Simultaneous determination of functionality type and molar mass distribution of oligo(1,3,6-trioxocane)s by supercritical fluid chromatography

Harald Pasch*, Hartmut Krüger and Helmut Much
Central Institute of Organic Chemistry, Division of Macromolecular Compounds, Rudower Chaussee 5, Berlin 0-1199, Germany

and Ulrich Just
Federal Institute for Materials Research and Testing, Department 3, Organic Materials, Unter den Eichen 87, 1000 Berlin 45, Germany
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Benzyloxy terminated oligo(1,3,6-trioxocane)s are separated into components of single molar mass and functionality by supercritical fluid chromatography. The assignment and quantification of the components is described. It is shown that molar mass and functionality type distribution may be determined simultaneously from one chromatogram.

(Keywords: oligomer; molar mass distribution; functionality; supercritical fluid chromatography)

INTRODUCTION

The chemical structure of a functional homopolymer (macromer, telechelic) is fully described by two parameters – the molar mass distribution (*MMD*) and the functionality type distribution (*FTD*). *FTD* may be obtained by liquid chromatography at the critical point of adsorption[1], and *MMD* is usually determined by size exclusion chromatography (s.e.c.). The two-dimensional separation critical chromatography *versus* s.e.c. was demonstrated to be useful for *FTD* and *MMD* determination[2]. In a previous report[3] we described the analysis of benzyloxy terminated oligo(1,3,6-trioxocane)s by supercritical fluid chromatography (s.f.c.). S.f.c. has been shown to be a unique method for the separation of this type of product into its oligomers and the oligomers into species of different functionality. The problem of quantification and the calculation of *FTD* and *MMD* from s.f.c. chromatograms are discussed.

EXPERIMENTAL

The preparation of the oligo(1,3,6-trioxocane) samples is described elsewhere[4].

The s.f.c. experiments were conducted on a Dionex SFC 600 D using a 10 m × 50 μm i.d. capillary column SB Biphenyl-30 (Lee Scientific). The mobile phase was 100% carbon dioxide (Scott). Flame ionization detection at 380°C was used and an oven temperature of 130°C was maintained. Timed split injection was carried out on a Valco injection valve. All samples were injected as 30 wt% solutions in methylene chloride. The density programme was as follows: initial density 0.2 g ml^{-1}, then increase density to 0.5 g ml^{-1} with a ramp rate of 0.03 g ml^{-1} min^{-1}, followed by increase density to 0.67 g ml^{-1} with a ramp rate of 0.02 g ml^{-1} min^{-1}, and hold for 20 min.

The h.p.l.c. separations were carried out on equipment consisting of a Jasco HPLC pump 880-PU (Jasco International Co.), an electric six-port injection valve (Knauer) and a differential refractometer RIDK 101 (Laboratorni pristroje, Prague). The stationary phase was a Bioselect 100 C-18 column (Knauer), 250 mm × 4 mm i.d., with a particle diameter of 5 μm. The mobile phase consisted of acetonitrile and water (50/50 vol%), and the flow rate was 0.5 ml min^{-1}. Twenty microlitres of a 10 wt% polymer solution were injected for each separation. A column temperature of 25°C was maintained.

RESULTS AND DISCUSSION

The cationic ring-opening polymerization of 1,3,6-trioxocane in the presence of benzyl alcohol results in the formation of α,ω-dihydroxy (I), α-hydroxy-ω-benzyloxy (II) and α,ω-dibenzyloxy oligo(1,3,6-trioxocane)s (III). In addition, small amounts of cyclic oligomers may be formed. However, the concentration of these species is usually <1%.

According to previous results, s.f.c. of benzyloxy oligo(1,3,6-trioxocane)s yielded a superposition of fractions of different functionality and degree of polymerization (*DP*). A tentative assignment indicated

*To whom correspondence should be addressed. Now at: Deutsches Kunststoff-Institut, Schlossgartenstrasse 6, 6100 Darmstadt, Germany

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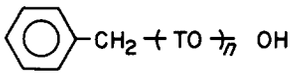
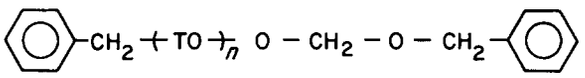
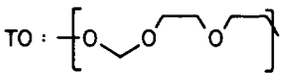
I $HO-CH_2-CH_2-O-CH_2-CH_2-(TO)_n-OH$

II 

III 

TO : 

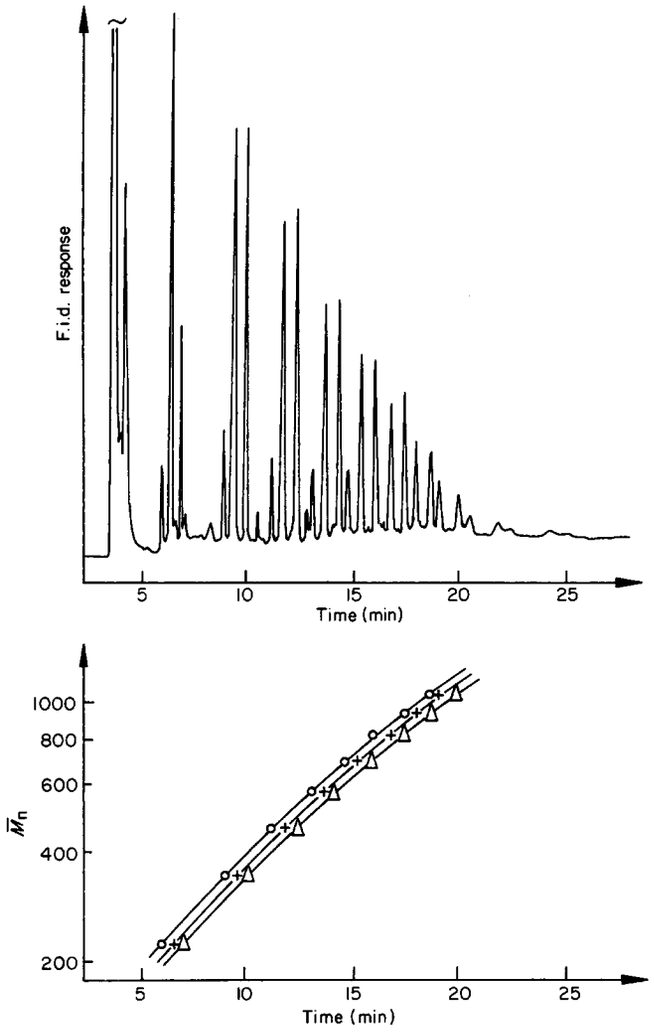


Figure 1 S.f.c. chromatogram and calibration curve of sample 1: column, SB Biphenyl-30; oven temperature, 130°C; mobile phase, carbon dioxide; f.i.d.

that separation occurred according to molar mass and with respect to the functionality in the order: I < II < III[3].

In order to support this interpretation, the starting material (*Figure 1*) was separated into fractions of single functionality I, II and III. In a previous study it was demonstrated that oligo(1,3,6-trioxocane)s may be separated into fractions of different functionality by liquid chromatography at the critical point of adsorption (critical chromatography)[4]. In this way oligomer mixtures of a single functionality are obtained, which may serve as 'calibration standards' for the assignment of peaks in s.f.c. chromatograms. It is a major advantage of critical chromatography that even 10 wt% polymer solutions may be separated without problems.

The critical chromatogram of a benzyloxy poly(1,3,6-trioxocane) is shown in *Figure 2*. In agreement with Krüger *et al.*[4] the first peak corresponds to the α,ω-dihydroxy oligomers (I); the second, third and fourth peaks correspond to cyclic oligomers, α-hydroxy-ω-benzyloxy (II) and α,ω-dibenzyloxy oligomers (III), respectively.

The fractions were collected and subjected to s.f.c. The resulting chromatograms showed typical oligomer distributions for the main functionalities and minor amounts of other functionalities (*Figure 2*). Oligomers with a $DP = 1-8$ were obtained for the three types of oligomers (I, II and III). For the cyclic oligomers a similar oligomer distribution could not be obtained because the concentration of these species in the sample was too low. Based on these separations a complete assignment of the peaks in *Figure 1* was possible. In addition, the molar mass *versus* retention time diagram gave parallel curves for all three functionalities, opening the opportunity of extrapolation towards higher molar masses.

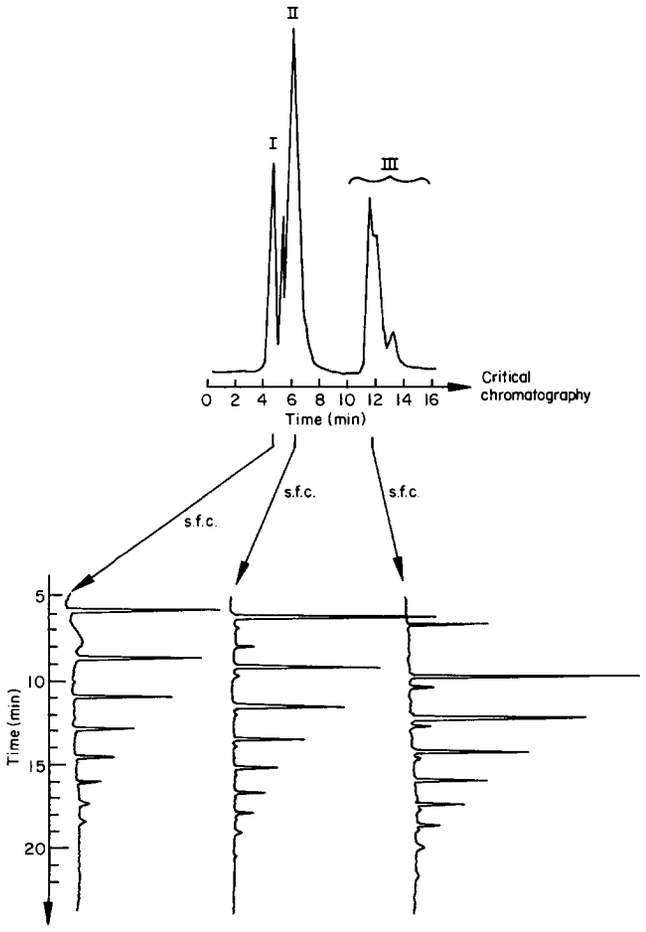
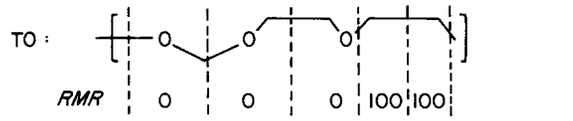


Figure 2 Two-dimensional separation critical chromatography *versus* s.f.c.: column, RP-18; mobile phase, acetonitrile/water (50/50 vol%); RI detector; s.f.c. (see *Figure 1*)

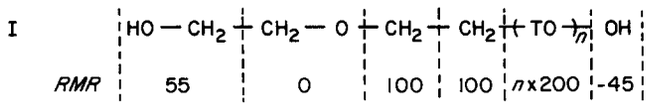
In s.f.c. as well as in gas chromatography, where a flame ionization detector (f.i.d.) is used, one of the major problems is quantification. The f.i.d. signal intensity does not only depend on the amount of the eluted component but also on its composition and chemical structure. In general, the number of carbon atoms and the types of linkages determine the signal intensity of the f.i.d.[5].

For complex mixtures, i.e. mixtures of oligomers, reference compounds for all components are normally not available. However, in a number of cases, namely for homologous series, the f.i.d. response may be calculated using increment methods[6]. For certain structural groups relative mass response (*RMR*) increments are known, which may be combined to give the relative f.i.d. response for a certain molecule (cf. *Table 1*).

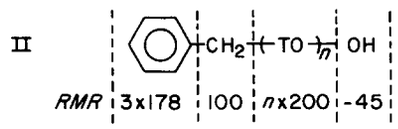
In order to calculate the relative response of the oligomer series I, II and III using the increments given in *Table 1*, the scheme below may be followed:



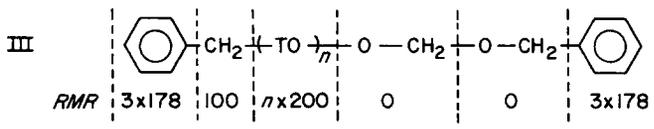
RMR = 200



RMR = 210 + 200*n*



RMR = 589 + 200*n*



RMR = 1168 + 200*n*

From the relative response of each component and the peak area in the s.f.c. chromatogram the number of molecules of component i, n_i, may be calculated. Accordingly the molar mass averages may be determined:

$$n_i = A_i/RMR_i$$

$$\bar{M}_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

$$\bar{M}_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

where A_i and RMR_i are the peak area and relative response of component i.

Table 2 summarizes the data for sample 1, i.e. the retention time, A_i, RMR_i, n_i and the molar mass of component i.

Using the given equations the average molar masses of series I, II and III were calculated from the s.f.c. chromatogram of sample 1 (*Figure 1*). Similarly the average molar masses of the isolated fractions of I, II and III (*Figure 2*) were determined and the results compared (*Table 3*). As can be seen, there is excellent agreement between the molar mass values, determined from the s.f.c. chromatogram of the total sample 1 (method A) and the s.f.c. chromatograms of the functionality fractions I, II and III (method B). For comparison with molar mass values obtained by size exclusion chromatography (s.e.c.) and vapour pressure osmometry (v.p.o.), the number average molar mass of total sample 1 was calculated using the data summarized in *Table 2*: $\bar{M}_n$ (s.f.c.) = 418; $\bar{M}_n$ (s.e.c.) = 390; $\bar{M}_n$

Table 1 *RMR* increments for f.i.d. response according to Ackman[6]

Structural group	*RMR* increment
$-CH_2-$	100
$-CH_2-O-$	0
$-CH_2-OH$	55
	178
	0

Table 2 Data for sample 1 from the s.f.c. chromatogram

	HO〰〰OH (I)					Ph〰〰OH (II)					Ph〰〰Ph (III)				
DP	RT[a] (min)	A_i (1000)	RMR_i	n_i	M_i[b]	RT[a] (RT)	A_i (1000)	RMR_i	n_i	M_i[b]	RT[a] (min)	A_i (1000)	RMR_i	n_i	M_i[b]
0											6.52	465	1168	0.398	228
1	5.92	240	410	0.585	224	6.33	1346	789	1.706	226	9.90	888	1368	0.649	346
2	8.85	225	610	0.369	342	9.35	1128	989	1.141	344	12.32	822	1568	0.524	464
3	11.15	125	810	0.154	460	11.70	831	1189	0.699	462	14.38	590	1768	0.334	582
4	13.08	117	1010	0.116	578	13.72	587	1389	0.423	580	16.12	406	1968	0.206	700
5	14.78	100	1210	0.083	696	15.43	405	1589	0.255	698	17.52	270	2168	0.124	818
6	16.12	77	1410	0.055	814	16.85	298	1789	0.167	816	18.73	177	2368	0.075	936
7	17.52	69	1610	0.043	932	18.05	198	1989	0.100	934	20.07	95	2568	0.037	1054
8	18.73	50	1810	0.027	1050	19.17	103	2189	0.047	1052					

[a]RT, retention time
[b]M_i, molar mass of component i

Table 3 Average molar masses and functionality of sample 1 calculated from the s.f.c. chromatogram of sample 1 (method A) or the s.f.c. chromatograms of the functionality fractions I, II and III (method B)

	I			II			III		
	$\bar{M}_n$	$\bar{M}_w$	U^a	$\bar{M}_n$	$\bar{M}_w$	U^a	$\bar{M}_n$	$\bar{M}_w$	U^a
Method A	395	508	1.29	398	493	1.24	472	555	1.18
Method B	372	452	1.22	391	484	1.24	488	576	1.18

[a] U, polydispersity ($= \bar{M}_w/\bar{M}_n$)

Table 4 *FTD* of sample 1

	I		II		III	
	mol%	wt%	mol%	wt%	mol%	wt%
S.f.c.	17.2	16.3	54.6	51.9	28.2	31.8
Critical chromatography	–	18.3	–	51.9	–	29.2

Table 5 Average molar masses and functionalities of samples 2–4 determined by s.f.c.

	Sample		
	2	3	4
S.f.c.			
$\bar{M}_n$ (I)	426	516	429
$\bar{M}_n$ (II)	565	601	511
$\bar{M}_n$ (III)	–	623	566
$\bar{M}_n$ (total)	551	615	522
Mass			
I mol%	37.5	6.0	24.3
wt%	31.2	5.1	20.6
II mol%	62.5	8.2	48.3
wt%	68.8	8.1	48.7
III mol%	–	85.8	27.4
wt%	–	86.8	30.7
OH equivalent (total)	1.37	0.02	0.97
V.p.o.			
$\bar{M}_n$ (total)	550	680	610
Titrimetry			
OH equivalent (total)	1.33	0.04	1.01

(v.p.o.) = 385. Again, excellent agreement was obtained and it was evident that $\bar{M}_n$, $\bar{M}_w$ and polydispersity may be determined with high accuracy by s.f.c. Furthermore, from the mass fractions of the functionality series I, II and III in sample 1 the molar and weight percentage of I, II and III may be calculated and compared to data obtained by a functionality type separation using critical chromatography (*Table 4*). The resulting hydroxyl group equivalent was 0.9, which was very close to 1.05 determined titrimetrically.

Additional evidence of the validity of our approach is given in *Table 5*. Benzyloxy oligo(1,3,6-trioxocane)s with different hydroxyl equivalents, corresponding to different amounts of functionality fractions I, II and III were investigated by s.f.c. As expected, the calculated molar masses and hydroxyl equivalents were in good agreement to the corresponding data of v.p.o. ($\bar{M}_n$) and titrimetry (hydroxyl equivalent).

CONCLUSIONS

Using s.f.c. it has been shown to be possible to determine the molar mass and the functionality of benzyloxy oligo(1,3,6-trioxocane)s. The assignment of each peak to a certain *DP* and type of functionality and the quantification of the peaks via an increment scheme enables the *FTD* and *MMD* to be determined simultaneously from one s.f.c. chromatogram. Thus, time consuming two-dimensional separations may at least partially be substituted by capillary s.f.c. However, resolution in s.f.c. strongly depends on the molar mass of the sample. The application range of the method may be extended by optimization of resolution and selectivity of the chromatographic system. These problems will be dealt with in subsequent experiments.

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