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Determination of functional type distribution of oligocaprolactonediols by liquid chromatography under critical conditions

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SUMMARY

Functional type separation of oligocaprolactonediols by liquid chromatography of macromolecules under critical conditions was investigated. The analysis was performed with the aid of a novel variant of HPLC in the critical region on the boundary of the exclusion and adsorption separation modes. This method is characterized by practically complete disappereance of separation by molecular masses thus giving only information on the type of functionality.

The critical conditions have been found on two systems. The first consists of a Lichrospher Si 100 column and a hexane-acetone mixture as eluent, while the second consists of a Zorbax NH2 column and a diethylether-acetone mixture.

INTRODUCTION

Reactive oligomers (telechelics) play an important role in the synthesis of various polymers (e.g. polyurethanes). Therefore well known characteristics like molecular mass, molecular mass distribution (MMD) and functionality are essential. Entelis et al. described a new and very useful characteristic: the Functional Type Distribution, FTD (1).

Recently a new method for chromatographic analysis of FTD has been proposed and substantiated experimentally: a Separation in the Critical Region (SCR). With this method the FTD of reactive oligomers like oligocarbonates (2) and butyleneterephthalate oligomers (3) was determined. In the present work the SCR method has been applied to determine the FTD of oligocaprolactonediols.

EXPERIMENTAL

Oligocaprolactonediols (OCLD) with the following structure were studied:

$$H-[-O-(CH_2)_5-C(O)-]_x-O-R-O-[-C(O)-(CH_2)_5-O-]_y-H$$

The values for x and y vary independently between 0 and 10. For determination of retention volumes of OCLD with different functionalities, partially acetylated OCLD samples were prepared.

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Acetylation was carried out by treatment of OCLD with acetic anhydride at 60°C for a period of 1 hour.

Lichrospher Si 100 (pore diameter 100Å) and Zorbax NH2 (pore diameter 80Å) were used as adsorbent and the binary mixtures acetone-hexane and diethylether-acetone respectively served as the mobile phase. The experiments were carried out on a modular HPLC system (Waters Ass.), consisting of a M6000A pump, a R401 refractive index detector and a U6K injection system.

RESULTS AND DISCUSSIONS

The chromatograms as shown in fig. 1 reflect the contents of bifunctional molecules in the sample OCLD 1000. The critical conditions in this case were realised on Lichrospher Si100 in hexane/acetone (50/50 by volume). However this separation system is not sufficiently suitable for OCLD because the critical point of adsorption is near solubility limits of the sample.

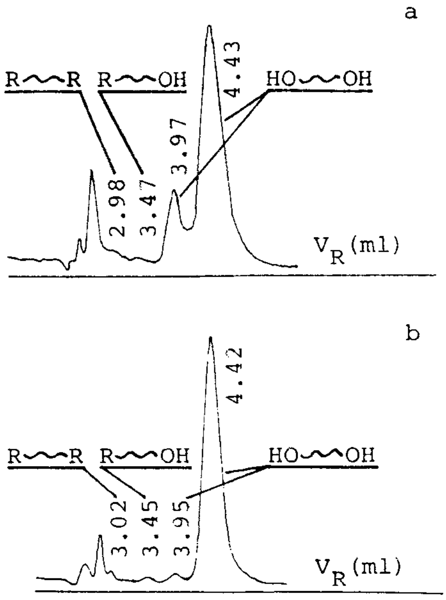

Fig. 1, FTD chromatograms of oligo(caprolactone)diol samples 3 (a) and 4 (b) from table 1 in critical conditions. Column: Lichrosphere Si100, hexane/acetone (50/50 vol) mixture, flow: 1 ml/min, RI detector.

It is very simple to find the critical conditions for any polymer. For this purpose it is necessary to select two solvents in one of which the exclusion mode is realised while in the other the adsorption mode is realised.

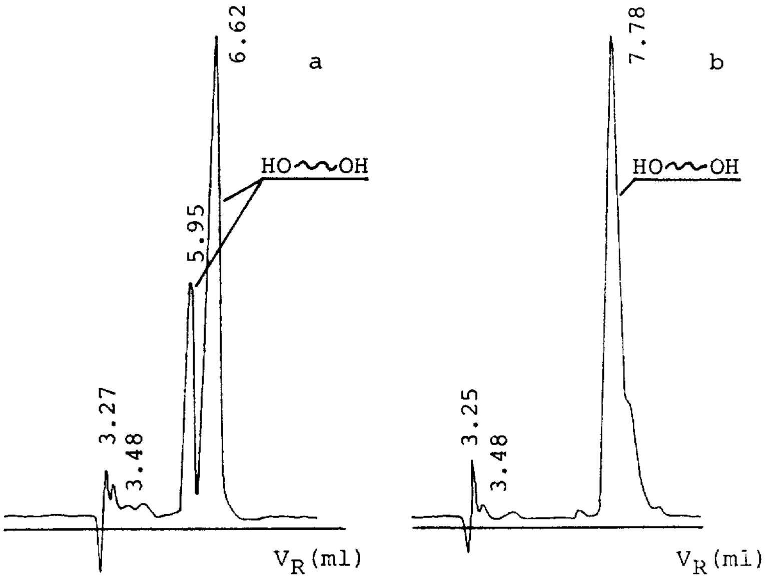

Fig. 2, FTD chromatograms of oligo(caprolactone)diol samples 3 (a) and 2 (b) from table 1 in optimized critical conditions.Column: Zorbax NH2, diethylether/acetone (78/22 vol) mixture, flow: 1 ml/min, RI detector.

For OCLD such solvents are acetone and diethylether respectively. By smoothly changing the acetone content in the mixture, it is possible to pass over from adsorption to exclusion through the critical conditions (3). In this way optimal conditions were obtained by taking diethylether - acetone (78/22 by volume) as a mobile phase and Zorbax NH2 as the stationairy phase. The typical chromatograms obtained by this system are shown in figure 2.

For the identification of the different functional type fractions the acetylated samples were studied under the same conditions (fig 3 a,b,c).

The quantity of different types of OH-functionality for the OCLD samples are summarized in table 1.

Table 1. FTD of OCLD samples

sample			functional type distribution (weight %)		
no.	type	Mn	HO-R-OH	HO-R	R
1	CAPA 200	590	98,9	<0,1	1,0
2	CAPA 215	1250	98,4	1,4	0,2
3	CAPA 212	1000	77,1 + 19,2	0,6	2,2
4	CAPA 225	2000	93,4 + 3,6	1,9	1,1

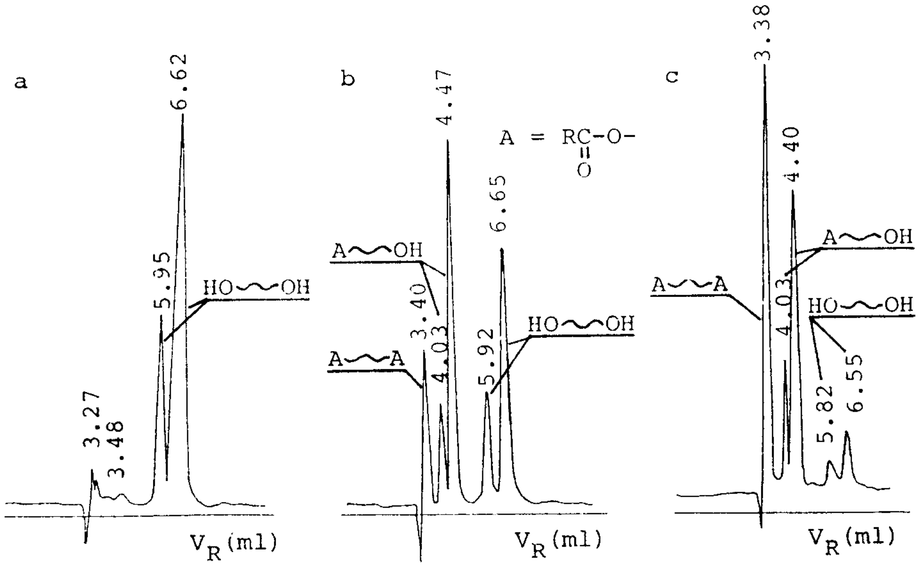

Fig. 3, FTD chromatograms of partially acetylated oligo(caprolactone)diol samples in optimized critical conditions (a = untreated, b = 33% acetylated, c = 67% acetylated). Column: Zorbax NH2, diethylether/acetone (78/22 vol) mixture, flow: 1 ml/min, RI detector.

In this table it is shown that the diol fraction appears as two separate fractions. This splitting was also observed in the acetylated samples (fig. 3) and reflects the different local structure of hydroxyl groups. This could be caused by the original starting diol in the OCLD synthesis (x or y=0 in the structural formula).

Furthermore it was found that the character of the OH groups present in samples 1 and 2 differs from samples 3 and 4, as it is shown in figure 2.

References

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