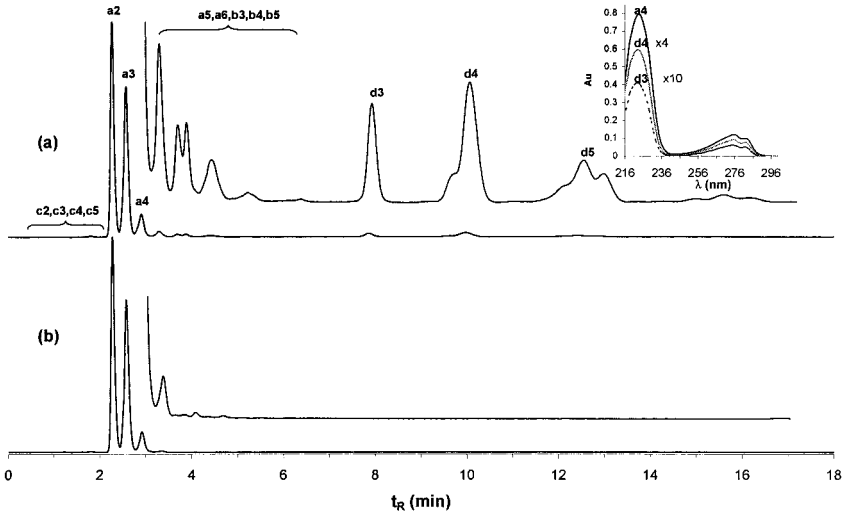
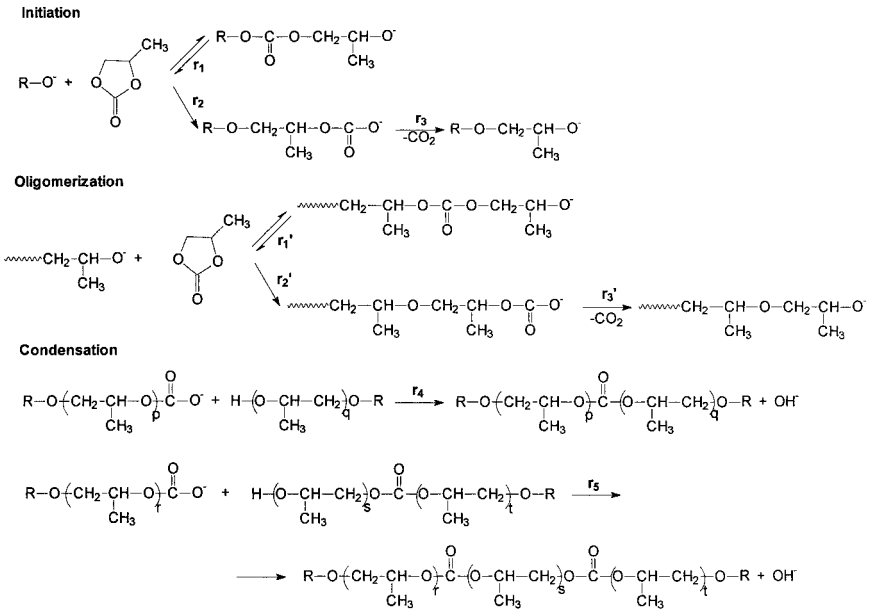


Figure 3. HPLC/UV traces recorded at 273 nm of the oligomer mixture before (**a**) and after hydrolysis (**b**). The inset shows the UV spectra of a_4, d_3 and d_4 fractions. The designation of the fractions is the same as given in Table 1. Experimental conditions: see Fig. 1 caption.

The mechanism of the Oligomerization

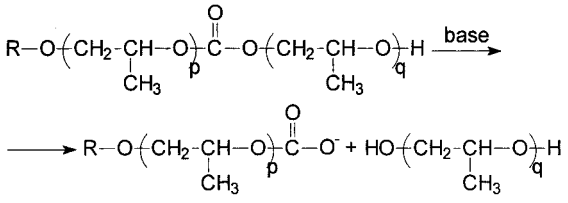
Based on the experimental results a mechanism is proposed for the formation of the observed oligomer series (Scheme 1). The phenolate and the alkoxylate chain-ends may react with the propylene carbonate reversibly by carbonyl carbon attack (r_1 and r_1'), or irreversibly by attack on the alkylene carbon (r_2 and r_2'). The carbonyl carbon attack yields alkoxylate chain-ends and carbonate linkage inside the chain, while the alkylene carbon attack produces carbonate chain-

ends. However, the nucleophilicity of the carbonate group is much lower than that of the alkoxylate; therefore, oligomerization can no longer proceed from this chain-end. The fate of the carbonate endgroups is to lose CO_2, thereby regenerating alkoxy chain-ends (r_3 and r_3') allowing the oligomerization to continue, or to condense with the oligomers having hydroxy endgroups (r_4, r_5).



Scheme 1. Proposed mechanism for the oligomerization of propylene carbonate initiated by the tert-butylphenol/$KHCO_3$ system.

The appearance of series **c** in the MS spectra demonstrates that chain-cleavage at the carbonate links takes place under our conditions according to Eq. 4.



(4)

Conclusions

We investigated the anionic ring-opening oligomerization of propylene carbonate initiated by the tert-butylphenol/$KHCO_3$ system. The analysis of the reaction mixture by MALDI-TOF and ESI-TOF MS methods showed that different oligomer series were formed. The presence of the carbonate linkage in the oligomers was proved by comparison of the MS spectra and HPLC traces of the reaction mixture obtained before and after hydrolysis. It was also demonstrated that liquid chromatography is capable of separating the oligomers. The PSD MALDI-TOF MS/MS method was applied to determine the position of the carbonate link, information which can hardly be obtained by other, non-mass spectrometric methods.

Acknowledgment

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