

CHROM. 22 197

## **Phase transition chromatography of polyesters on macroporous glycidyl methacrylate–ethylene dimethacrylate copolymers**

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### **ABSTRACT**

The chromatographic behaviour of oligoesters of phenolphthalein and terephthalic acid in columns packed with a polymeric sorbent based on the macroporous strongly cross-linked copolymer glycidyl methacrylate–ethylene dimethacrylate was studied. The possibility of the effective separation of oligomers according to the type of terminal groups was demonstrated. For comparison the sorbent Silasorb 600 was used.

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### **INTRODUCTION**

During the last decade, methods for the separation of oligomers according to the type of terminal groups (functionality) have been developed<sup>1</sup>. It has been demonstrated<sup>2</sup> that the shift from size-exclusion chromatography to the adsorption mode by changing the adsorption energy, of the polymer unit by decreasing the eluent polarity is connected with the phase transition of the polymer. At this boundary, named the “critical region”, the size separation of linear chains disappears and separation according to structural heterogeneity, particularly its functionality, can be achieved. The critical regions have been found for a number of polymers and sorbents.

Hydrolysed macroporous glycidyl methacrylate–ethylenedimethacrylate (GMA–EDMA) copolymers have been used previously<sup>3</sup> as universal sorbents for the high-performance gel permeation chromatography (GPC) of polymers with both aqueous and weakly polar organic mobile phases.

In this work, the possibility of separating aromatic oligoesters according to the types of terminal groups on GMA-EDMA copolymers was studied.

## EXPERIMENTAL

The functionality types of oligoesters of terephthalic acid and phenolphthalein were investigated, where the functionality  $f = 0, 1, 2$  represents 0, 1 and 2 terminal phenolic hydroxy groups per molecule, respectively.

The samples were prepared by high-temperature or heterophase<sup>4</sup> polycondensation and characterized<sup>5</sup> by osmometry, GPC and high-performance liquid chromatography. The molecular weights and functionality values of the oligoesters are given in Table I.

TABLE I

NUMBER- ( $\bar{M}_n$ ) AND WEIGHT-AVERAGE ( $\bar{M}_w$ ) MOLECULAR WEIGHTS AND NUMBER-AVERAGE FUNCTIONALITY VALUES ( $\bar{f}_n$ ) OF OLIGOESTERS

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{f}_n$
1	1770	2060	1.30
2	2240	3790	0.90
3	1750	2080	1.95
4	1090	1140	0.00

Chromatographic experiments were carried out using a Milichrom 1 apparatus (Scientific Instruments, Orel, U.S.S.R.). Columns of  $62 \times 2$  mm I.D. and  $280 \times 2$  mm I.D. were packed with polymeric sorbents based on hydrolysed macroporous strongly cross-linked GMF-EDMA copolymers (G5 and 6/11H). Mixtures of hexane with tetrahydrofuran (THF) or methylene chloride were used as the mobile phase.

The results were compared with those obtained with a  $62 \times 2$  mm I.D. silica column (Silasorb 600; Lachema, Brno, Czechoslovakia).

## RESULTS AND DISCUSSION

Fig. 1 shows the transition from the size-exclusion separation mode to the adsorption mode on (a) 6/11H and (b) G5 sorbents using THF/hexane mixtures. The critical region for these sorbents was found at 30% (v/v) of hexane (6/11H) and between 10 and 20% of hexane (G5) in the mixture. The distribution coefficients ( $K_d$ ) of bifunctional molecules [ $K_d^{(2)}$ ] under these conditions were found to be too small [ $K_d(2) = 1.3$  for 6/11H and  $1.23 < K_d(2) < 2$  for G5] for separation according to functionality.

A similar shift from the size-exclusion to the adsorption mode was observed<sup>5</sup> on the Silasorb 600 column. The critical region corresponds to a hexane content equal of 30% in the THF-hexane mixture, and  $K_d(2) = 1.5$ . Hence the oligoesters cannot be separated according to functionality in THF-containing mobile phases.

Fig. 2 shows the shift in chromatographic mode at the critical region for GMA-EDMA sorbents using methylene chloride-hexane mixtures. The critical

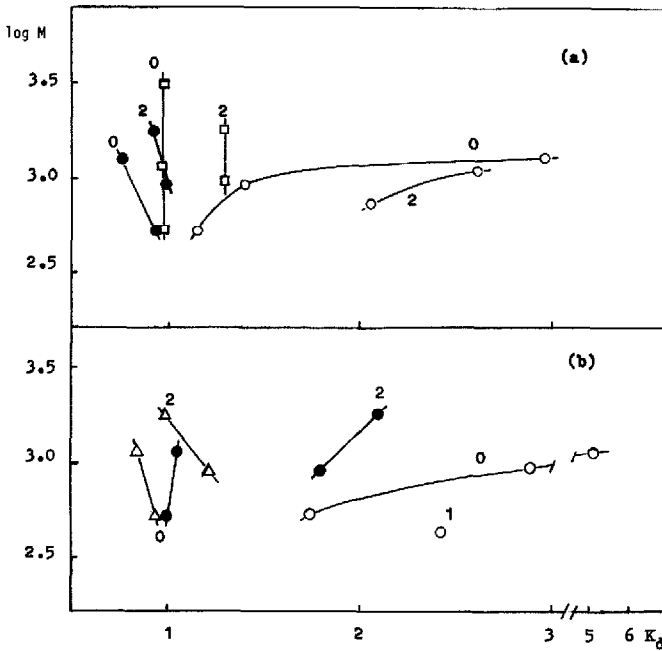


Fig. 1. Transition from the exclusion separation mode to the adsorption mode on (a) 6/11H and (b) G5 sorbents using THF-hexane mixtures. The numbers on the curves correspond to the functionality values. Hexane content in mobile phase:  $\Delta$  = 10;  $\bullet$  = 20;  $\circ$  = 30;  $\square$  = 40%.

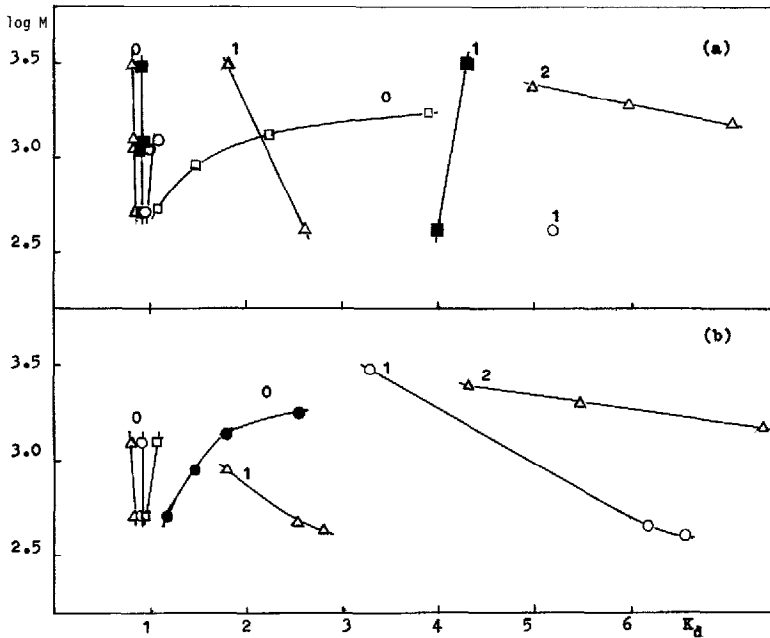


Fig. 2. Transition from the exclusion separation mode to the adsorption mode on (a) 6/11H and (b) G5 sorbents using methylene chloride-hexane mixtures. The numbers on the curves correspond to the functionality values. Hexane content in mobile phase:  $\Delta$  = 0;  $\blacksquare$  = 20;  $\circ$  = 30;  $\square$  = 40;  $\bullet$  = 50%.

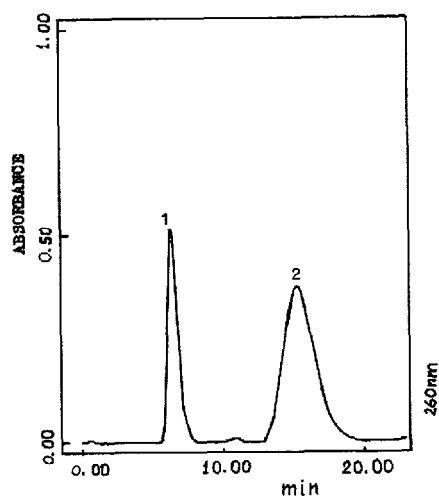


Fig. 3. Chromatogram of sample 1 obtained in the critical region on the 6/11H column. Eluent: methylene chloride-hexane (70:30); flow-rate, 100  $\mu$ l/min. Peaks: 1 = non-functional fraction; 2 = monofunctional fraction.

region corresponds to a 20% content of hexane in the mixture for 6/11H and between 30 and 40% of hexane for G5. The retention times of functional molecules are very large in these mobile phases [ $K_d(1) = 4$  for 6/11H and  $K_d(1) > 10$  for G5]. The bifunctional molecules proved to be irreversibly adsorbed on G5.

Fig. 3 shows a chromatogram obtained in the critical region on the 6/11H column. The two peaks correspond to non-functional and monofunctional fractions of oligoesters.

The results were compared with those obtained on a Silasorb 600 column using methylene chloride-containing mobile phases. In pure methylene chloride, separation of oligoesters by adsorption occurs. A stronger eluent, *e.g.*, 1–2% of 2-propanol, must be added in order to reach the critical region, as illustrated in Fig. 4. In the critical region irreversible adsorption of bifunctional molecules was observed on both the silica and organic sorbents.

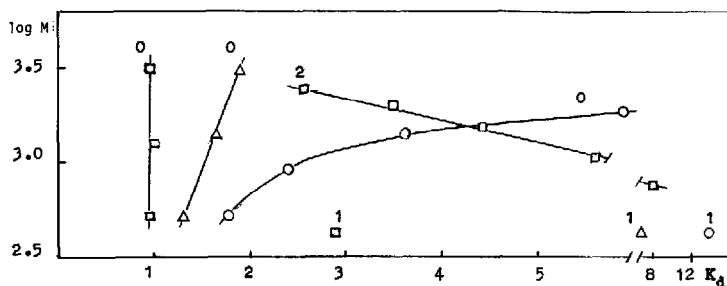


Fig. 4. Transition from the exclusion separation mode to the adsorption mode on Silasorb 600 using methylene chloride-2-propanol mixtures. 2-Propanol content in mobile phase:  $\circ = 0.5$ ;  $\triangle = 1$ ;  $\square = 2\%$ .

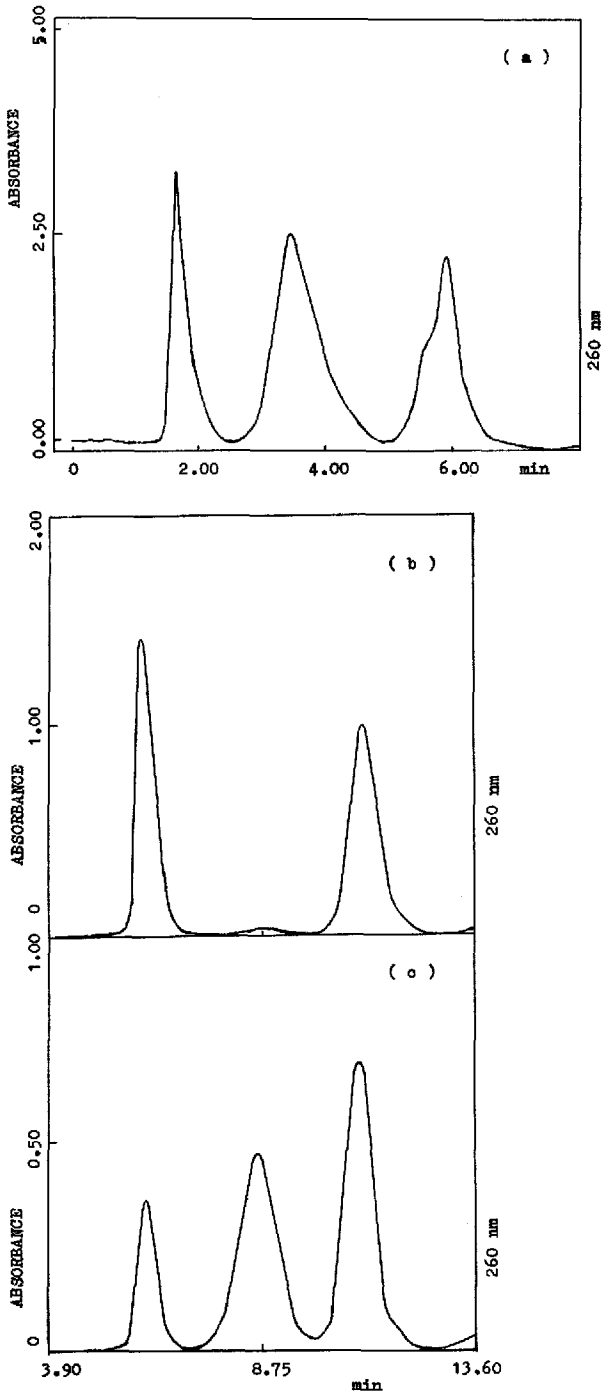


Fig. 5. Chromatograms of samples (c) 1 and (a) 2 and (b) a mixture of samples 3 and 4, obtained by the gradient elution technique on (a) the G5 column and (b and c) the 6/11H column. Mobile phases: (a) step 1 (up to 4 min); methylene chloride-hexane (60:40); step 2 (up to 8 min); methylene chloride-hexane-THF (30:20:50); step 3 (up to 12 min); THF; (b and c) step 1 (up to 6 min): methylene chloride-hexane (70:30), step 2 (up to 15 min): methylene chloride-hexane-THF (47:20:33). Flow-rate is 100  $\mu$ l/min.

From the comparison of the two types of sorbent the following conclusions can be drawn. These sorbents contain different functional groups on the the surface, *i.e.*, silanol groups on silica and hydroxy groups on organic sorbents. In a solvent such as methylene chloride, which does not show specific interactions with the sorbent and sorbate, the adsorption energy of the polymer unit is different for each sorbent. The energy reaches a critical value in solvents of different elution strengths calculated according to Snyder's theory<sup>6</sup> for alumina ( $0.62 < \epsilon < 0.66$  on Silasorb 600 and  $\epsilon = 0.40$  on 6/11H).

In contrast, the critical regions both for sorbents in THF-containing solvents approximately coincide ( $\epsilon = 0.43$ ). This means that specific interactions of the solvent with both the sorbate and sorbent cause a decrease in the adsorption energy of the polymer unit on the silica surface to the same extent as on hydroxy groups and simultaneously decreases the difference between the adsorption energies of a middle unit and the terminal group.

The results of this work show that the chromatography in the critical region must be modified for the effective separation of the studied oligoesters by the gradient elution technique. A concave profile of the gradient was obtained with a stepwise change in the eluent composition. The first stage of elution was accomplished with the critical mixture of methylene chloride and hexane and then, after elution of the non-functional fraction peak, the composition of the eluent was changed by addition of THF (two or three stages). Examples of such chromatograms are shown in Fig. 5. Samples 1 and 2 consisted of three fractions of different functionality (Fig. 5c and a). Fig. 5b shows for comparison the chromatograms of a mixture of the non-functional sample 4 and the bifunctional sample 3.

## REFERENCES

- 1 S. G. Entelys, W. W. Evreinov and A. I. Kusaev, *Reakcionnospobnyye Olygomery*, Khimiya, Moscow, 1985.
- 2 M. B. Tennikov, P. P. Nefedov, M. A. Lasareva and C. J. Frenkel, *Vysokomol. Soedin., Ser. A*, 19 (1977) 657.
- 3 T. B. Tennikova, D. Horák, F. Švec, J. Kolář, J. Čoupek, S. A. Trushin, V. G. Maltzev and B. G. Belenki, *J. Chromatogr.*, 435 (1988) 357.
- 4 I. V. Blagodatskikh, S.-S. A. Pavlova, L. V. Dubrovina, T. P. Bragina and V. V. Korshak, *Dokl. Akad. Nauk SSSR*, 281 (1985) 353.
- 5 I. V. Blagodatskikh, L. V. Dubrovina and S.-S. A. Pavlova, *Vysokomol. Soedin., Ser. A*, 30 (1988) 2622.
- 6 L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography*, Wiley-Interscience, New York, 1979.