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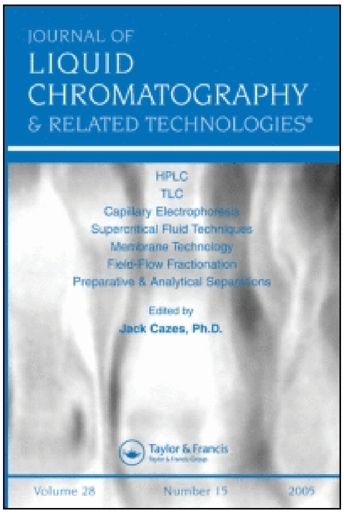

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Characterization of Macrocycles Formed from Cationic Copolymerization of Tetrahydrofuran with Propylene Oxide by GPC and GC/MS

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JOURNAL OF LIQUID CHROMATOGRAPHY, 5(8), 1423-1430 (1982)

CHARACTERIZATION OF MACROCYCLES FORMED FROM CATIONIC COPOLYMERIZATION OF TETRAHYDROFURAN WITH PROPYLENE OXIDE BY GPC AND GC/MS *

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ABSTRACT

The copolymers obtained from a THF/PO-$BF_3O(C_2H_5)_5$-glycerin-ethylene chloride cationic copolymerization system were analyzed by GPC. The chromatograms show two groups of peaks, one located in the high molecular weight (MW) region and the other in the low MW region. In order to examine the low MW region in detail, the oligomers were separated from the copolymer by distillation under high vacuum, and further identified by GC/MS, NMR. It was found that these were an expected series of cyclic oligomers, i.e., PO:THF crown ethers: 1:2, 3:1, 2:2, 1:3, 3:2, 2:3, 1:4, 4:2, 3:3, 2:4, 4:3. Through the study of the elution behavior of these crown ethers in toluene with GPC, a linear relationship of the elution time against the logarithm of their MW's was obtained. Under the same GPC conditions, the relationship between the elution time and MW of n-alkanes was also determined. It was found that the hydrodynamic volume of the crown ethers is less than that of the n-alkanes with same MW, and they can be treated as homologous series as in the case of n-alkanes on the study of GPC elution behavior ignoring the influence of PO:THF composition ratios in crown ether rings.

INTRODUCTION

Previous reports(1-4) have shown that in the cationic copolymerization of tetrahydrofuran(THF) and propylene oxide (PO) with boron fluoride-ethyl ether ($BF_3O(C_2H_5)_2$) as catalyst, low MW by-products formed simultaneously with the copolymer appeared clearly in the GPC chromatogram of the total polymerization product. From the total product, Hammond and co-workers (2) have isolated cyclic cotetramers, which are apparently mixtures of cyclic entities containing o,1, and 2 THF units, and inferred the existence of pentamer and hexamer by

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GPC. Similar results were obtained by us (3). Recently, Li Pengfei and coworkers (4) identified some oligomers from the total product by GC/MS, indicating that they are composed of cyclic cotetramers, i.e., PO:THF crown ethers: 3:1, 2:2, 1:3.

To further clarify the oligomer contents in the total product and to examine GPC elution behavior of these oligomers in detail, it seems interesting to identify the oligomer species which were isolated by high vacuum distillation. This paper describes the characterization of these oligomers by GC/MS, NMR, and their elution behavior of GPC.

EXPERIMENTAL

Materials

The cationic copolymerization of THF and PO was carried out as previously described (3,4). $BF_3O(C_2H_5)_2$, glycerin (GLYC) and ethylene chloride (EC) were used as catalyst—co-catalyst—solvent system. Molar ratios of PO:THF:$BF_3O(C_2H_5)_2$: GLYC:EC are 1:2:0.03:0.03:6. Total conversion to polymer was about 75% after 3 hours at 0°C. The number average molecular weight, $\bar{M}n$ of total product determined by vapor-pressure osmometry is 920(3,4). $\bar{M}n$ of linear copolymer calculated by GPC is 1900. The THF:PO mole composition ratio of total product is 1.33:1. The content of the oligomers was about 25% of total product.

The total product was distilled and redistilled under high vacuum. The oligomer fractions collected were identified by GC, MS, NMR.

Apparatus

GC chromatograms of various fractions were obtained on a Model SP-501 gas chromatography with flame ionization detector. (South-Santong Chemical Instru. Co. China) A column packed with 5% OV-101 on Chromsorb W AW-DMCS (60-80 mesh) with 200 cm in length was used. Column temperature was maintained at 200, 230, or 270°C for different fractions, respectively. For total polymerization product, a temperature program, 150-280°C (10°C/min), was used.

Chemical ionization mass spectra were obtained with a Finnigan 4021 model gas chromatograph-mass spectroscopy system with methane as the reagent gas.

For GPC study, the chromatograms were carried out on Waters Model 244 Liquid Chromatograph with a differential refractometer and a Model 730 Data Module. Waters μ-STYRAGEL-100Å Column (30 cm x 7.8 mm I.D.) was used. The instrument was operated at ambient temperature and a flow rate of 1 ml/min with toluene as solvent.

^1H NMR spectra were determined in carbon tetrachloride solution and tetramethylsilane (TMS) as internal reference on a Varian EM-360L-60MHz NMR spectrometer.

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RESULTS AND DISCUSSION

The total polymerization product and seven oligomer fractions obtained from high vacuum distillation were analyzed by GC as shown in Figure 1,2 and Table 1, respectively. They indicate that total product contains more than eleven components and that each oligomer fraction is composed of a major component and several minor components, except Fraction G.

The ^1H NMR spectra of seven fractions all show the same result as follows: doublet δ 1.06, $C\text{-}CH_3$; δ 1.60, $C\text{-}CH_2$; multiplet δ 3.38, O-CH and $O\text{-}CH_2$ protons. To compare with the results of NMR obtained for homopolymer of PO and THF (1-3), It seems that these seven fractions all comsist of THF and PO units.

In order to confirm the nonhydroxylic structure for these oligomers, the total product was separated into non-, mono-, di-, and tri-hydroxyl-functional fractions by liquid-solid silica gel column chromatography (5). The GC chromatogram of the nonfunctional fraction was found to coincide with

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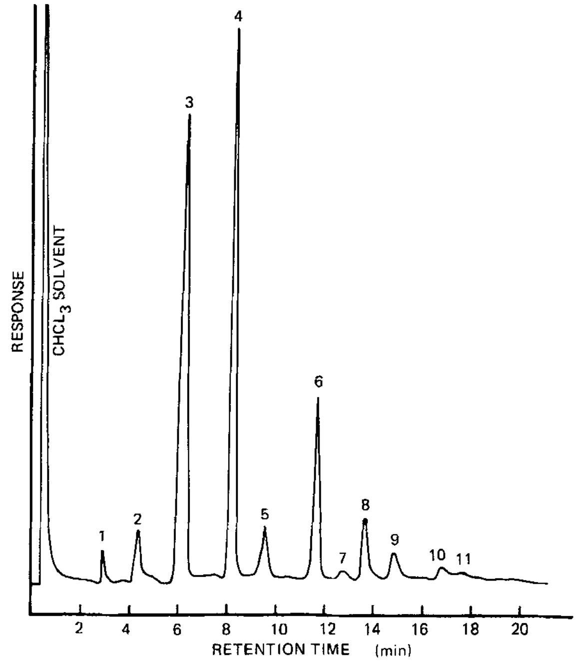

Figure 1. GC Chromatogram of Total Polymerization Product. Oligomer components were expressed with peak numbers.

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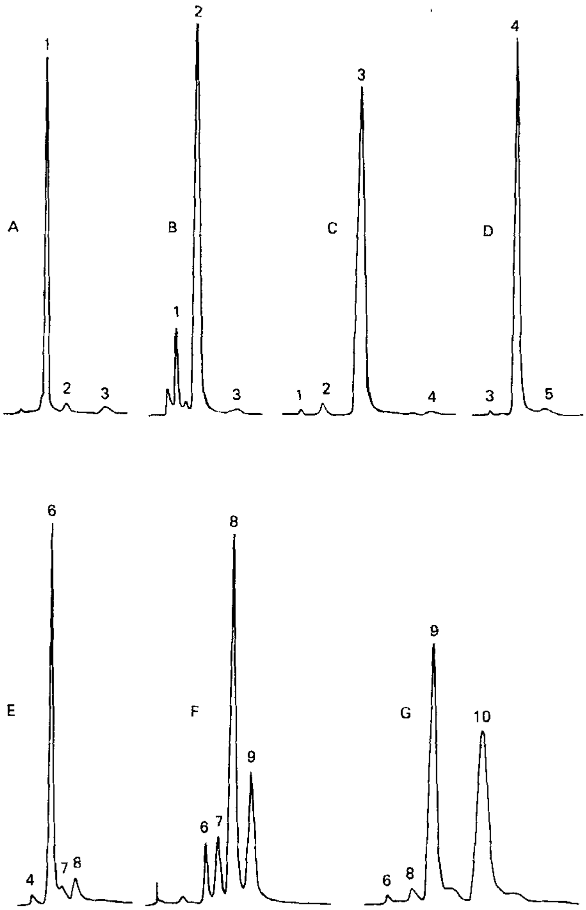

Figure 2. GC Chromatograms of Seven Oligomer Fractions A to G. The bp of seven fractions were listed in Table 1.

Figure 1, while GPC chromatograms of nono-, di-, and trifunctional fractions show absence of the low MW component as expected. The number average functionality (6) measured on the nonfunctional fraction is 0.037-0.91. Hence, the cyclic structure was assumed for all oligomer fractions.

Moreover, the oligomers evaporated from total product were identified by chemical ionization mass spectroscopy. It was observed that these oligomers are an expected series of cyclic oligomers, i.e., PO:THF crown ethers. Their

TABLE 1

The Major Component of the Oligomer Fractions in GC

Sample	bp °C/mm	Major Component*
Fraction A	48/0.01	1
B	58/0.01	2
C	68/0.007	3
D	80/0.01	4
E	117/0.01	6
F	125/0.0003	8
G	143/0.0003	9,10

*The major component of each fraction was expressed with the peak number shown in Figure 2.

MW and corresponding ring structure are correlated in Table 2, which shows that, at the comonomer ratios studied, only mixed PO:THF crown ether will exist and that the largest ring indentified is the PO:THF crown ether 4:3, i.e., cyclic coheptamer. Relatively larger rings may also be present, as shown by GC peaks at longer retention times, but these were not unambiguously assigned yet.

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TABLE 2

Crown Ethers Identified by Chemical Ionization Mass Spectroscopy in Total Product

Peak Number(a)	Mol. Wt. (m/e-1)	Crown Ethers Composition (PO:THF)
1	202	1:2
2	246	3:1
3	260	2:2
4	274	1:3
5	318	3:2
6	332	2:3
7	376	4:2
8	346	1:4
9	390	3:3
10	404	2:4
11	448	4:3

a. The oligomer components in total product were expressed with peak number in Figure 1.

b. The Robinson's mixed macrocycle crown ether nomenclature (7) is used in this paper.

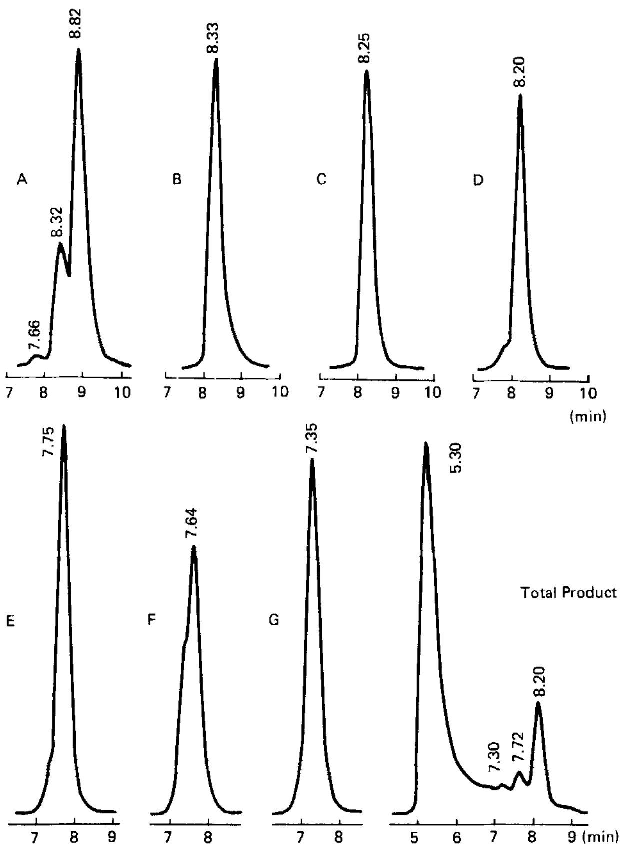

Figure 3. GPC Chromatograms of Seven Oligomer Fractions A to G, and Total Polymerization Product.

*The main peak represents high MW copolymer in the total product, 5.30 min. is exclusion limit time of this column.

Then, by using the seven oligomer fractions with known MW and composition, the elution behavior of the PO:THF crown ethers in GPC was studied.

Figure 3 shows the GPC chromatograms of seven fractions and total polymerization product. The μ-STYRAGEL-100Å column can provide efficient separation for these macrocycles (MW 200-400) in short time.

A linear relationship between the elution time of these macrocycles and logarithm of their MW was obtained (see Figure 4.). Under the same GPC con-

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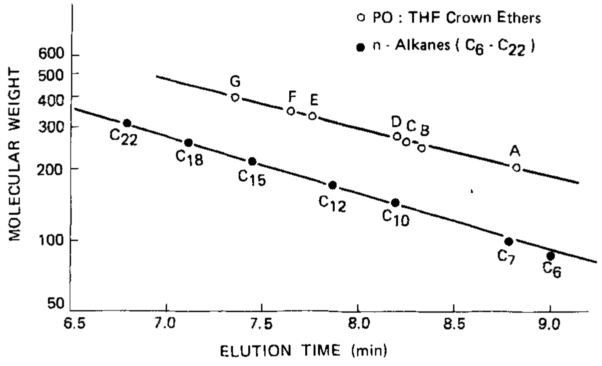

Figure 4. Correlation between GPC Elution Time and Molecular Weight of the PO:THF Crown Ethers and n-Alkanes.

ditions, correlation between the elution time and log MW for n-alkanes was also determined. (also see Figure 4.) The calibration curve in Figure 4 shows that the line for the macrocycles was located above that of n-alkanes, indicating that their hydrodynamic volumes were less than that of n-alkanes with the same MW's. The PO:THF crown ethers can be treated as homologous series as in the case of n-alkanes on the study of GPC elution behavior (8), mo matter what the composition ratios is.

The GPC chromatogram of total product in Figure 3 shows three small peaks corresponding to the cyclic cotetramer, cyclic copentamer and cohexamer mixtures, respectively, and clearly indicates that the cyclic cotetramer mixtures predominates, as is frequently observed in other cyclization systems (7). This agrees with that shown from GC determination of total product in Figure 1. In order to understand the factors affecting formation of cyclic oligomers under different polymerization conditions, the content of cyclic oligomers in total product can be estimated from the GPC chromatogram. For example, the content of oligomers is reduced from 10.4% to 1.0% when glycerin concentration is increased from 0 to 8.0% during the bulk copolymerization process (9).

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