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Mechanism of ring-opening and elimination cooligomerization of cyclic carbonates and ε-caprolactone: Formation of cyclic cooligomers

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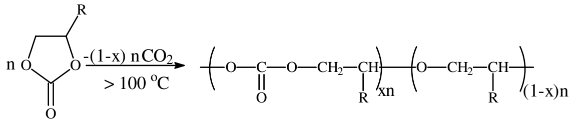
Abstract

The cooligomerization reactions of the comonomers ethylene carbonate–propylene carbonate, ethylene carbonate–ε-caprolactone and propylene carbonate-ε-caprolactone initiated by the *p*-*tert*-butylphenol/$KHCO_3$ system were investigated by means of electrospray ionization mass spectrometry combined with liquid chromatography. Three major cooligomer series were found in each case which were identified such as cooligomers with *tert*-butylphenol and hydroxyl headgroups. The presence of cyclic cooligomers was also unambigously observed. In addition, cooligomers carrying carbonate linkages were also identified, however, their fraction was very small compared to the cooligomer series without carbonate linkages. Besides the cooligomerization reaction, homooligomerization of ethylene and propylene carbonate was observed, as well as no linear homooligomers of ε-caprolactone were detected. Based on the LC-ESI MS results a mechanism is proposed for the formation of cyclic co-oligomers and the chain degradation of cooligomers containing carbonate linkages.

Keywords: Copolymerization; Macrocyclics; Ethylene carbonate; Propylene carbonate; ε-caprolactone; Chromatography/mass spectrometry

1. Introduction

Cyclic carbonates e.g. ethylene- and propylene carbonate undergo ring-opening polymerization (ROP) at elevated temperatures (>100 °C) in the presence of initiators such as Lewis acids, bases, or transesterification catalysts to yield poly(ether carbonates) [1–8] as outlined below.



In the presence of Lewis acids or transesterification catalysts, formation of polymers with $x = 0.4–0.5$ carbonate content was reported [1–6]. Initiation of anionic ROP of propylene carbonate with a Brønsted base such as potassium hydroxide yielded polymers with lower carbonate content ($x = 0.1–0.3$) [7,8].

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The ring opening oligomerization of ethylene- and propylene carbonate is of great industrial importance [9] as ethylene and propylene oxide, used for the production of epoxide-type resins, can be replaced by their corresponding, less harmful and "easy to handle" carbonates. On the other hand, ethylene- and propylene oxide oligomers of low molecular weight are basic components of industrial adhesives. Our previous reports [10,11] have shown that the oligomerization of PC initiated by the bisphenol-A/base and monofunctional phenol derivatives/base systems [12] resulted in the formation of both oligomers with all propylene oxide units and some oligomer series containing carbonate linkages as studied by means of matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) [13,14] and electrospray time-of-flight (ESI-TOF) [15] mass spectrometric methods.

Cooligomers with different hydrophilic/hydrophobic units (such as ethylene oxide-caprolactone, and ethylene oxide–propylene oxide) and/or different flexibilities (e.g. propylene oxide-caprolactone) may be valuable starting materials for the synthesis of resins with special properties. Therefore, our aim was to investigate the possibilities of the formation of such biner cooligomers under bulk conditions.

As an extension of our work, in this article, the liquid chromatographic/electrospray ionization mass spectrometric characterization of the cooligomers formed in the biner cooligomerization reaction of ethylene carbonate–propylene carbonate, ethylene carbonate-ε-caprolactone and propylene carbonate-ε-caprolactone initiated by the *p-tert*-butylphenol/$KHCO_3$ system is discussed.

2. Experimental

2.1. Chemicals

Ethylene carbonate (EC), propylene carbonate (PC), ε-caprolactone (CL), $KHCO_3$ and *p-tert*-butyl phenol (TBP) (analitical grade, Merck, Germany) were used without further purification. The eluent acetonitrile (HPLC grade, Multisolvent) was received from Scharlau. The HPLC grade water was prepared by a Millipore type water purifier instrument.

2.2. General procedure for the preparation of the cooligomers

A 50 ml three-necked flask equipped with a magnetic stirrer, thermometer, and nitrogen inlet/outlet in an oil bath was charged with the appropriate amount of *p-tert*-butylphenol, propylene carbonate, ethylene carbonate, ε-caprolactone and $KHCO_3$ under nitrogen atmosphere. The reaction mixtures were mixed at room temperature under N_2 atmosphere for 1 h and continuously heated to 160 °C in about 1 h, and it was kept at 140 °C for additional 23 h. The products were light yellow viscous liquids. The composition of the initial reaction mixture was 20/4/100/100 mmol *p-tert*-butylphenol, $KHCO_3$, comonomer 1 and comonomer 2, respectively.

2.3. Instrumentation

High performance liquid chromatography (HPLC)/electrospray ionization time-of-flight mass spectrometry (ESI-TOF MS). The separation of the cooligomers were performed using a Waters 2695 Separations Module equipped with a Waters 2996 Photodiode Array Detector on a C-18 reversed phase column (Waters XTerra® RP-18, 100 × 4.6, 3.5 μm) thermosted at 35 °C (Waters, Milford, MA). 30 μl of the analyte solutions (prepared in acetonitrile in a concentration of 1 mg/ml) were injected and the chromatographic separation were accomplished at a flow rate of 0.7 ml/min using gradient elution. The elutions were started with a 50% (v/v) solution of acetonitrile (ACN) and water, and the ACN content was gradually increased from 50% to 80% (v/v) in the time interval of 10–25 min.

The effluent was introduced into the ESI source of a BioTOF II instrument (Bruker Daltonics, Billerica, MA) by a high pressure splitter valve (P-470 UpChurch Scientific) (split ratio was 1:40). The temperature of the drying gas (N_2) was kept at 200 °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. Both the HPLC and the ESI MS instruments were controlled by the HyStar 2.3 software from Bruker. The UV and MS signals recorded were processed by the DataAnalysis 3.2 software (Bruker Daltonik GmbH, Germany).

3. Results and discussion

The bulk anionic, ring-opening and elimination cooligomerization reaction of the biner comonomer mixtures of ethylene carbonate–propylene carbonate, ethylene carbonate-ε-caprolactone and propylene carbonate-ε-caprolactone was initiated with the *p-tert*-butylphenol/$KHCO_3$ system. The cooligomerization started above 110 °C when intense evolution of CO_2 was observed indicating decarboxylation of the carbonates. The representative ESI MS spectrum obtained with the cooligomerization reaction mixture of propylene carbonate and ε-caprolactone is shown in Fig. 1.

As seen in Fig. 1 three different cooligomer series appeared in the ESI MS spectrum. Two of these series originated from the cooligomers containing *tert*-butylphenol (TBP) and hydroxyl (HO) headgroups, the third series

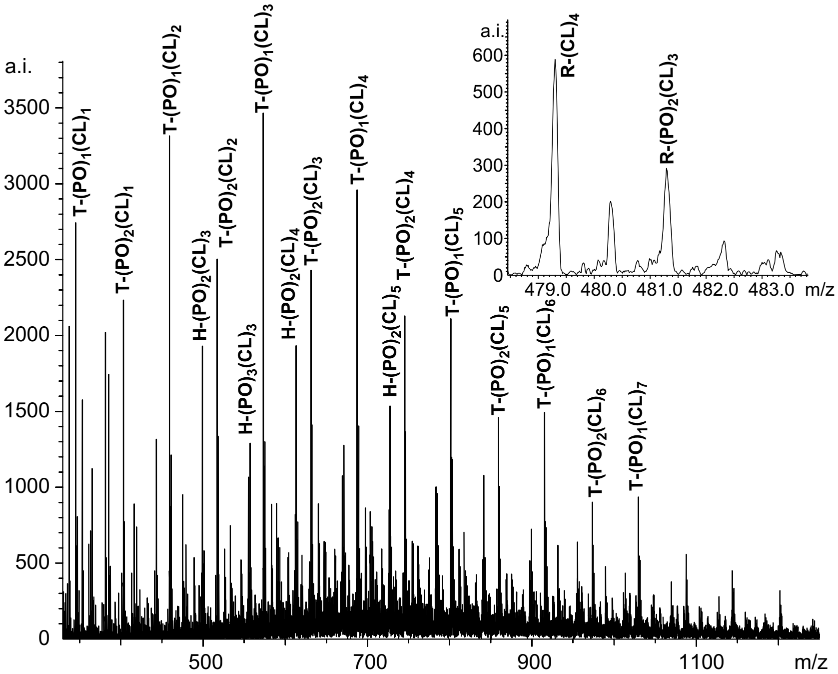


Fig. 1. ESI-TOF MS spectrum of the cooligomerization mixture of propylene carbonate-ε-caprolactone initiated by the *tert*-butylphenol/$KHCO_3$ system (oligomers are cationized with sodium ions). PO and CL stand for the repeat unit propylene oxide and ε-caprolactone, respectively. T and H denote the cooligomers with *tert*-butylphenol and hydroxyl headgroups, respectively. R stands for the ring (cyclic) cooligomers. Subscript numbers represent the number of repeat units.

came from cyclic cooligomers. The assignations of the cooligomers were made according to Eq. (1).

$$M_{\text{cooligomer}} = M_{\text{endgroups}} + M_{\text{cation}} + \sum M_i \cdot n_i \tag{1}$$

where $M_{\text{cooligomer}}$ is the mass of an individual cooligomer, appeared in the ESI MS spectra (for the singly charged one), $M_{\text{endgroups}}$ and M_{cation} are the mass of the endgroups and the cation attached to the cooligomer chain, respectively. M_i and n_i stand for the mass and the number of the ith repeating unit in the cooligomer, respectively.

In this case, Eq. (1) for the mass of the cooligomers with *tert*-butylphenol (M_T) and hydroxyl headgroups (M_H) and cyclics (M_R) reads as:

$$M_T = 150 + 23 + 58n_{PO} + 114n_{CL} \tag{2}$$

$$M_H = 18 + 23 + 58n_{PO} + 114n_{CL} \tag{3}$$

$$M_R = 0 + 23 + 58n_{PO} + 114n_{CL} \tag{4}$$

where 58, 114 and 23 are the mass of propylene oxide, the caprolactone units and sodium ion, respectively and n_{PO} and n_{CL} are the number of the PO and CL units, respectively.

Linear cooligomers with carbonate linkages, i.e., mass series differing 44 mass units from those mentioned above were found, however, their intensity was very low compared to the main cooligomer series. Interestingly, cyclic cooligomers containing carbonate units were not found. The mass of the cooligomers composed of n_{PO} and n_{CL} units differs only by 2 mass units from those of the cooligomers carrying $n_{PO} + 2$ and $n_{CL} - 1$ repeat units (having the same headgroup). For instance, in Fig. 1 inset cyclic oligomers with 4 CL units (R-$(CL)_4$) appear at a nominal mass 479, while cyclic cooligomers having 2 EO and 3 CL units (R-$(PO)_2(CL)_3$) are assigned at nominal mass 481. However, the peak $M + 2$ of R-$(CL)_4$ (i.e. appearing at m/z 481) coincides with the monoisotopic peak of R-$(PO)_2(CL)_3$. The relative intensity of the $M + 2$ peak of R-$(CL)_4$ to its monoisotopic peak is 5% as calculated from the isotopic distribution for the composition $C_{20}H_{40}O_8Na$ (sodiated adduct ion of R-$(CL)_4$). As seen in Fig. 1 inset the peak intensity at m/z 481 is much larger than that expected from the isotopic contribution of the $M + 2$ peak of R-$(CL)_4$ indicating the presence of R-$(PO)_2(CL)_3$. On the other hand, separation of the reaction mixture by liquid chromatography and coupling it on-line with ESI, the identification of these cooligomers becomes more unambiguous. Indeed, separation of cooligomers were successfully achieved: ion chromatograms extracted at masses 479 and 481 yielded well-resolved peaks for R-$(CL)_4$ and R-$(PO)_2(CL)_3$ appearing with 11.6 and 9.8 min retention times, respectively.

The cooligomerization of ethylene carbonate with ε-caprolactone in the presence of *tert*-butylphenol/KHCO$_3$ was also achieved. Applying Eq. (1) for the ESI MS spectra obtained for the cooligomerization reaction mixture (not shown) and considering similar cooligomeric series as those formed in the case of the PC-CL system one can establish the following mass series:

$$M_T = 150 + 23 + 44n_{EO} + 114n_{CL} \tag{5}$$

$$M_H = 18 + 23 + 44n_{EO} + 114n_{CL} \tag{6}$$

$$M_R = 0 + 23 + 44n_{EO} + 114n_{CL} \tag{7}$$

where 44, 114 and 23 are the mass of ethylene oxide, the caproctone units and sodium ion, respectively, n_{EO} and n_{CL} are the number of EO and CL units, respectively, for the co-oligomers with *tert*-butylphenol (M_T) and hydroxyl headgroups (M_H), and for the cyclics (M_R). Cooligomeric series obeying Eqs. (5)–(7) were found in the ESI MS spectrum. Moreover, it is also evident that co-oligomers with n_{EO} and n_{CL} units carrying *tert*-butylphenol headgroup and those with n_{EO} + 3 and n_{CL} units bearing hydroxyl headgroup occur at the same nominal mass (the exact mass difference is 0.01526 Da, which exceeds the resolution of our instrument). In addition, the nominal masses of the cooligomers with hydroxyl headgroup and with n_{EO} and n_{CL} units also overlap with those of the cyclics containing $n_{EO} + 3$ and $n_{CL} - 1$ units. It is clear that due to several coinciding masses of different cooligomeric series, a single ESI MS spectrum does not give unambiguous evidences for the presence of some cooligomers. Therefore, we used the LC-ESI MS method to separate and analyze the co-oligomers formed. The ion chromatograms extracted at masses 261, 305, 375 and 489 Da are plotted in Fig. 2.

As shown in Fig. 2, each extracted ion chromatogram reveals two distinct peaks at smaller and larger retention times. At small retention times, i.e., at around 2.5 min cooligomers with hydroxyl headgroups, and at larger retention times cooligomers with *tert*-butylphenol headgroups appeared. The assignation of the two series of the same mass was carried out on the basis of an UV-Chromatogram recorded parallel with the MS detection. No UV-absorption in the time interval of 0–4 min was observed indicating the absence of a chromophore moiety, (i.e. hydroxyl headgroup), while at larger retention time significant UV-absorption was monitored (i.e. *tert*-butylphenol headgroup). In Fig. 2c–d one can also realize that multiple chromatographic peaks appeared at larger retention time, i.e., peaks originated from the co-oligomer with TBP headgroups. This is most probably due to the sequence distribution of the EO and CL units within the chain. It should be kept in mind, however, that the nominal mass of CO$_2$ and the EO unit is equal (the exact mass difference is 0.03638 Da), thus 2 EO and one EC unit cannot be distinguished on the basis of their mass. Therefore, one may suppose that the additional peaks shown in Fig. 2c–d come from the cooligomers T-(EC)(CL) and T-(EC)(CL)$_2$. However, we also observed multiple elution peaks, for the cooligomers with TBP headgroups in the case of the PC–CL system, (where no mass interference exists) indicating a sequence distribution of the PO and CL units. On the other hand, investigating the extracted ion chromatograms of the homooligomers of EO (where the effect of sequence distribution is absent) we observed two single elution peaks up to n_{EO} = 4 (one originating from the cooligomers containing HO headgroup, the other comes from the cooligomers with TBP headgroup) and at n_{EO} = 5 additional peaks appeared close to the TBP series.

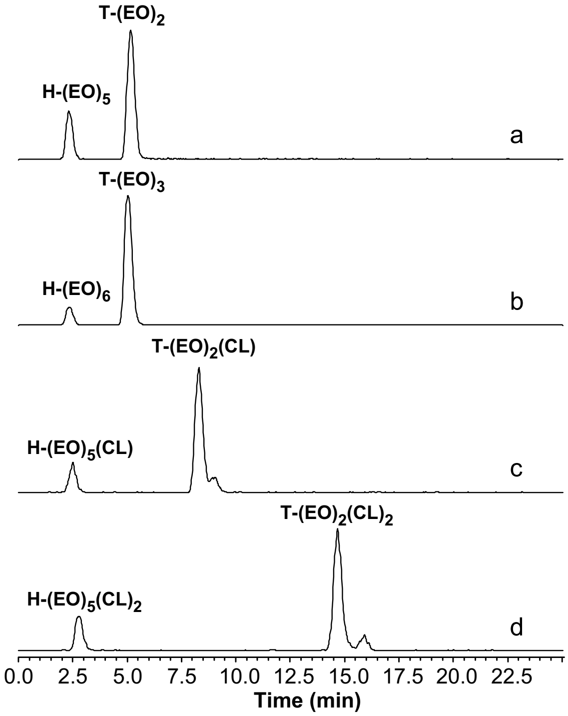


Fig. 2. Extracted ion chromatogram (EIC) of the cooligomerization reaction mixture of ethylene carbonate-ε-caprolactone initiated by the *tert*-butylphenol/KHCO$_3$ system extracted at masses 261 Da (a), 305 Da (b), 375 Da (c) and 489 Da (d) (oligomers are cationized with sodium ions).

This additional peak was attributed to the presence of T-(EO)$_n$(EC) oligomers carrying carbonate linkages. We also observed that the intensity of the additional peak increased with n_{EO} relative to those of the T-(EO)$_n$ series, and H-(EO)$_n$ was not found with n_{EO} larger than 9. This finding may indicate that incorporation of carbonate linkages occurs at larger n_{EO}, therefore, additional elution peaks in Fig. 2c–d originate from sequence distribution of the EO and CL units rather than due to the presence of a EC unit.

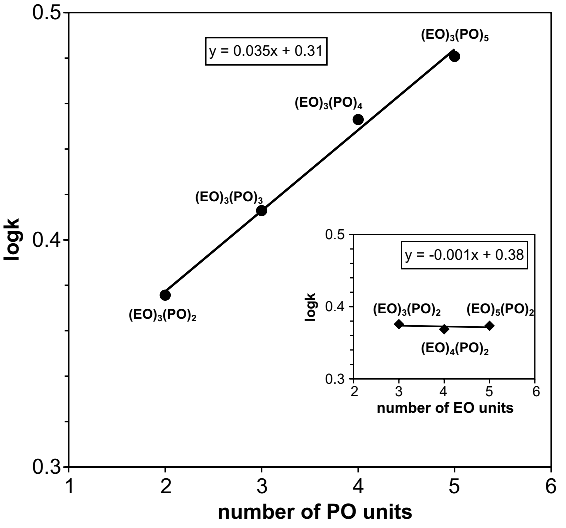


Fig. 3. log$k$ versus number of propylene oxide units plot for the cyclic cooligomers formed in the cooligomerization reaction of ethylene carbonate–propylene carbonate initiated by the *tert*-butylphenol/$KHCO_3$ system. The inset shows the dependence of log$k$ as a function of the number of ethylene oxide units. The retention factor k is defined as $(V_R - V_o)/V_o$, where V_R and V_o are the retention and column hold-up volume, respectively (C-18 reversed phase column).

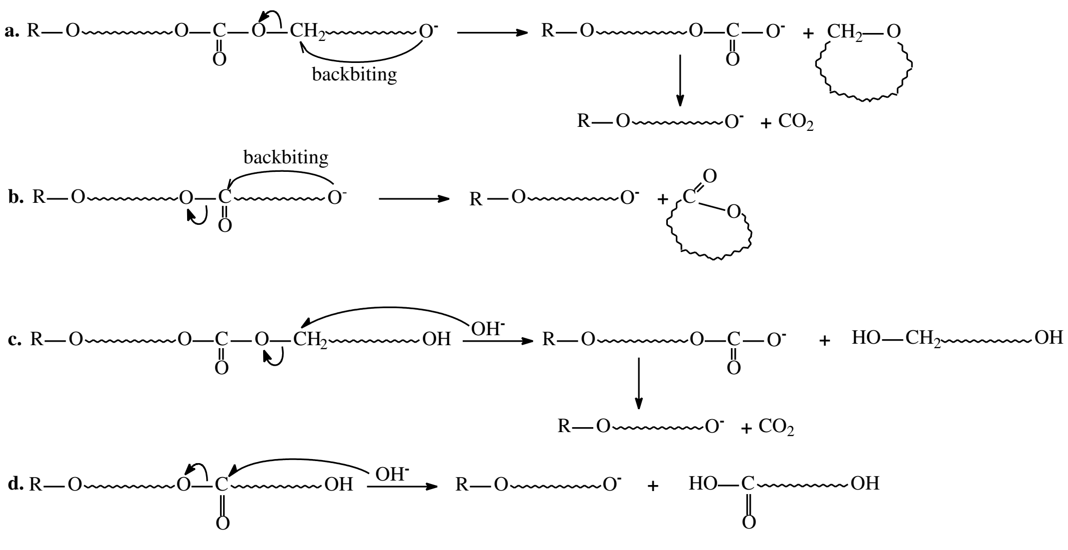
Ethylene carbonate was cooligomerized with propylene carbonate under the same experimental conditions as the previous systems. The ESI MS spectrum and LC-ESI MS data for this cooligomerization mixture (not shown) indicated the presence of three major series, i.e. cooligomers with TBP and OH headgroups, as well as cyclics. The cooligomeric series were identified similarly to the previous systems using Eq. (1). The chromatographic behavior of cyclics consisting of EO and PO units was also investigated using the extracted ion chromatograms. It has been shown for linear EO–PO block copolymers [16] that the retention factor k changes with number of the EO and PO units according to Eq. (8).

$$\log k = \log\beta + n_{EO}\log\alpha_{EO} + n_{PO}\log\alpha_{PO} \qquad (8)$$

where α_{EO} and α_{PO} are the separation selectivities of EO and PO, respectively, and $\log\beta$ expresses the partition of the endgroups to the total retention. In Fig. 3. The log$k$ values are plotted as a function of n_{PO}, while the inset shows the log$k$ versus n_{EO} plot.

As turns out from Fig. 3, log$k$ changes linearly with n_{PO}, while no dependence of log$k$ on n_{EO} was found in the case of cyclic cooligomers. This finding indicates that Eq. (8) is valid for cyclic cooligomers, too. In the light of our results, the proposed mechanism for the formation of linear and cyclic cooligomers is depicted in Scheme 1.

According to Scheme 1, nucleophilic attack of the alkoxide chain-end on the alkylene carbon by backbiting can occur to yield cyclic cooligomers and cooligomers with alkoxide termini after decarboxylation (reaction **a**). Similar attack on the carbonyl carbon of the carbonate group would yield cooligomers containing carbonate linkages. However, we practically did not observe the formation of these cyclic cooligomers, therefore, this route may not operate under the employed experimental conditions. Moreover, nucleophilic attack on the carbonyl carbon of the ester group may readily take place affording cyclics and alkoxide-terminated cooligomers (reaction **b**). Formation of linear cooligomers with



Scheme 1. Proposed mechanism for the formation of linear and cyclic cooligomers.

TBP and hydroxyl headgroups takes place by chain-degradation at the carbonate linkages (reaction **c**) and at the ester group (reaction **d**) initiated by hydroxyl ions (formed from $KHCO_3$).

Acknowledgement

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