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Analysis of benzyloxy-terminated poly(1,3,6-trioxocane)s by supercritical fluid chromatography

H. Pasch*,☆, H. Krüger and H. Much

Central Institute of Organic Chemistry, Division of Macromolecular Compounds, Rudower Chaussee 5, O-1199 Berlin (Germany)

U. Just

Federal Institute for Materials Research and Testing, Department 3, Organic Materials, Unter den Eichen 87, 1000 Berlin 45 (Germany)

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ABSTRACT

Benzyloxy-terminated poly(1,3,6-trioxocane)s are separated into oligomers by supercritical fluid chromatography. Depending on the chemical structure of the polytrioxocane, two to three peaks are obtained for each degree of polymerization, corresponding to different types of functionality. Up to a degree of polymerization of $n=7$ the α,ω-dihydroxy, α-hydroxy-ω-benzyloxy and α,ω-dibenzyloxy species are well separated.

INTRODUCTION

Macromers and telechelics are known to be oligomers with exactly one or two functional endgroups. Therefore, they are important intermediate products for further polymer reactions. An exact knowledge of the macromer and telechelic functionality is necessary for the application. The separation of functional polymers according to the type of functional groups is possible using liquid chromatography at the critical point of adsorption [1]. In this case a functionality-type distribution is obtained; the corresponding molar mass distribution of the fractions may also be obtained when size-exclusion separations of the fractions are carried out in a second dimension [2].

The use of a single liquid chromatographic method usually yields separations in which different distribution functions overlap (functionality, molar mass, chemical composition). The resolution of these methods is not sufficient to separate a polymer into its oligomers and the oligomers into components of different functionality.

Supercritical fluid chromatography (SFC) has become a popular tool to separate polymers into their oligomers [3–6]. Using highly efficient and selective capillary columns, unique separations may be achieved. However, so far only limited experimental data are available on simultaneous separation according to functionality and molar mass. Therefore, it is the aim of the present paper to study the potential of SFC in regard to this problem.

EXPERIMENTAL

The preparation of the poly(1,3,6-trioxocane) samples is described in ref. 7.

In brief, 1,3,6-trioxocane was cationically polymerized in the presence of benzyl alcohol (Table I, samples 1–3). Additionally, for sample 1 an extraction of the aqueous solution with diethyl ether was

☆ Present address: Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, W-6100 Darmstadt, Germany.

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TABLE I
CHARACTERISTICS OF SAMPLES TESTED

Sample	$\bar{M}_n$[a]	Hydroxyl number	Hydroxyl group equivalent
1	550	135.0	1.33
2	1410	53.1	1.34
3	385	164.0	1.13
4	680	3.5	0.04
5	960	113.7	1.95

[a] $\bar{M}_n$ = Number-average molecular weight, as determined by vapour pressure osmometry (VPO).

carried out to remove the α,ω-dibenzyloxy oligomers.

For sample 4, 1,3,6-trioxocane was polymerized in the presence of dibenzyl formal. As a result the product consists mostly of α,ω-dibenzyloxy oligomers.

Sample 5 was synthesized according to a route described in ref. 8. The first set of experiments was carried out on a Carlo Erba SFC 3000 instrument with flame ionization detection (FID). The mobile phase was 100% carbon dioxide (Linde). Samples were injected through a pneumatically operated Valco injection valve in a timed-split mode. An SE-54 10 m × 100 μm I.D. capillary column (Carlo Erba) was used. The oven temperature was 120°C and the FID temperature was maintained at 330°C.

The second set of experiments was carried out on an SB Biphenyl-30 10 m × 50 μm I.D. capillary column (Lee Scientific) using Dionex SFC 600 D equipment. Oven temperatures of 100 and 130°C were maintained. Timed-split injection was carried out on a Valco injection valve.

All polymer samples were injected as 30% (w/w) solutions in methylene chloride.

RESULTS AND DISCUSSION

The cationic ring-opening polymerization of 1,3,6-trioxocane in the presence of benzyl alcohol results in the formation of components with different endgroups. In agreement with the active chain-end mechanism, α-hydroxy-ω-benzyloxy oligo (1,3,6-trioxocane)s (I) and cyclic oligomers (II) are formed along with α,ω-dihydroxy (III) and α,ω-dibenzyloxy oligo (1,3,6-trioxocane)s (IV) (Fig. 1) [7].

Accordingly two types of distribution functions are expected: molar mass distribution and functionality-type distribution. In a first set of experiments a number of samples (see Table I) were investigated on a methylsiloxane capillary column (SE-54) using Carlo Erba SFC 3000 equipment. A density program was applied consisting of an initial isobaric step, in which the sample solvent was eluted, and two linear ramp steps for the separation of the oligomers. After optimization of the ramp rates and the hold times, chromatograms were obtained, showing the expected oligomer distribution (see Fig. 2). For each degree of oligomerization two peaks, a smaller one and a bigger one, were obtained, indicating a second type of distribution. Obviously components of two different types of functionality were present in the samples. However, the expected three to four different types of functional components could not be separated.

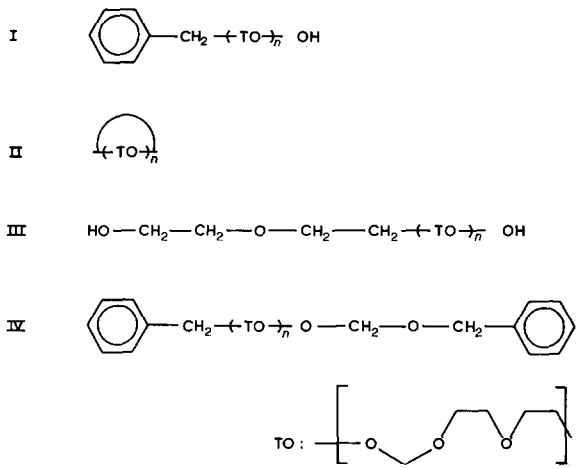


Fig. 1. Structures of compounds I–IV.

A higher resolution was expected when the polarity of the stationary phase was increased. In addition, a 50 μm I.D. instead of a 100 μm I.D. column was used.

The separation of a low-molecular-weight poly-(1,3,6-trioxocane) on an SB Biphenyl-30 stationary phase is shown in Fig. 3. Again density programming was used but the hold steps were deleted. In program A (see Fig. 4), consisting of two ramp steps with rates of 0.03 and 0.02 g ml^{-1} min^{-1}, well resolved peaks were obtained in the first part of the chromatogram. In the second part of the chromatogram the peaks were very close to each other. Accordingly the first ramp rate was increased to 0.1 g ml^{-1} min^{-1} and the second ramp rate was de-

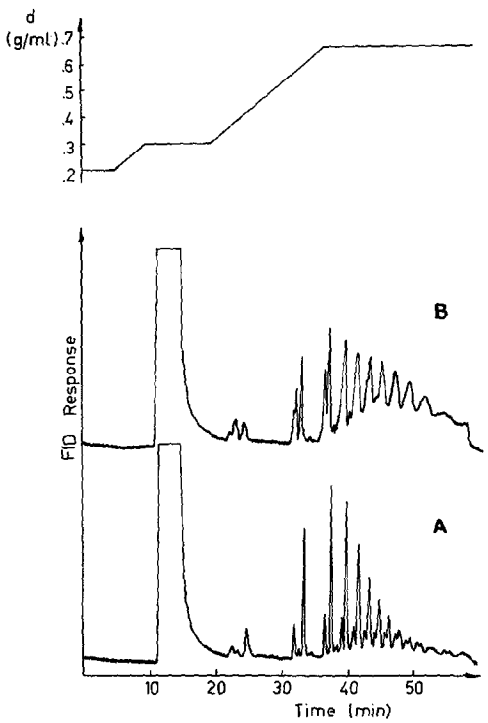


Fig. 2. SFC chromatograms of samples 1 (A) and 2 (B) on a methylsiloxane capillary column, density programming, oven temperature 120°C.

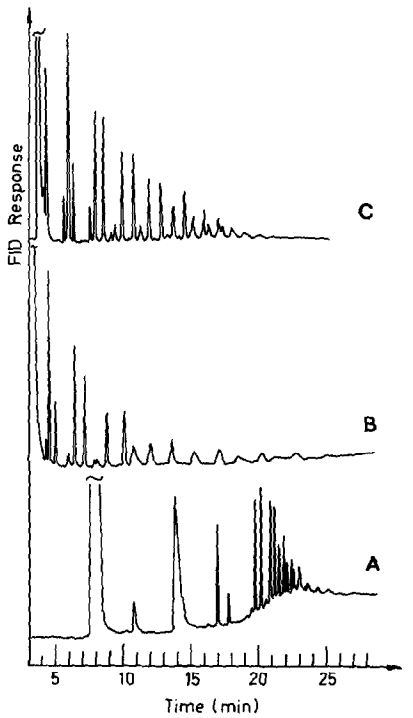


Fig. 3. SFC chromatograms of sample 3 on a SB-Biphenyl 30 capillary column with different density programmes, oven temperature 100°C.

creased to 0.01 g ml^{-1} cm^{-1}. In this case very broad peaks were obtained in the second part of the chromatogram. Optimum resolution was achieved using ramp rates of 0.06 and 0.02 g ml^{-1} min^{-1} (see Fig. 3C).

A further improvement was expected when the oven temperature was increased from 100 to 130°C. After adjusting the density programming to an optimum resolution, well resolved peaks were obtained (see Fig. 5). With respect to the previously discussed molar mass and functionality-type distributions, the number of peaks indicated that for each degree of polymerization more than two peaks were obtained. For sample 3 the hydroxyl group equivalent was determined to be 1.13, and it was assumed that all types of functionalities (I–IV) might be present.

In order to assign the peaks, samples which contain predominantly one type of functionality were investigated. As can be seen in Fig. 6A, sample 4 exhibits a normal oligomer distribution with minor peaks of other functionalities.

This sample was prepared in the presence of dibenzyl formal, which finally leads nearly exclusively to dibenzyl-functionalized oligomers. Accordingly the hydroxyl equivalent is very low. The following

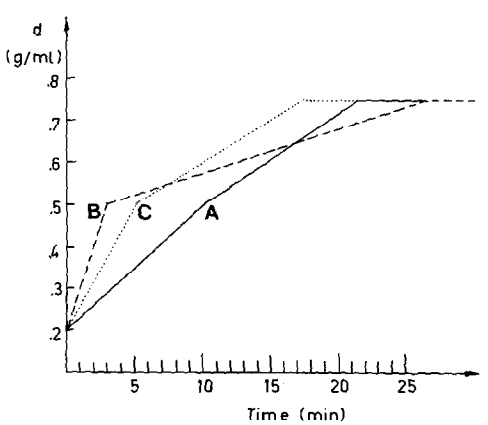


Fig. 4. Density programming for Fig. 3.

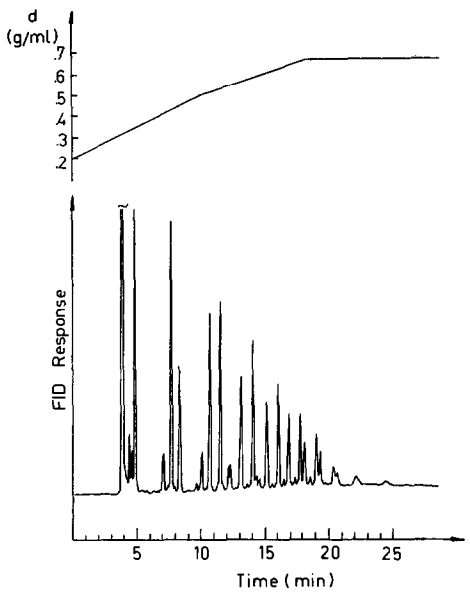


Fig. 5. SFC chromatogram of sample 3 on a SB-Biphenyl 30 capillary column, oven temperature 130°C.

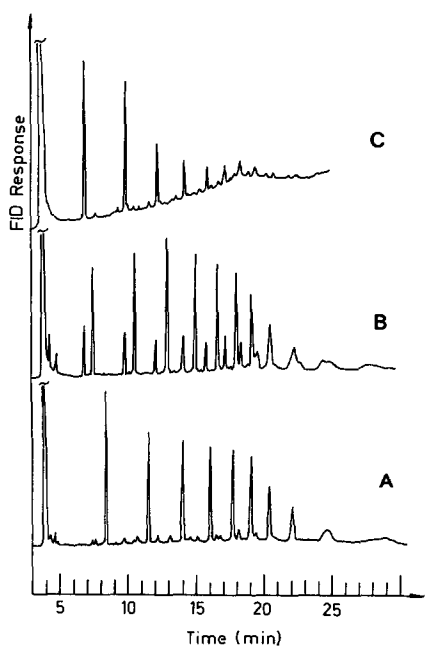
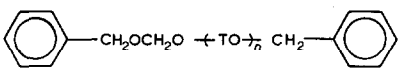


Fig. 6. SFC chromatograms of samples 4 (A), 1 (B) and 5 (C) on a SB-Biphenyl 30 capillary column. For density programme, see Fig. 5.

average structure could be assumed which corresponds to the functionality type IV.



The polymerization of 1,3,6-trioxocane without dibenzyl formal was supposed to give an oligomer mixture containing exclusively α,ω-dihydroxy components (functionality type III). Fig. 6C shows a typical oligomer distribution, however, the efficiency of the separation was less than in Fig. 6A. The reason is thought to be higher polarity of the α,ω-dihydroxy oligomers, causing solubility problems with the mobile phase.

A polytrioxocane sample in which the α,ω-dibenzyl components were removed by extraction in water–diethyl ether is shown in Fig. 6B. Accordingly, this sample contains mainly α,ω-dihydroxy and α-hydroxy-ω-benzyloxy oligomers.

Based on the interpretation of the chromatograms in Fig. 6A–C, the peaks in Fig. 5 could be assigned. Within one degree of oligomerization the components of different functionality were eluted in the order III–I–IV. The lowest molar mass components of I and III ($n = 0$), *i.e.* benzyl alcohol and diethylene glycol, were eluted shortly after the sample solvent at 4–5 min. Therefore the peak at 7.12 min corresponds to III with $n = 1$, the peak at 7.73 min corresponds to I with $n = 1$ and the peak at 8.37 min corresponds to IV with $n = 0$. The assignment of the other peaks is summarized in Table II.

A number of minor peaks in Fig. 5 could not be assigned to either a certain degree of oligomerization or functionality type III, I or IV. Some of them may correspond to a cyclic oligomer series (functionality type II), however an unambiguous assignment was not possible. According to Krüger *et al.* [7] the amount of cyclic oligomers is of the order of 1% (w/w).

After assigning the oligomer peaks to the different functionalities, calibration curves of molar mass *versus* retention time could be obtained (see Fig. 7). In our case, for the three functionality types similar calibration curves were obtained, indicating that the separation occurred according to the size of the oligomer molecule. From the shape of the curves it

TABLE II

ASSIGNMENT OF THE OLIGOMER PEAKS IN THE SFC CHROMATOGRAM OF SAMPLE 3

n	III		I		IV	
	M^a (g/mol)	$t_R{}^b$ (min)	M (g/mol)	t_R (min)	M (g/mol)	t_R (min)
0	–	–	–	–	228	8.37
1	224	7.12	226	7.73	346	11.55
2	342	10.08	344	10.78	464	14.07
3	460	12.38	462	13.18	582	16.10
4	578	14.35	580	15.20	700	17.73
5	696	16.10	698	16.85	818	19.05
6	814	17.42	816	18.20	936	20.38
7	932	18.55	934	19.37	1054	22.12
8	1050	–	1052	20.62	1172	24.50

[a] M = Molar mass.
[b] t_R = Retention time.

could be assumed that increasing the oligomer chain length by one TO-unit resulted in an increase in the retention time by a constant increment.

CONCLUSIONS

Benzyloxy-terminated poly(1,3,6-trioxocane)s are distributed according to molar mass and end functionality. The first distribution can be described by size-exclusion chromatography, the second by high-performance liquid chromatography. Using SFC it is possible to characterize both distributions by one chromatographic technique. The molar mass as well as the functionality-type distribution could be described in detail, assigning the single peaks to a certain type of functionality and degree of polymerization. It has been shown that a biphenyl siloxane capillary column is most suited for this problem. The calculation of average molar masses and functionalities simultaneously from the intensity of the single peaks would be a very fast method for the determination of structural parameters. This problem will be dealt with in forthcoming investigations.

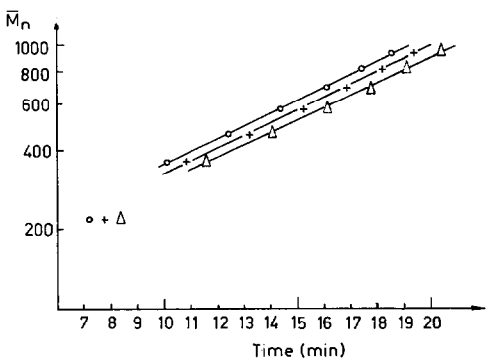


Fig. 7. SFC calibration curves of the functionality fractions III (○), I (+) and IV (△).

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