RING-OPENING AND ELIMINATION POLYMERIZATION OF PROPYLENE CARBONATE

Thesis of PhD

Author:

János Török

Supervisor:

Dr. Miklós Zsuga

Professor and Head

University of Debrecen,

Department of Applied Chemistry

Debrecen, 2005.

I. 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)

The oligomerization of ethylene (EC) and propylene carbonates (PC) in the presence of bisphenol-A (BPA) yielding oligo(ethers) is of great industrial importance. Since ethylene and propylene oxides can be replaced with their carbonates, a more convenient synthesis of the corresponding oligo(ethers) can be obtained. However, our previous SEC studies on the oligomerization of PC showed that dimeric and trimeric products of the oligomers also formed using the BPA/base system. This inspired us to scrutinize the di- and trimerization and investigate the mechanism of the oligomerization.

As an extension of our work, we intended to investigate the reaction mechanism of the oligomerization of PC in the presence of monofunctional phenol derivatives, such as *p-tert*-butylphenol, phenol, *p-Cl*-phenol, *p*-cresol and synthetise heterotelechelic oligomers.

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 specific properties. Our aim was to investigate the possibilities of the formation of random biner cooligomers (such as PO-EO, PO-CL and EO-CL) under bulk conditions.

II. Applied polimerization and instrumental methods

Preparation of telechelic oligomers

The telechelic oligomers were prepared under bulk conditions. The calculated amount of initiator, catalyst ($KHCO_3$) and monomer (propylene carbonate) were weighed into a resin kettle. The applied bifunctional initiator was bisphenol-A, and the monofunctionals were phenol derivatives, such as phenol, p-tert-butylphenol, p-cresol, p-Cl-phenol. In the copolymerization reaction p-tert-butyl phenol was the initiator and propylene carbonate, ethylene carbonate and ε-caprolactone were the comonomers. The components were mixed under slow N_2 stream at ambient temperature and heated up to 160 °C in about 1 hour and they were kept at 160 °C for additional 23 hours. The reactions were quenched by cooling the system.

Characterization of telechelic oligomers

To determine the molecular weights and molecular weight distributions of the oligomer formed, size-exclusion chromatography (Waters W600 pump, W490 UV and W410 RI detectors) and mass spectrometric (Bruker BiFlexIII MALDI-TOF and Bruker BioTOF II ESI-TOF) measurements were taken. The identification of the end-groups based on the mass spectrometric results. The copolymers were studied by HPLC/MS (Waters W2695 Separations Module, W2996 DAD detector and Bruker BioTOF II ESI-TOF).

For additional structural information ^{1}H and ^{13}C NMR (Bruker AM 360) and PSD MALDI-TOF MS/MS spectra (Bruker BiFlexIII MALDI-TOF) were collected.

III. New scientific results

1. Preparation and study of homotelechelic oligomers

The decarboxilation 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. These series were later completely identified.

The first series of peaks corresponds to the oligomers containing propylene oxide units with the BPA moiety. The second series corresponds to the oligomers containing BPA and propylene oxide units in which only one propylene carbonate unit is incorporated. The third series is assigned as the peaks of the oligomers formed in the reaction from the oligomers of the first series with oligomers of the second *via* condensation by loss of H_2O. The fourth series originates from the product of condensation of two oligomers of the second series. The last series is derived from the product of the reaction of oligomers of the first series with two members of the second series *via* condensation with loss of two H_2O.

The first observation indicates that the frequency of formation of carbonate linkages in the oligomers is very low at 160 °C. The second finding reveals that the oligomer should contain carbonate groups at the chain-end for dimerisation and trimerisation to take place. These findings also indicate that the alkoxide anion chain-end is not able to activate the dimerization and/or trimerization.

The results of the MS studies agreed well with those obtained by ^{1}H, ^{13}C NMR and Size Exclusion Chromatography (SEC). Based on our investigation, the following mechanism for the oligomerization is proposed:

There are two possible routes for the alkoxide anion to react with PC. 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 accompained 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, since the carbonate anion is a much weaker nucleophile than the alkoxide anion, it can not open the ring of PC, and would rather react with the alcohol group.

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

The PSD MALDI-TOF MS/MS measurement can obtain structural information on the oligomers in question.

We observed an intensive fragmentation of a 160 Da unit which we attributed to the loss of the propylene carbonate+propylene oxide units. In order to support the presence of carbonate linkages in oligomer series, the product of the oligomerization reaction was hydrolized under alkaline conditions. The hydrolized oligomers do not carry carbonate groups, all of the resulting oligomers belong to the first series i.e., they consist of propylene oxide units and BPA. These results indicate that both of the mechanism operate under the applied experimental conditions.

2. Preparation and study of heterotelechelic oligomers

The ring-opening oligomerization reaction of propylene carbonate in the presence of different monofuctional phenol derivatives/$KHCO_3$ 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 first series corresponds to

the oligomers containing the initiator moiety with all propylene oxide chains. The second series comes from the oligomers containing the initiator moiety, the propylene oxide repeating units, and one of the propylene carbonate units. The position of the carbonate linkage in this series may be in the chain or at the chain-end. The position of this linkage cannot be judged from simple MS measurements. The third series is assigned as propylene glycol oligomers bearing hydroxyl termini. The last two series can be derived from the first two series *via* condensation reaction.

The structures of the oligomers carrying carbonate linkages were determined by the post-source decay (PSD) MALDI-TOF MS/MS method and the results imply that carbonate linkages in the second series are not located at the chain-end. To support chemically the presence of the carbonate linkages the reaction mixtures were treated with an ethanolic solution of KOH. Indeed, the MALDI-TOF MS and ESI-TOF MS spectra of the reaction mixtures obtained after hydrolysis showed only the first and third series appeared in the MS spectra.

Most of the oligomers were separated by liquid chromatography. The assignments of the peaks on the chromatogram was made by the off-line MALDI-TOF and ESI-TOF MS methods.

Based on the MS results, a mechanism for the oligomerization reaction is actually the same as proposed for the homotelechelic oligomers. The appearance of hydroxyltelechelic series in the MS spectra demonstrates that chain-cleavages at the carbonate links take place under our conditions.

3. Preparation and LC/MS study of biner copolymers

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 as cooligomers with *tert*-butylphenol and hydroxyl headgroups. The presence of cyclic cooligomers was also unambigouosly observed. In addition, cooligomers carrying carbonate linkages were also identified, however, their fraction was very small compared to those of the cooligomer series without carbonate linkages. Interesingly, cyclic cooligomers containing carbonate units were not found. 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.

In the case of copolymeryzation of ethylene carbonate and ε-caprolactone it is also evident that co-oligomers with n_{EO} and n_{CL} units carrying *tert*-butylphenol headgroups and those with $n_{EO}+3$ and n_{CL} units bearing hydroxyl headgroup occur at the same nominal mass. 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 cooligomers formed. Extracted ion chromatogram at the relevated masses reveals two distinct peaks at smaller and larger retention times. At small retention times 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. One can also realize that multiple chromatographic peaks appeared at larger retention time, i.e., peaks originated from the cooligomer with TBP headgroups. This is most probably due to the sequence distribution of the EO and CL units within the chain.

Ethylene carbonate was cooligomerized and the cooligomeric series were identified similarly to the previous systems. The chromatographic behavior of cyclics consisting of EO and PO units was also investigated using the extracted ion chromatograms. The capacity factor (logk) changes linearly with n_{PO}, while no dependence of logk on n_{EO} was found in the case of cyclic cooligomers. In the light of our results, the proposed mechanism for the formation of linear and cyclic cooligomers is the following:

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. 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.

IV. Scientific publications and lectures

1. Publications in the field of dissertation

1. S. Kéki, **J. Török**, Gy. Deák, M. Zsuga, „*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" Macromolecules*, **34**, 6850 (2001) I.F.: 3,73

2. S. Kéki, L. Sz. Szilágyi, J. Török, Gy. Deák, M. Zsuga, *„MALDI-TOF MS Characterization of Synthetic Polymers"*, Studia Universitatis "Vasile Goldis", Arad, Seria B, **3,** 11 (2001)

3. S. Kéki, J. Török, Gy. Deák, M. Zsuga, „*Mechanism of the Anionic Ring-Opening Oligomerization of Propylene Carbonate Initiated by the tert-Butylphenol/$KHCO_3$ System" Macromolecular Symposia*, **215,** 141 (2004) IF: 0,89

4. S. Kéki, J. Török, Gy. Deák, M. Zsuga, „*Ring-Opening and Elimination Cooligomerization of Cyclic Carbonates and ε-Caprolactone: Identification of the Reaction Products by Liquid Chromatographic/Electrospray Mass Spectrometric Methods" European Polymer Journal*,
közlésre elfogadva, IF: 1,09

5. Török János, Kéki Sándor, Deák György, Zsuga Miklós, *„Polimerek molekulatömeg meghatározása tömegspektrometriával" Műanyag és Gumi,* közlésre beküldve

6. Török János, Kéki Sándor, Deák György, Zsuga Miklós, *„Telekelikus polimerek előállítása gyűrűfelnyílásos polimerizációval" Műanyag és Gumi,* közlésre beküldve

2. Other publications

1. S. Kéki, L. Sz. Szilágyi, J. Török, Gy. Deák, M. Zsuga, *„High aggregation number silver clusters by matrix-assisted laser desorption/ionization: Role of matrixes on the gas-phase reduction of silver ions" J. Phys. Chem. B.* **107**, 4818 (2003), IF: 3,68

2. S. Kéki, J. Török, Gy. Deák, L. Daróczi, M. Zsuga, *„Silver Nanoparticles by PAMAM-Assisted Photochemical Reduction of* Ag^+*" Journal of Colloid and Interface Science,* **229,** 550 (2000) IF: 1,49

3. J. Török, K. Kovács-Hadady, E. Micsnovics, *„Distribution of cationic ion-pairing reagents on thin-layers after continuous overpressured layer chromatography" J. Chrom. A.,* **803** 235 **(**1998) IF: 2,32

3. Lectures in the fileld of dissertation

1. László Sz. Szilágyi, Sándor Kéki, János Török, György Deák, Miklós Zsuga: A MALDI-TOF MS alkalmazása a kémiai szerkezetfelderítésben, Nemzetközi Vegyészkonferencia, Arad, Románia (2001) (előadás)

2. S. Kéki, I. Bodnár, J. Borda, J. Török, Gy. Deák, M. Zsuga, *"MALDI MS Characterization of Polar Synthetic Polymers"*, IUPAC World Polymer Congress 2002: 39th International Symposium on Macromolecules, Beijing, China, July 7-12 2002. (előadás)

3. S. Kéki, I. Bodnár, J. Borda, J. Török, Gy. Deák, M. Zsuga, *„MALDI MS characterization of biologically degradable polymers"*, MoDeSt 2002. Second International Conference on Polymer Modification, Degradation and Stabilisation Budapest, Hungary, 30 June - 4 July 2002. (Keynote lecture)

4. Sándor Kéki, János Török, György Deák, Miklós Zsuga, *„Heterotechelic Polypropylene Oxide Oligomers by Anionic Ring Opening Polymerization of Propylelene Carbonate*", IUPAC International Symposium on Ionic Polymerization, Boston, MA, June 30-July 04. 2003. (előadás)

5. Török János, Kéki Sándor, Deák György, Zsuga Miklós, *"Propilén-karbonát gyűrűfelnyílásos polimerizációja fenolátokkal"*, Vegyészkonferencia Kolozsvár, Románia, 2000. november 17-19. (előadás)

6. Török János, Kéki Sándor, Deák György, Zsuga Miklós, *„Ring-opening oligomerization of propylene carbonate initiated by the Bisphenol-A/$KHCO_3$ sysytem: a matrix-assisted laser desorption/ionization mass spectroscopic study of the oligomers formed"*, Zilele Academice Aradene, Arad, 2001. május 18-20. (előadás)

7. Deák György, Kéki Sándor, Török János és Zsuga Miklós, *„Etilén- és propilén-oxid oligomerek szintézise és karakterizálása"*, VII. Vegyész-konferencia, Félixfürdő, 2001. november 16-18. (előadás)

8. Török János, Deák György, Kéki Sándor, Zsuga Miklós, *„Heterotelekelikus propilén-karbonát-oligomerek szintézise"*, VII. Vegyészkonferencia, Félixfürdő, 2001. november 16-18. (előadás)

9. Török János, Deák György, Kéki Sándor, Zsuga Miklós, *„A propilén-karbonát gyűrűfelnyílásos/eliminációs polimerizációja: fenol/bázis iniciátor-rendszerrel"*, Mechanoplast 2002, Gyula, 2002. március 12-14. (előadás)

10. Deák Gy., Török J., Kéki S., Zsuga M., *„Propilén-karbonát alapú heterotelekelikus polimerek szintézise"*, Aradi Akadémiai Napok, Arad, 2003. május 16-17. (előadás)

11. Török J., Deák Gy., Kéki S., Zsuga M. *„Propilén-oxid tartalmú kopolimerek előállítása és karakterizálása",* IX. Vegyészkonferencia, Kolozsvár, 2003. november 14-16. (előadás)

12. Kéki Sándor, Török János, Bodnár Ildikó, Borda Jenő, Deák György, Zsuga Miklós, *„Szintetikus polimerek vizsgálata MALDI-TOF MS módszerrel",* MTA Anyagtudományi és Technológiai Komplex Bizottságának Modern anyagtudomány: szerkezet, funkció, vizsgálati módszerek című ülése. Budapest, MTA, 2002. május 10. (előadás)

4. Other lectures

1. Szilágyi Sz. László, Kéki Sándor, Török János, Deák György, Zsuga Miklós, *„Ezüst-klaszterek előállítása MALDI körülmények között”* Nemzetközi Vegyészkonferencia, Arad, Románia (2003)(előadás)

2. J. Török, S. Kéki, Gy. Deák, L. Daróczi, M. Zsuga, *„Association of Starburst^{TM} (PAMAM) Dendrimer Generation 4 in the Presence of Metal Ions”*, 1st International Dendrimer Symposium, Frankfurt, Main (3-5 october 1999) (poszter)

3. S. Kéki, J. Török, G. Deák, L. Daróczi, M. Zsuga, *„Dendrimer Nanophotoreactor Synthesis and Characterization of Silver-Nanoclusters”*, 1st International Dendrimer Symposium, Frankfurt, Main (3-5 october 1999) (poszter)

4. Kéki, S.; Török, J.; Deák, Gy.; Daróczy, L.; Zsuga, M., *„Synthesis and characterization of silver-nanoclusters in the presence of Pamam dendrimers”*, International seminar on polymer materials in 21st century, New Delhi, India, 21-23 February 2000. (előadás)

5. J. Török, S. Kéki, Gy. Deák, L. Daróczi, M. Zsuga *„Photochemical Reduction of Ag^{+} in the Presence of Carboxyl and Amino Terminated PAMAM Dendrimers”*, World Polymer Congress, IUPAC Macro 2000, Warsaw, Poland, 9-14 July 2000 (poszter)

6. Török J., Kéki S., Deák Gy., Zsuga M. *„Fém-nanoklaszterek szintézise dendrimerekkel”*, Vegyészkonferencia ’99, Kolozsvár, 1999. november 26-28. (előadás)

7. Kéki Sándor, Török János, Szilágyi Sz. László, Deák György, Zsuga Miklós, *„Ezüstklaszterek kialakítása Gőzfázisban”*, VIII. Vegyészkonferencia, Kolozsvár, Románia (2002. november 15-17.) (előadás)

8. Török János, Kovácsné Hadady Katalin, *„Különböző módszerekkel előállított kationos felületaktív anyagra érzékeny membránok vizsgálata”,* Vegyészkonferencia, Eger, 1996

9. J. Török, K. Kovács-Hadady, *„Impregnation of Thin-Layers with Cationic Ion-Pairing Reagents by Using Personal OPLC Instrument”,* 9th International Symposium on Instrumental Planar Chromatography, Interlaken, Switzerland, 1997.