Journal of Chromatography, 257 (1983) 327–335
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 15,478

SEPARATION OF OLIGOMERS BY HIGH-PERFORMANCE MICRO GEL PERMEATION CHROMATOGRAPHY

TOYOHIDE TAKEUCHI* and DAIDO ISHII
Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya-shi 464 (Japan)
and
SADAO MORI
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514 (Japan)
(Received October 29th, 1982)

SUMMARY

High-resolution gel permeation chromatography (GPC) has been attained on 2 m × 0.35 mm I.D. micro packed fused-silica columns and applied to the separation of epoxy and phenol–formaldehyde resins. More peaks were resolved on these micro-GPC columns than on conventional GPC columns, 1 m × 8 mm I.D. The use of high-resolution micro GPC combined with reversed-phase liquid chromatography gave some information regarding the structure of by-products of epoxy resins.

INTRODUCTION

The separation mechanism of gel permeation chromatography (GPC) is very simple, solute molecules being separated according to their effective molecular size in solution; larger solute molecules are eluted earlier than smaller ones. This predictable elution pattern offers a substantial advantage in the identification of unknown components if their molecular structures can be estimated. However, higher numbers of theoretical plates are required to resolve components in GPC since the selection of the mobile phase and the peak capacity are restricted. Higher numbers of theoretical plates can generally be obtained on a longer column coupled in series[1], but this may be more costly.

In micro high-performance liquid chromatography (micro-HPLC), the consumption of the stationary phase as well as of the mobile phase is reduced, leading to low-cost HPLC. We have found that flexible fused-silica tubings are good column materials in micro-HPLC[2–4] and have prepared 20–50 cm micro packed fused-silica columns and coupled several columns in series to obtain high-resolution columns[3,4]. Around 100,000 theoretical plates were obtained on 1.5–2 m columns.

In this study, high-resolution micro-GPC columns were prepared and applied to the separation of oligomers of epoxy and phenol–formaldehyde resins.

0021-9673/83/0000–0000/$03.00

EXPERIMENTAL

The apparatus for micro-GPC was assembled from a Micro Feeder (Azumadenki Kogyo, Tokyo, Japan) equipped with a 500-μl gas-tight syringe as a pump, a micro valve injector (0.02 μl; Japan Spectroscopic, Tokyo, Japan), a micro packed fused-silica column and a UV spectrophotometer UVIDEC-100 (Japan Spectroscopic) equipped with a modified flow cell (cell volume 0.04 μl). Polyimide-coated fused-silica tubings (0.35 mm I.D.) were obtained from Gasukuro Kogyo (Tokyo, Japan) and manually packed with materials taken out of commercially available columns. TSK-GEL G 1000H (5 μm; Toyo Soda Manufacturing, Tokyo, Japan), G 3000H (5 μm; Toyo Soda Manufacturing) and KF-802.5 (6 μm; Showa Denko K.K., Tokyo, Japan) were employed as the materials for micro GPC separation columns. 50-cm Columns were prepared as described previously[2] and coupled in series.

A conventional gel permeation chromatograph was composed of a TRI ROTAR (Japan Spectroscopic) as a pump, a separation column and a UV spectrophotometer UVIDEC-254 (Japan Spectroscopic). Two 50 cm × 8 mm I.D. columns packed with A-802 (10 μm, Showa Denko K.K.) were coupled and employed as the separation column.

Epoxy resins, Epikote 828 and 1001, were commercially available. Phenol–formaldehyde resins, phenol-resol and phenol-novolak, were prepared in the laboratory.

A micro fused-silica column, 20 cm × 0.26 mm I.D., packed with silica ODS SC-01 (5 μm, Japan Spectroscopic) was employed to separate by-products of epoxy resins in the reversed-phase mode.

Tetrahydrofuran was obtained from Wako (Osaka, Japan) and employed without any treatment as the mobile phase in micro-GPC.

RESULTS AND DISCUSSION

Fused-silica tubings have frequently been employed as the column material in capillary gas chromatography, owing to their smooth and inert surface, mechanical strength and ease of handling. These advantages are appreciated in liquid chromatography (LC) and some studies using fused-silica tubings have been reported[2–7].

More than 5000 theoretical plates per 10 cm are obtained on a micro packed fused-silica column, which may be due to the smooth and inert surface of the fused-silica tubings. Since more than 100,000 theoretical plates can easily be obtained on a longer micro-GPC column[3,4], 2-m columns were employed to separate oligomers in this work.

Separation of epoxy oligomers

The structures corresponding to the main peaks of epoxy resins are illustrated in Fig. 1 (m_n); at both ends of them are epoxide groups. Besides the main peaks, some by-products which have functional groups other than epoxide groups either as end-groups or as side chains pendant to the main chain are produced according to the reaction conditions[8,9], as shown in Fig. 1. Since these by-products affect the properties of epoxy resins, their characterization is of practical importance.

A lot of effort has been devoted to characterizing epoxy resins: GPC[4,10–13],

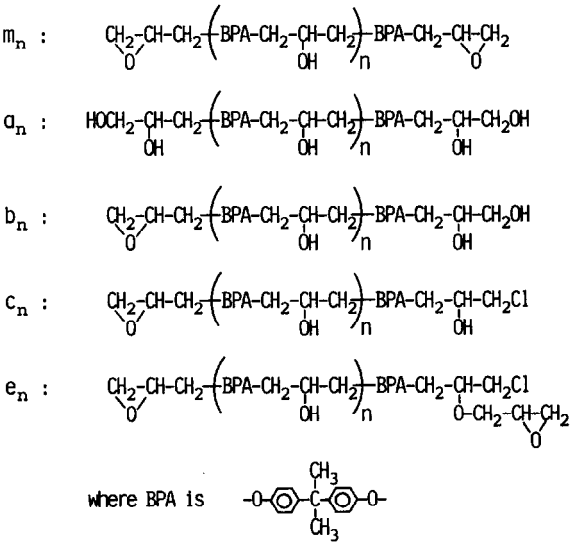


Fig. 1. Structures of epoxy oligomers and by-products.

reversed-phase LC (RPLC) combined with various spectroscopies[14,15] and field-desorption mass spectrometry (FD-MS)[9] have been utilized. The last work gave much information regarding the by-products. Saito *et al.*[9] characterized epoxy resins by FD-MS and gave the relative intensity of main and by-products.

Typical chromatograms of the separation of epoxy resins obtained by conventional GPC are shown in Figs. 2 and 3. Some peaks based on by-products appeared between main peaks or in their shoulders.

Fig. 4 shows separations of Epikote 828 obtained on 50-cm and 2-m micro-GPC columns packed with KF-802.5. The high resolution of micro-GPC can be seen. Three by-product peaks appear between the $n = 0$ and $n = 1$ main peaks in Fig. 4B, while one overlapped by-product peak appears in conventional GPC, as shown in Fig. 2. The flow-rate in Fig. 4B is only 1.04 μl/min, consuming only 120 μl of the mobile phase.

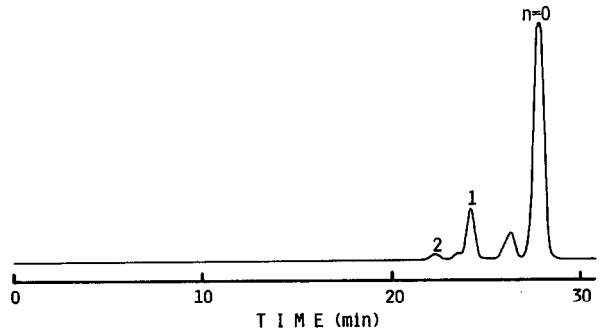


Fig. 2. Separation of Epikote 828 by conventional GPC Column: A-802, 0.5 m × 8 mm I.D. × 2. Mobile phase: tetrahydrofuran. Flow-rate: 1 ml/min. Injection volume: 200 μl. Wavelength of UV detection: 254 nm.

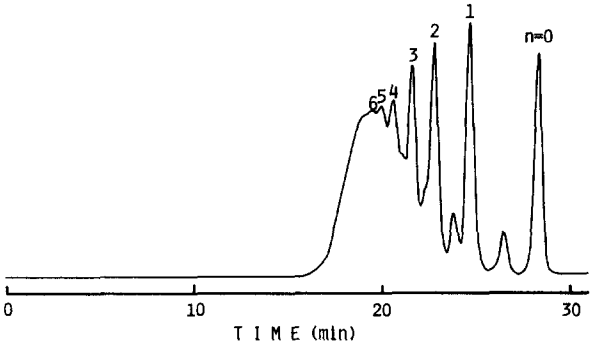


Fig. 3. Separation of Epikote 1001 by conventional GPC. Operating conditions as in Fig. 2.

Fig. 5 shows separations of Epikote 1001 obtained on 50-cm and 2-m micro-GPC columns packed with KF-802.5. The resolution power of micro-GPC is greater than of conventional GPC and comparable to high-resolution GPC[1]. Main peaks ranging from $n = 0$ to 10 and peaks based on by-products ranging from $n = 0$ to $n = 4$ appear in Fig. 5B.

Separations of epoxy oligomers on a 2-m micro-GPC column packed with G 1000H are shown in Figs. 6 and 7. Fig. 8 also shows a separation of Epikote 1001 on a G 3000H micro GPC column. Since the dimensions of the pores of G 1000H and G 3000H are different from those of KF-802.5 different elution profiles are obtained. In

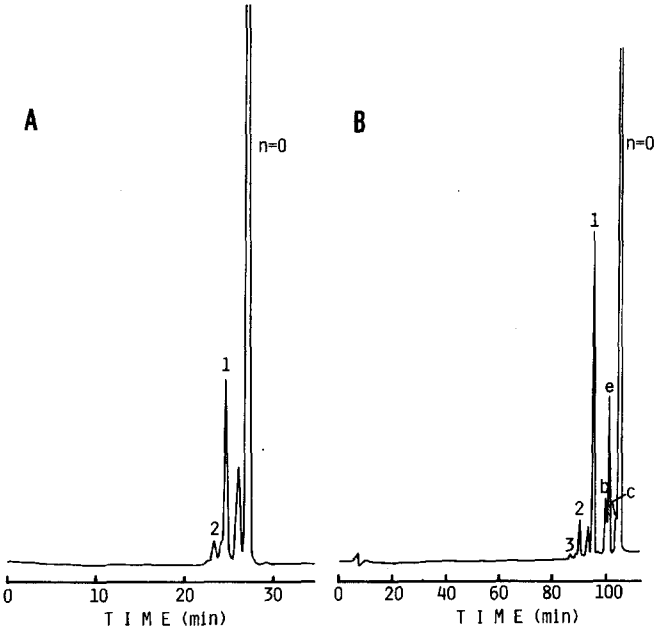


Fig. 4. Separations of Epikote 828 by micro GPC. Column: KF-802.5, 0.5 m × 0.3 mm I.D. (A); 0.5 m × 0.35 mm I.D. × 4 (B). Mobile phase: tetrahydrofuran. Flow-rate: 1.04 μl/min. Injection volume: 0.02 μl. Wavelength of UV detection: 280 nm.

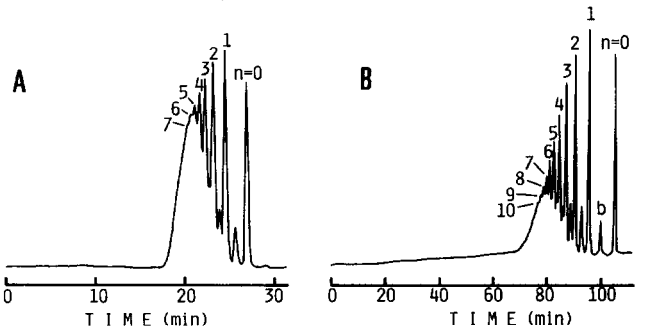


Fig. 5. Separations of Epikote 1001 by micro GPC. Operating conditions as in Fig. 4.

the case of Epikote 1001, one peak based on the by-product (b) appears between main peaks of $n = 0$ and $n = 1$ on KF-802.5 and G 1000H columns, while two by-product peaks (a and b) appear for G 3000H. In the first two cases, the by-product (a) may be overlapped by the main peak of $n = 1$.

Solutes are separated according to their effective molecular size in solution in GPC, while the retention of solutes is highly dependent on their polarity in RPLC.

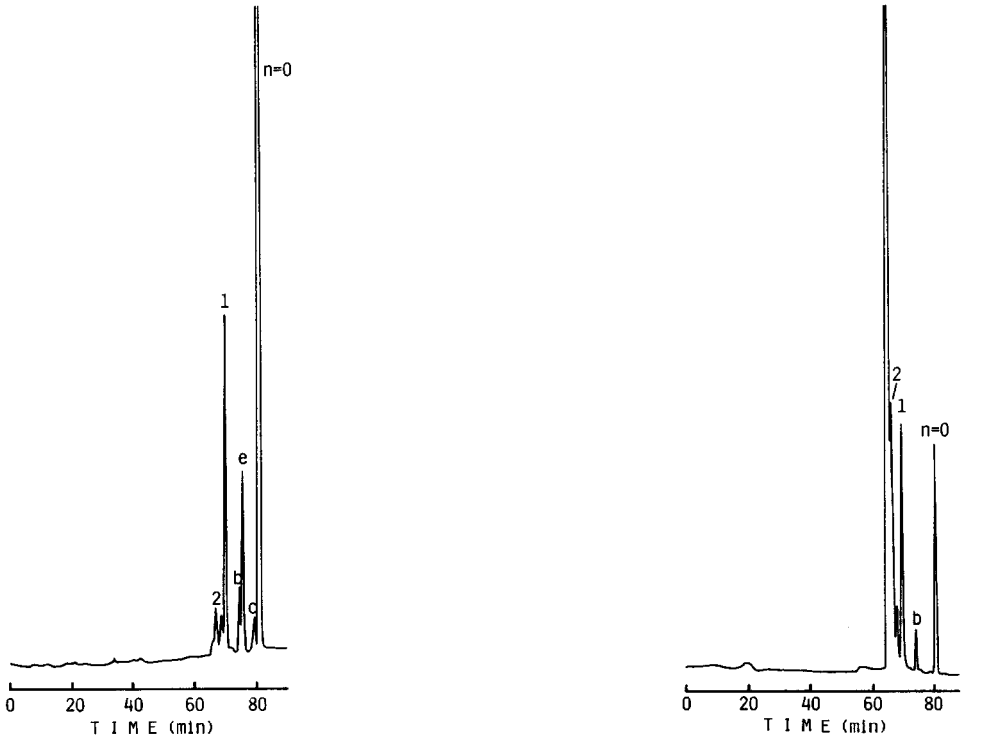


Fig. 6. Separation of Epikote 828 on a G 1000H micro-GPC column. Operating conditions as in Fig. 4 except the column, G 1000H, 0.5 m × 0.35 mm I.D. × 4.

Fig. 7. Separation of Epikote 1001 on a G 1000H micro-GPC column. Operating conditions as in Fig. 6.

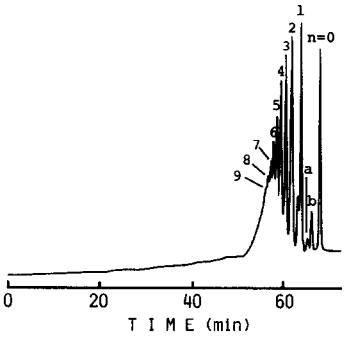
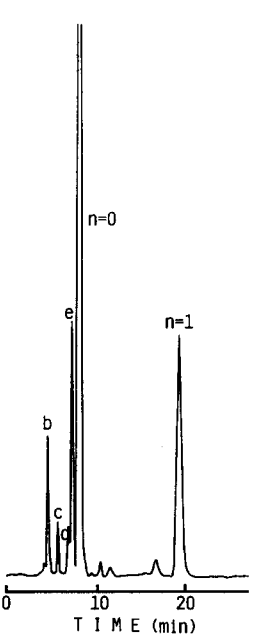


Fig. 8. Separation of Epikote 1001 on a G 3000H micro-GPC column. Operating conditions as in Fig. 7 except the column, G 3000H, 0.5 m × 0.33 mm I.D. × 4.

Thus, the contrasting elution orders of by-products in GPC and RPLC give some information on the structure of the by-products. Figs. 9 and 10 show separations of a low-molecular-weight portion of Epikote oligomers by RPLC. Several peaks based on main and by-products are well resolved although higher-molecular-weight species are not eluted in reasonable time under these operating conditions. It is possible to assign main and by-product peaks in Figs. 9 and 10 to those in GPC chromatograms, taking account of the peak height ratios. A wavelength of 225 nm was chosen in RPLC because of the increase in sensitivity, while 280 nm was chosen in GPC with the



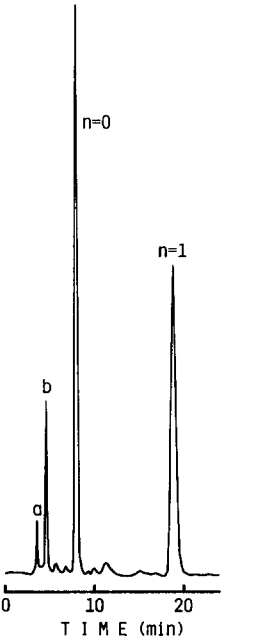


Fig. 9. Separation of Epikote 828 on a reversed-phase micro column. Column: silica ODS SC-01, 20 cm × 0.26 mm I.D. Mobile phase: acetonitrile–water (7:3). Flow-rate: 2.08 μl/min. Injection volume: 0.02 μl. Wavelength of UV detection: 225 nm.

Fig. 10. Separation of Epikote 1001 on a reversed-phase micro column. Operating conditions as in Fig. 9.

restriction of large UV absorption of tetrahydrofuran at low wavelengths. By-product peaks marked with a, b, c and e in Figs. 9 and 10 correspond to peaks similarly denoted in Figs. 4–8. The structures of main and by-products can be presumed by considering the elution orders in GPC and RPLC. Main peaks of $n = 0$ and 1 are m_0 and m_1 in Fig. 1, respectively. By-products a, b, c and e may correspond to a_0, b_0, c_0 and e_0 in Fig. 1, respectively.

Separation of phenol–formaldehyde resin oligomers

Phenol–formaldehyde resins are produced by condensation or addition reactions between phenol and formaldehyde and their structures are dependent on the reaction conditions. With an acid catalyst, condensation is dominant, leading to the formation of the linear polynuclear novolak bound by methylene links. With an

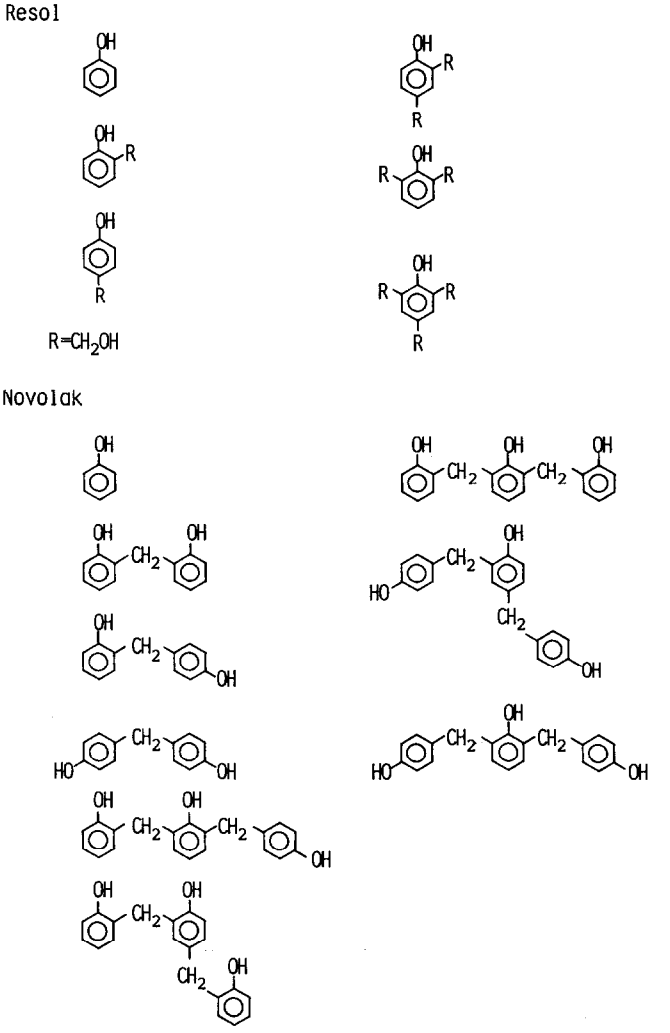


Fig. 11. Structures of representative species in phenol–formaldehyde resin.

alkaline catalyst, the addition reaction is dominant, producing resol with numerous methylol groups. Although analyses of novolak and resol have been reported by GPC[16–18] and RPLC[15], resolution of the components is unsatisfactory. Representative species in phenol–formaldehyde resins are shown in Fig. 11. Since the structures and the sizes of these species are similar, resolution of the individual species is very difficult.

Figs. 12 and 13 show separations of phenol–formaldehyde resin oligomers obtained by conventional GPC and high-resolution micro-GPC, respectively. More peaks appeared in the latter chromatograms than in the former due to the high resolution of micro-GPC. Since some species in Fig. 11 are commercially available, it will be possible to assign structures to these species.

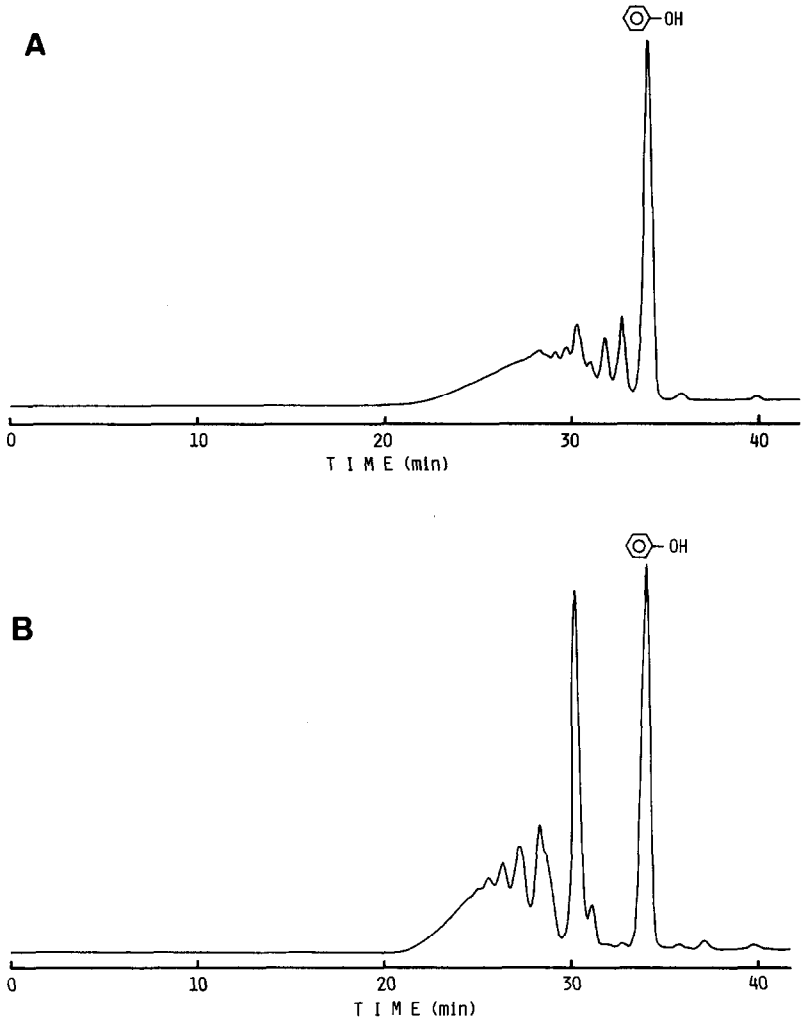


Fig. 12. Separations of phenol–formaldehyde resin oligomers by conventional GPC. Operating conditions as in Fig. 2. A, Resol; B, novolak.

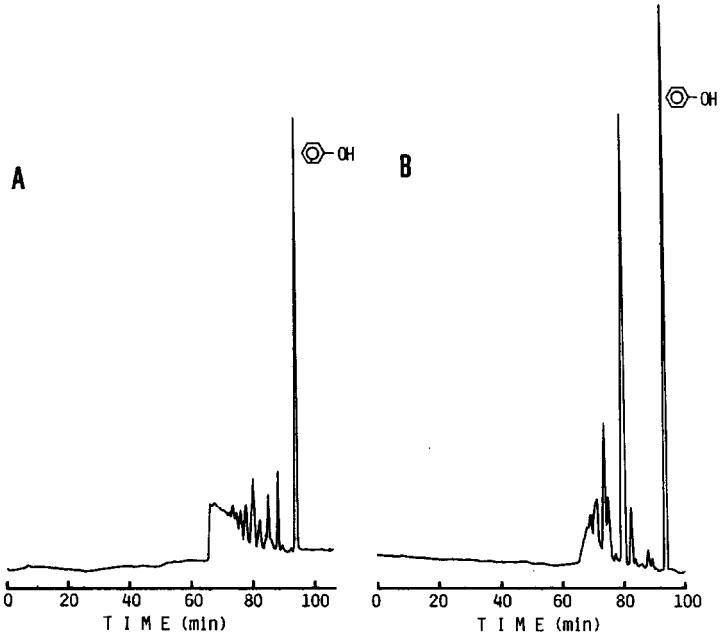


Fig. 13. Separations of phenol–formaldehyde resin oligomers by micro-GPC. Operating conditions as in Fig. 6: A, Resol; B, novolak.

CONCLUSION

The high resolution of micro-GPC in the analysis of oligomers has been demonstrated. More species could be resolved on micro-GPC columns than on conventional GPC columns. It will be possible to apply micro-GPC to the analysis of polymers.

REFERENCES

1 S. Ishiguro, Y. Inoue and T. Hosogane, *J. Chromatogr.*, 239 (1982) 651.
2 T. Takeuchi and D. Ishii, *J. Chromatogr.*, 213 (1981) 25.
3 T. Takeuchi and D. Ishii, *J. Chromatogr.*, 238 (1982) 409.
4 D. Ishii and T. Takeuchi, *J. Chromatogr.*, 255 (1983) 349.
5 F. J. Yang, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 589.
6 T. Takeuchi and D. Ishii, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 469.
7 F. J. Yang, *J. Chromatogr.*, 236 (1982) 265.
8 S. Shiono, I. Karino, A. Ishimura and J. Enomoto, *J. Chromatogr.*, 193 (1980) 243.
9 J. Saito, S. Toda and S. Tanaka, *Bunseki Kagaku (Jap. Anal.)*, 29 (1980) 462.
10 H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, 19 (1975) 585.
11 H. Batzer and S. A. Zahir, *J. Appl. Polym. Sci.*, 19 (1975) 609.
12 D. Braun and D. W. Lee, *Angew. Makromol. Chem.*, 48 (1975) 161.
13 D. Braun and D. W. Lee, *Angew. Makromol. Chem.*, 57 (1977) 111.
14 W. A. Dark, E. C. Conrad and L. W. Crossman, Jr., *J. Chromatogr.*, 91 (1974) 247.
15 F. P. B. van der Maeden, M. E. F. Biemond and P. C. G. M. Jansen, *J. Chromatogr.*, 149 (1978) 539.
16 E. J. Quinn, H. W. Osterhoudt, J. S. Heckles and D. C. Ziegler, *Anal. Chem.*, 40 (1968) 547.
17 E. W. Wagner and R. J. Greff, *J. Polym. Sci., Part. A-1*, 9 (1971) 2193.
18 M. Duval, B. Bloch and S. Kohn, *J. Appl. Polym. Sci.*, 16 (1972) 1585.