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Analysis

Separation and Characterization of ε-Caprolactone Oligomers by Gel Permeation Chromatography

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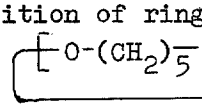
SUMMARY

It is shown that the combined use of gel permeation chromatography and the isocyanate method of determination of hydroxyl end groups extends the possibilities for studying complex oligomer mixtures of ε-caprolactone. Oligomer mixtures of ε-caprolactone obtained by $(C_6H_5)_3CSbCl_6$ and by $(C_6H_5)_3CK$ are investigated. At initiation by both the initiators the cationic and the anionic one - a covalent bond between the initiator and the polymer chain is formed. In the case of the initiation by $(C_6H_5)_3CK$ intramolecular transesterification proceeds which results in cyclic oligomers. At initiation by $(C_6H_5)_3CSbCl_6$ linear oligomers are formed. It is assumed that the ε-caprolactone polymerization by $(C_6H_5)_3CSbCl_6$ proceeds by alkyl-oxygen bond scission.

INTRODUCTION

Oligomers - cyclic (I) or linear (II) are often formed in the course of the ε-caprolactone polymerization. The initial group (In) of the linear oligomers depends on the initiator nature and the type of the end group depends on the position of ring scission (IIa and IIb).



(I)

$$In\text{-}[O\text{-}CO\text{-}(CH_2)_5]_n\text{-}OH \qquad \text{(IIa)}$$

$$In\text{-}[O\text{-}(CH_2)_5\text{-}CO]_n\text{-}OH \qquad \text{(IIb)}$$

The complex character of the oligomer mixtures strongly complicates the study of the mechanism of the ε-caprolactone polymerization. That is one of the reasons for the lack of a common concept on the initiation mechanism. A convenient method of studying the oligomer products is gel permeation chromatography (GPC) combined with chemical methods of end groups determination.

In the present work an attempt is made to show that by the combined use of the isocyanate method of determination of hydroxyl end groups (1,2,3) and GPC information may be received about the initiation mechanism, the type of the end groups and the type of some of the side reactions. Oligomer mixtures were investigated which were obtained by ε-caprolactone polymerization by a cationic initiator-$(C_6H_5)_3CSbCl_6$ and by an anionic one - $(C_6H_5)_3CK$.

EXPERIMENTAL

Purification of the solvents and the monomer

ε-Caprolactone monomer (Fluka AG) was twice dried over CaH_2 and distilled under vacuum. Dichloromethane was dried over CaH_2 and sodium mirror, tetrahydrofuran was dried over K/Na alloy under vacuum.

Synthesis of the initiators

$(C_6H_5)_3CSbCl_6$ and $(C_6H_5)_3CK$ were synthesized as already described (4,5).

Polymerization procedure

ε-Caprolactone polymerization was carried out under vacuum. The reaction was terminated by adding of moist solvent (at the cationic polymerization) or of HCl (in the case of the anionic polymerization). The polymerization mixtures obtained by anionic polymerization were fractionalized by precipitation in ethyl ether. The soluble in ether part which consists of oligomers with molecular mass below 2500 was investigated.

Treating of the polymerization products

The reaction mixtures obtained by cationic polymerization and the oligomers formed by anionic polymerization were reacted with phenylisocyanate or with 4,4'-diphenylmethanediisocyanate. A twofold excess of isocyanate dissolved in toluene was added to a solution of the oligomer products in toluene. The reaction mixture was stirred at room temperature for 3 hrs.

GPC analyses

A "Waters 150C" apparatus equipped with 5 columns ultra-Styragel (100, 500, 500, 1000 and 10000 Å pore size), two detectors - differential refractometer and an UV (254 nm) detector was used. The analyses conditions were: 35°C, tetrahydrofuran as an eluent, flow rate 1 ml/min.

Synthesis of standard oligomer mixtures

Cyclic and linear oligomers of ε-caprolactone were used as standards. They were obtained under the action of graphite intercalation compounds of K and $SbCl_5$ as described elsewhere (6,7).

RESULTS AND DISCUSSION

1. Choose of standard mixtures and reagents

It is known that by the use of homogeneous anionic initiators cyclic oligomers are formed with the cyclic dimer prevailing (8). It was shown in our previous work (6) that at initiation of ε-caprolactone polymerization by KC_{24} under certain conditions 5-10% cyclic oligomers are formed with $\overline{DP}$ up to 10 and higher. Such oligomer mixture is sufficiently separated under the above described conditions of GPC analysis (Figure 1, curve 1). The linearity of the dependence of elution volume on lgM (Figure 2, curve 1, correlation coeff. 0.999) shows that the oligomers are members of one and the same polymerhomologous series. Since the linear polymerization products of ε-caprolactone contain end groups which react with isocyanates (-OH and -COOH) the linear and the cyclic products can be separated by reaction with isocyanate. There are no changes in the GPC chromatogram after treating of the oligomer

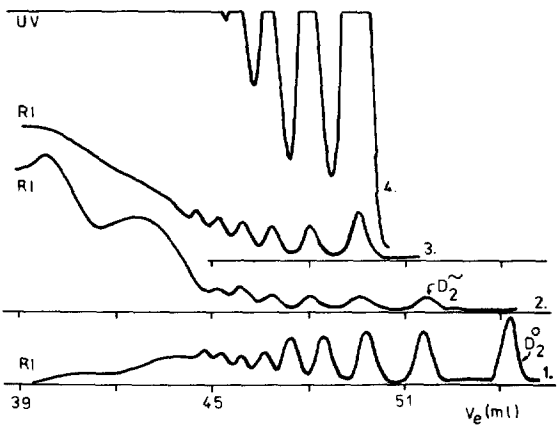


Figure 1. GPC traces of caprolactone oligomers:
Cyclic oligomers obtained by KC_{24} ($[M]_o$= 1 mol.l^{-1}, $[I]_o$=1.46 mol%, 20°C, 2 hrs, tetrahydrofuran (6)) - curve 1, D_2° - cyclic dimer;
Linear oligomers obtained by $C_{30}SbCl_5$,($[I]_o$= 1.47mol%, 20°C, 24 hrs, bulk (7))- curve 2, $D_2^{\sim}$ - linear dimer;
Linear oligomers treated with phenylisocyanate - refractometer trace - 3, UV trace - curve 4.

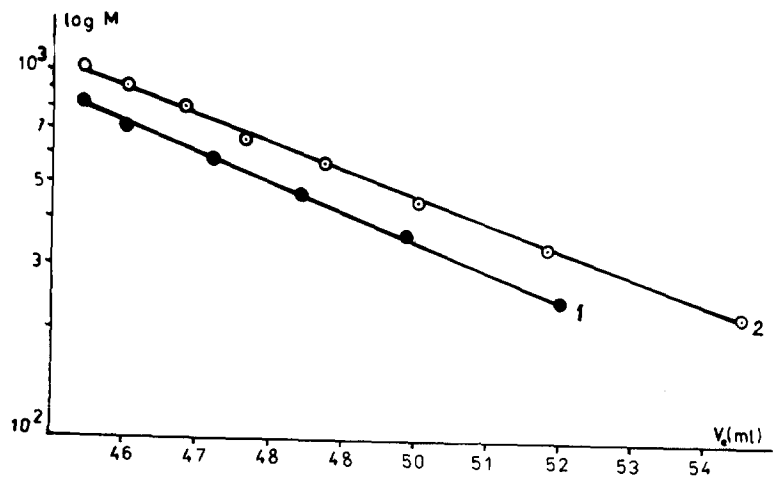


Figure 2. Dependence of the elution volume on lgM:
1 - cyclic oligomers, 2 - linear oligomers.

mixture obtained by KC_{24} with isocyanate. This shows the lack of "impurities" of linear products in the mixture. Therefore the oligomer mixture obtained by KC_{24} is a convenient standard for GPC of polyesters because of its purity as well as the presence of commensurable quantities of cyclic oligomers.

The oligomer mixture obtained by $C_{30}SbCl_5$ (7) was choosen as a standard of linear oligomers (Figure 1, curve 2). The dependence of elution volume on lgM is linear (Figure 2, curve 2, correlation coefficient 0.999). Bands at 3360 and 3460 cm^{-1} which may be assigned to -COOH and -OH groups are observed in the IR spectra of the oligomers. Furthermore, the retention times of these oligomers differ from the retention times of the cyclic oligomers. A linear structure of the oligomers obtained by $C_{30}SbCl_5$ was assumed on grounds of these facts. The linear structure was confirmed after an interaction with phenylisocyanate. A strong UV absorbance of each peak appears in the GPC chromatogram of the reaction mixture (Figure 1, curves 3a and 3b). The dependence of the retention time on lgM remaines linear but all points synchronously shift towards the higher molecular masses. This shows that the phenylisocyanate has added to each oligomer.

2. Determination of the composition of the polymerization products obtained by $(C_6H_5)_3CSbCl_6$

It was shown in our previous work (9) that the ε-caprolactone initiation by $(C_6H_5)_3CSbCl_6$ proceeds by addition of the triphenylmethylium cation. The GPC chromatogram in this case has a more complex character (Figure 3, curves 1a and 1b). The retention times of the oligomers differ from those of the cyclic standards as well as from those of the linear ones. A

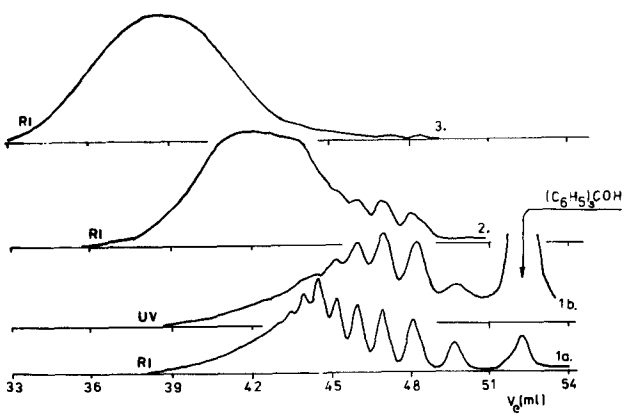


Figure 3. GPC traces of reaction mixture of caprolactone obtained by initiation by $(C_6H_5)_3CSbCl_6$ ($[M]_o$= 1 $mol.l^{-1}$, $[I]_o$= 1 mol%, 25°C, 2 hrs, solvent - toluene), refractometer trace - 1a, UV trace - 1b, after treatment with phenylisocyanate - curve 2, after treatment with 4,4'-diphenylmethanediisocyanate - curve 3.

strong UV absorbance is typical for each oligomer. That was ascribed to a covalently bound with the polymer chain triphenylmethyl group. The dependence of elution volume on lgM is linear (Figure 4, curve 1) with correlation coefficient 0.999. The isocyanate test was used in order to prove the type of the end groups. Changes occur in the oligomer mixture as a result of the treating with phenylisocyanate (Figure 3, curve 2). The peaks synchronous shift towards higher molecular masses. At that the linearity of the dependence of the elution volume on lgM remains unchanged (Figure 4, curve 2). The change in the GPC chromatogram is strongly expressed when the isocyanate test is performed by the use of 4,4-diphenylmethanediisocyanate (Figure 3, curve 3). The molecular mass of the product of addition of the initiator cation to one monomer molecule is 374. Oligomers with molecular mass about 1000 will be obtained at interaction between two moles of such a product and one mole diisocyanate (molecular mass 260). As seen from the chromatogram there are no products with molecular mass below 1000 in the reaction mixture treated by 4,4'-diphenylmethanediisocyanate. This confirms that in the reaction mixture of caprolactone and $(C_6H_5)_3CSbCl_6$ there are no cyclic oligomers with molecular mass below 1000. For the oligomers with a higher degree of polymerization a linear structure may also be assumed on grounds of their shift towards higher molecular masses. The data from IR and NMR spectroscopy give evidence of the presence of alcoholic hydroxyl groups (bands at 3440 cm^{-1} and signals at 4.35 ppm in DMSO-d_6 and 3.67 ppm in $CDCl_3$ correspondingly). Signals for carboxylic proton are not present.

These facts show that the oligomer mixture of ε-caprolactone obtained by $(C_6H_5)_3CSbCl_6$ is a polymerhomologous series with a general formula IIa. These findings provide grounds to assume that the ε-caprolactone polymerization

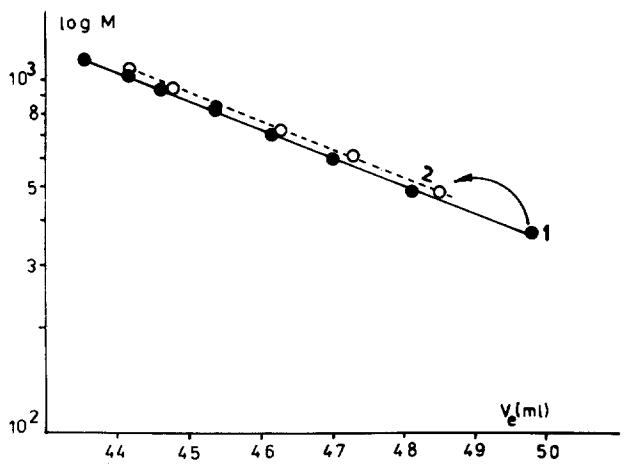


Figure 4. Dependence of the elution volume on lgM: caprolactone oligomers obtained by $(C_6H_5)_3CSbCl_6$ - curve 1, the same oligomers after treatment with phenylisocyanate -curve 2.

initiated by $(C_6H_5)_3CSbCl_6$ proceeds by alkyl-oxygen bond scission. This is in agreement with the recently reported by Penczek et al. (10) results on ε-caprolactone initiation by $(CH_3)_2Br^+SbF_6^-$.

3. Determination of the composition of the oligomer products obtained by initiation by $(C_6H_5)_3CK$

The GPC chromatogram of the oligomers formed at initiation by $(C_6H_5)_3CK$ is complex (Figure 5). The comparison of the retention times of these oligomers with the retention times of the standard cyclic and linear oligomers shows that they coincide only for some of the cyclic oligomers. Some of the oligomers unlike the standard oligomers possess UV absorbance. The retention times of the oligomers obtained by triphenylmethylpotassium differ from those of the oligomers obtained by triphenylmethylhexachloroantimonate as well. These facts provide grounds to assume that the oligomers formed at initiation by triphenylmethylpotassium are a mixture of cyclic and linear oligomers. In order to simplify the chromatogram the oligomer mixture was treated with 4,4'-diphenylmethanediisocyanate. At condensation of the linear products with the diisocyanate their molecular mass will grow up to 1000 or more and it will be possible to appreciate the presence of the unreactive towards isocyanates cyclic oligomers. In fact, the chromatogram of the treated oligomer mixture shows the presence of cyclic oligomers with $\overline{DP} \geq 3$. At that products with molecular mass below 1000 which absorb in the UV region are lacking. It may be accepted that the linear oligomers which show UV absorbance in the chromatogram of the oligomers before treating the mixture contain covalently bound triphenylmethyl group.

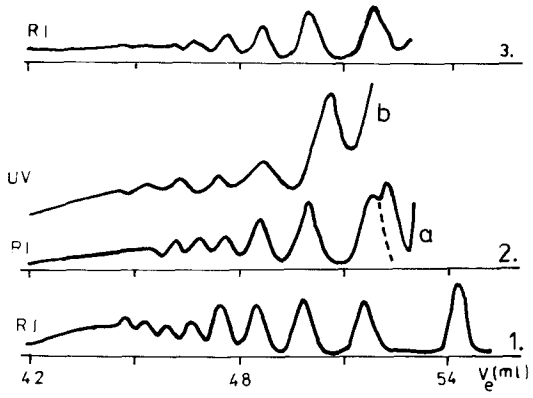


Figure 5. GPC traces of caprolactone oligomers obtained by $(C_6H_5)_3CK$: refractometer trace - curve 2a and UV trace - curve 2b; the oligomers after treatment with 4,4'-diphenylmethanediisocyanate - curve 3. The cyclic oligomers of caprolactone are shown for comparison - curve 1.

CONCLUSION

A polymerhomologous series of linear oligomers which contain initial $(C_6H_5)_3C-$ end groups and terminal $-CH_2OH$ groups is formed at initiation of ε-caprolactone polymerization by $(C_6H_5)_3CSbCl_6$. Probably the ring scission in this case proceeds at the alkyl-oxygen bond.

At initiation of caprolactone polymerization by $(C_6H_5)_3CK$ a covalent bond between the initiator and the monomer is also formed. In this case intramolecular transesterification proceeds to a considerable extent and besides the linear oligomers the reaction mixture contains cyclic oligomers as well. Regardless of the heterogeneous nature of the initiator $(C_6H_5)_3CK$ the polymerization products are mainly oligomers. The combined use of GPC and the isocyanate test extends the possibilities for investigation of complex oligomer mixtures of ε-caprolactone.

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