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## Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

### Size Exclusion Chromatography of Meiamine-, Urea-, and Phenolformaldehyde Resins Using N, N-Dimethylformamide as Eluent

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**To cite this Article** Matsuzaki, Takeshi , Inoue, Yoshinori , Ookubo, Tetsuo and Mori, Sadao(1980) 'Size Exclusion Chromatography of Meiamine-, Urea-, and Phenolformaldehyde Resins Using N, N-Dimethylformamide as Eluent', *Journal of Liquid Chromatography & Related Technologies*, 3: 3, 353 — 365

**To link to this Article:** DOI: 10.1080/01483918008069340

**URL:** <http://dx.doi.org/10.1080/01483918008069340>

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SIZE EXCLUSION CHROMATOGRAPHY OF MELAMINE-, UREA-, AND PHENOL-FORMALDEHYDE RESINS USING N,N-DIMETHYLFORMAMIDE AS ELUENT

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ABSTRACT

Resins, hardly soluble in THF or chloroform, in the oligomer region were analyzed using DMF as solvent and a polystyrene column for oligomers. This column, 25 cm x 8 mm i.d., is the exclusive use of DMF and has the number of theoretical plates of 6000 per 25 cm. Polynuclear methylol melamines were resolved into individual polynuclear species and peaks from mono- to penta nuclear methylol melamines were identified. The thermal stability of methylol melamines can be monitored by this system. Molecular weight distributions of urea-formaldehyde resins and phenol-formaldehyde resole resins were observed. This PSt gel - DMF system will be useful for the process control or the quality control of these resins.

INTRODUCTION

Recent improvements in the efficiency of small pore packing materials in high performance size exclusion chromatography (HPSEC, or GPC) have advanced the resolution of components in the lower molecular weight range (1). Crosslinked polystyrene (PSt) is the most commonly employed packing material in HPSEC. The solvents (the mobile phase) utilized in the ideal HPSEC with this packing

material should be limited to those which have solubility parameters as close as possible to that of polystyrene, such as tetrahydrofuran (THF), chloroform, and toluene (2). Lack of solubility in these solvents of melamine-formaldehyde resins and urea-formaldehyde resins, which are materials in oligomer region less than 10,000 molecular weight, constitutes inhibition for application of this technique.

Melamine- and urea-formaldehyde resins have been separated by SEC of a Sephadex LH-20 (alkylated dextran gel) - N,N-dimethylformamide (DMF) system (3-5). However, this technique is time consuming and its application is limited to mono-nuclear methylol melamines or low-molecular weight urea resins. Trimethylsilylated mono-nuclear methylol melamines have been separated by SEC of a PVAc gel - THF system (6). Methylated methylol melamines which are soluble in THF will be separated by a PSt gel - THF system. Separations of mono-nuclear methylol melamines by a reversed-phase liquid chromatography have been also attempted with a ODS - water or water/methanol system (7).

A PSt gel - DMF system is very attractive for SEC of polyacrylonitrile and other polar polymers (8,9), but DMF has never been applied with PSt gel of narrow pores to the separation of oligomers and low-molecular weight compounds, because the solvent contracts the swollen PSt gels of narrow pore sizes, resulted in the decrease of the number of theoretical plates of PSt columns used for oligomers and low-molecular weight compounds with THF or chloroform when these solvents are replaced by DMF.

The present report deals with the separation of resins of the title using DMF and a PSt column for HPSEC of oligomers. This column is the exclusive use of DMF which can not be replaced by the common solvents for SEC, such as THF.

#### MATERIALS

A Shodex GPC-AD-802S, which was packed with Shodex A802 GPC gel in a stainless-steel column 25 cm x 8 mm i.d., was used with

DMF as a mobile phase. The gel is polystyrene-divinyl benzene copolymer and has the exclusion limit of 8000 by polystyrene molecular weight. The column has the number of theoretical plates of 6000 measured by injecting 20  $\mu$ l of 1% acetone solution at a flow-rate of 1.0 ml/min and at 40 °C.

Standard samples were polystyrenes (PSt) (MW = 600, 4000 and 37000) and polyethylene glycols (PEG) (MW = 200, 1000, 4000, and 9000) of narrow molecular weight distributions. Melamine-, urea- and phenol-formaldehyde resins were prepared in our laboratory.

### METHODS

A JASCO (Nihon Bunko Kogyo Co., Ltd., Hachioji, Tokyo 192, Japan) TRIROTAR high performance liquid chromatograph was used with a differential refractometer Shodex SE-11 (Showa Denko Co., Ltd., Minato-ku, Tokyo 105, Japan). Eight Shodex GPC-AD-802S columns were connected in series and kept at 60 °C in a constant temperature bath. A flow-rate of DMF was 1.0 ml/min and a pressure drop was between 42 and 50 Kg/cm<sup>2</sup>. A sample injection volume was 100  $\mu$ l, if it is not specified. For the comparison purposes, two or four Shodex GPC-A-802 columns (each 50 cm x 8 mm i.d.) were used with THF as a mobile phase at a flow-rate of 1.0 ml/min at 23 °C. The attenuation of RI was x8.

### RESULTS AND DISCUSSION

#### Calibration curves

A chromatogram of PSt in DMF is shown in Figure 1 with that in THF obtained on a similar column set. The exclusion limit in DMF was nearly equal to that observed in THF, but the retardation of elution and the peak broadening for solutes were predominant in DMF except PSt 37000. The peak broadening effect resulted in the poor peak resolution of PSt 600. Though slight peak broadening of PSt 37000 was observed, it eluted at the exclusion limit

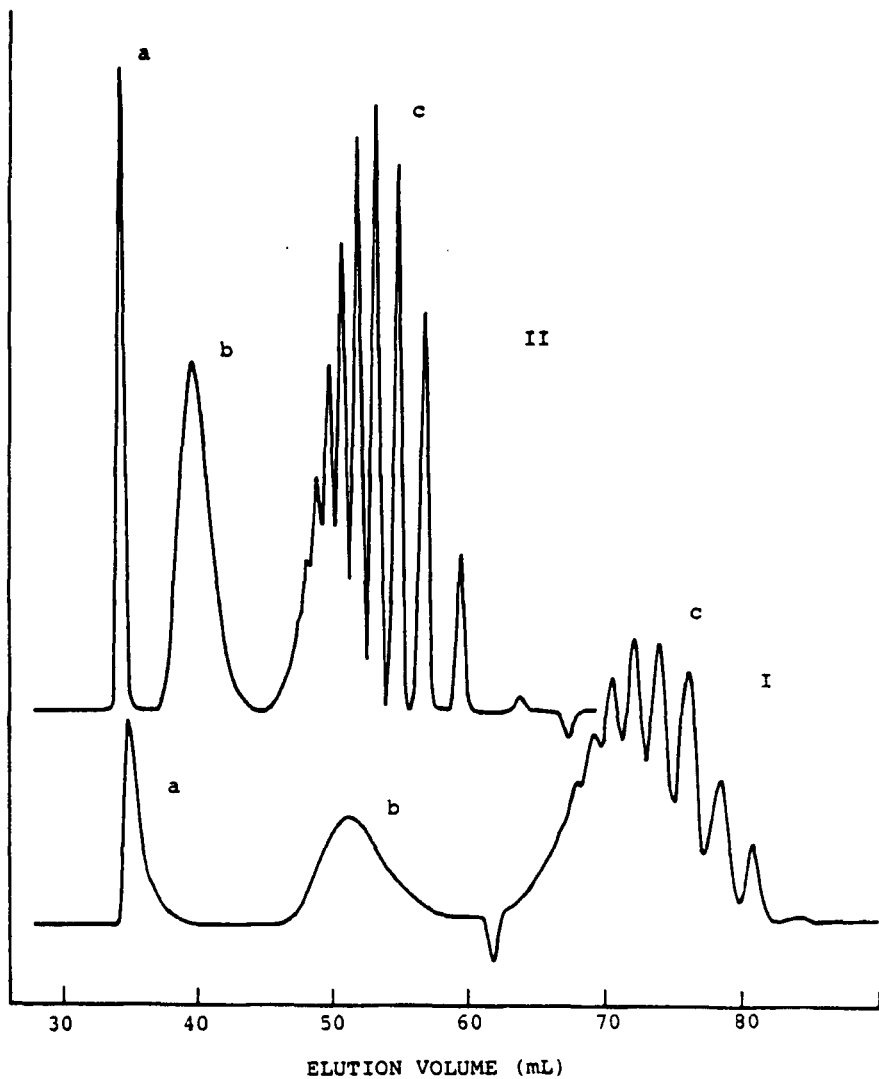


Figure 1. Chromatograms of polystyrenes in DMF (I) and THF (II). (a) PSt 37000 (0.1%); (b) PSt 4000 (0.2%); (c) PSt 600 (0.9%). Total column length in both solvents was 200 cm.

Figure 2 is calibration curves obtained by plotting the results in Figure 1 in addition to those of PEG in both solvents.

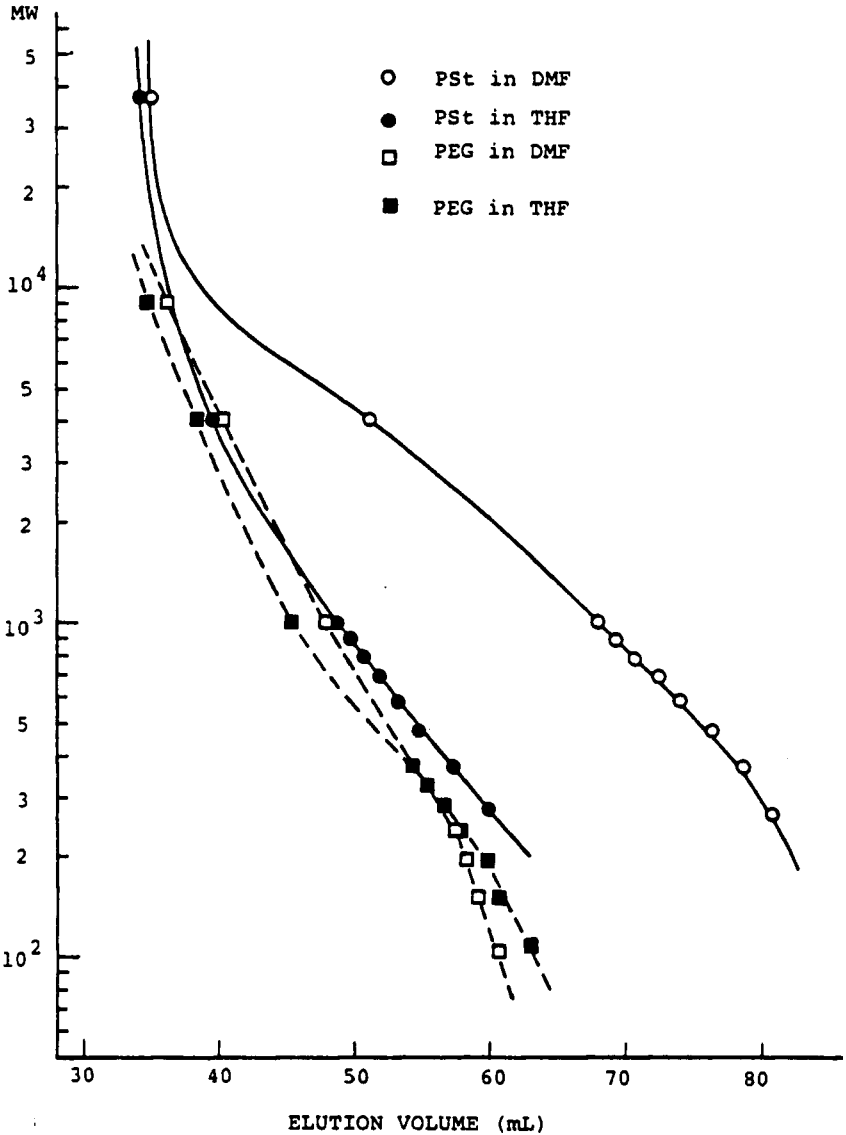


Figure 2. Relationship between molecular weight and peak elution volume for polystyrenes and polyethylene glycols in DMF and THF.

The divergence between calibration curves for PEG in DMF and THF was not so great as that for PSt. An increase in retention in

THF for PEG less than 300 MW was observed. The elution behavior of PSt in DMF may be explained by adsorption of the PSt on the apolar PSt gel (9). Hydrogen bonding of DMF to PEG probably decreases their elution volumes by enhancing their molecular volumes, resulting in the apparent convergence of their elution volumes in DMF and THF.

#### Melamine-formaldehyde resins

Polynuclear methylol melamines, which are soluble only in DMF and dimethylsulfoxide (DMSO), were resolved into individual polynuclear species using a PSt gel - DMF system. Figure 3 is a typical example of a methylol melamine condensate. Peak A is mononuclear methylol melamines which contain one melamine. Peak B is dinuclear ones which contain two melamines bridged by methylene ether or methylene. Peaks C, D, and E are estimated to be tri-, tetra-, and penta-nuclear methylol melamines. Trimethylol melamine may be a main component in Peak A. Resolution of mononuclear methylol melamines into individual methylol melamine was insufficient even with this column set (AD-802S x 8, 200 cm); only mono- and dimethylol melamines could be discriminated from the rest of methylol melamines (tri-, tetra-, penta-, and hexa-methylol melamines). A AD-801S column set may be needed for the separation of these mononuclear methylol melamines.

Alkyl ether derivatives of polynuclear methylol melamines obtained by the reaction of the methylol group with alcohol are soluble in THF. Figure 4 is the chromatogram of a methyl etherified product of polynuclear methylol melamines which are the similar resin as in Figure 3 but not identical. Description of peaks A, B, C, and D is the same as in Figure 3. Melamine number in peaks A' and B' may be the same as in peaks A and B, but the methylol number different. The retardation of the elution of the alkyl etherified sample in DMF was predominant, compared with the chromatogram in Figure 3, suggesting hydrogen bonding of DMF to a methylol group.

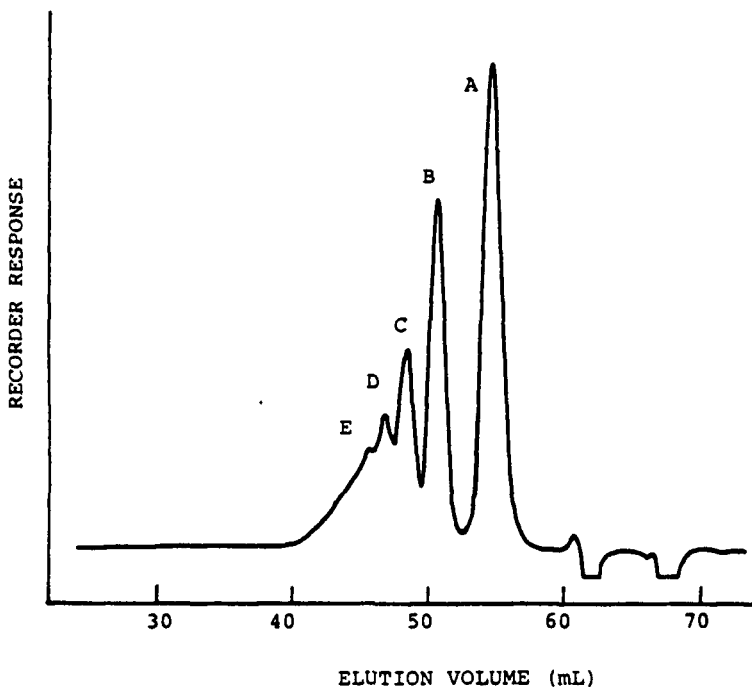


Figure 3. Chromatogram of a melamine-formaldehyde resin in DMF. Sample concentration was 1%. Description of A to E is in text.

The increase of molecular weights of methylol melamines in a condensation step when they are kept in high temperature can be monitored by using SEC of a PSt gel - DMF system as shown in Figure 5. A mixture of formaldehyde and melamine (mole ratio = 3 : 1) was reacted at pH 9.5 for 10 minutes (Figure 5, Ia), and was allowed to stand at 80 °C at pH 5.8 for 10 minutes (Ib), 20 minutes (Ic), and 30 minutes (Id). The number of melamine nucleus in methylol melamines increased with increasing the time allowed to stand in contrast to the decrease of a mononuclear methylol melamine. The stability of a 40% melamine-formaldehyde resin solution at pH 9.7 was estimated by leaving it at 70 °C for several hours (Figure 5, II). Polynuclear methylol melamines increased with increasing the time allowed to stand.



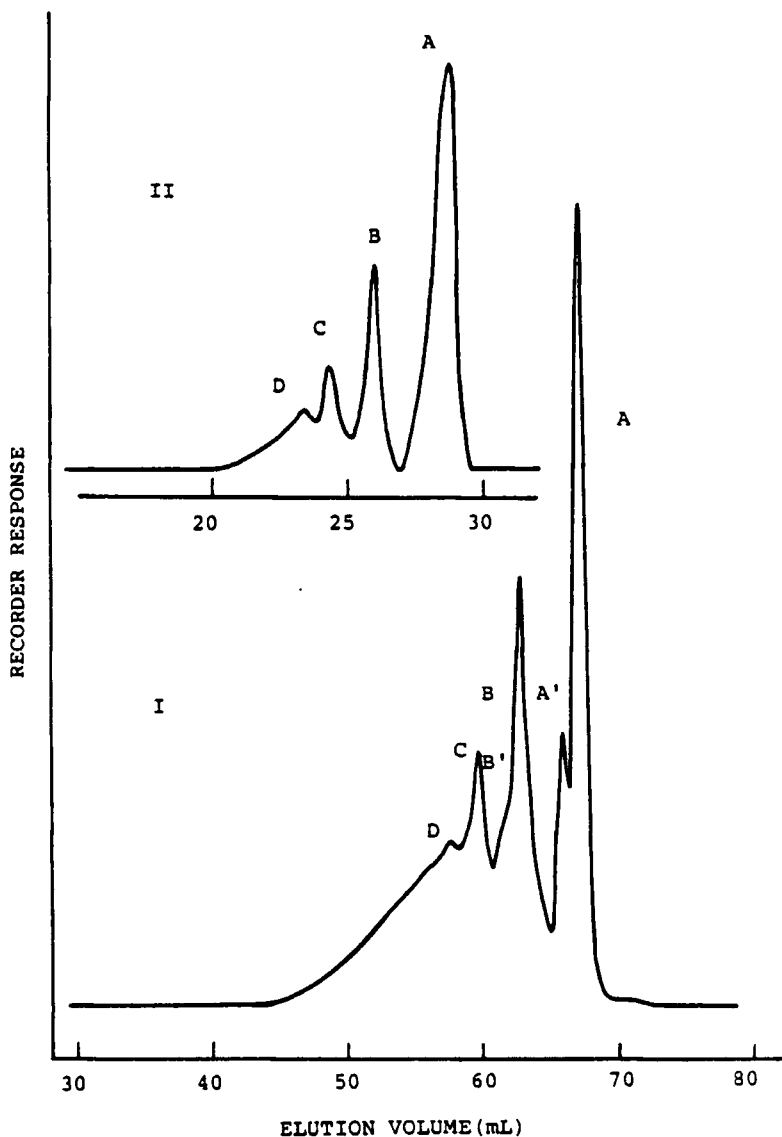


Figure 4. Chromatogram of a melamine-formaldehyde resin methyl ether in DMF (I) and THF (II). Description of A to D is the same as in Figure 3. Column length : (I) 200 cm; (II) 100 cm. Sample concentration and injection volume : (I) 1%, 100  $\mu$ l; (II) 0.2%, 250  $\mu$ l.

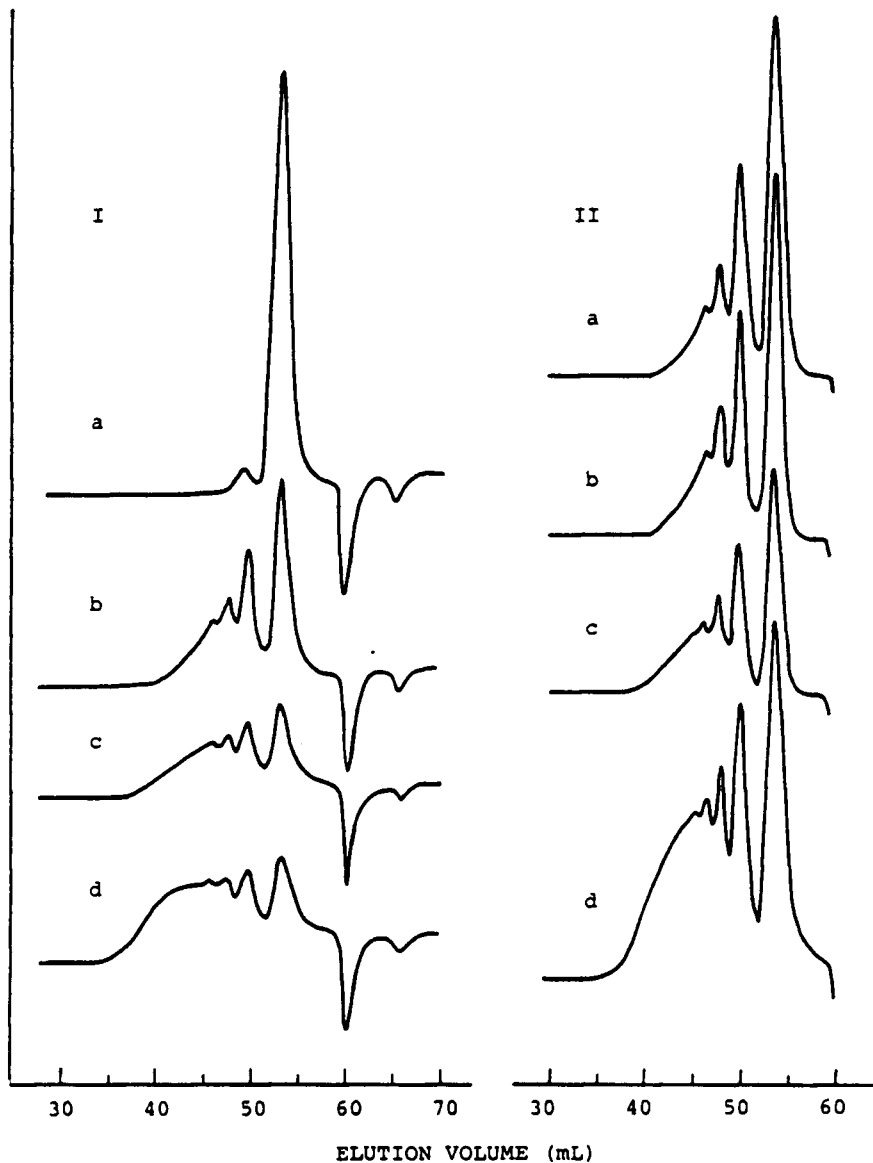


Figure 5. Variation of Chromatograms of methylol melamines in a condensation step under high temperature. (I) reaction time (minutes): (a) 0; (b) 10; (c) 20; (d) 30. (II) reaction time (hours): (a) 0; (b) 4; (c) 19; (d) 25. For the description of (I) and (II), see text.

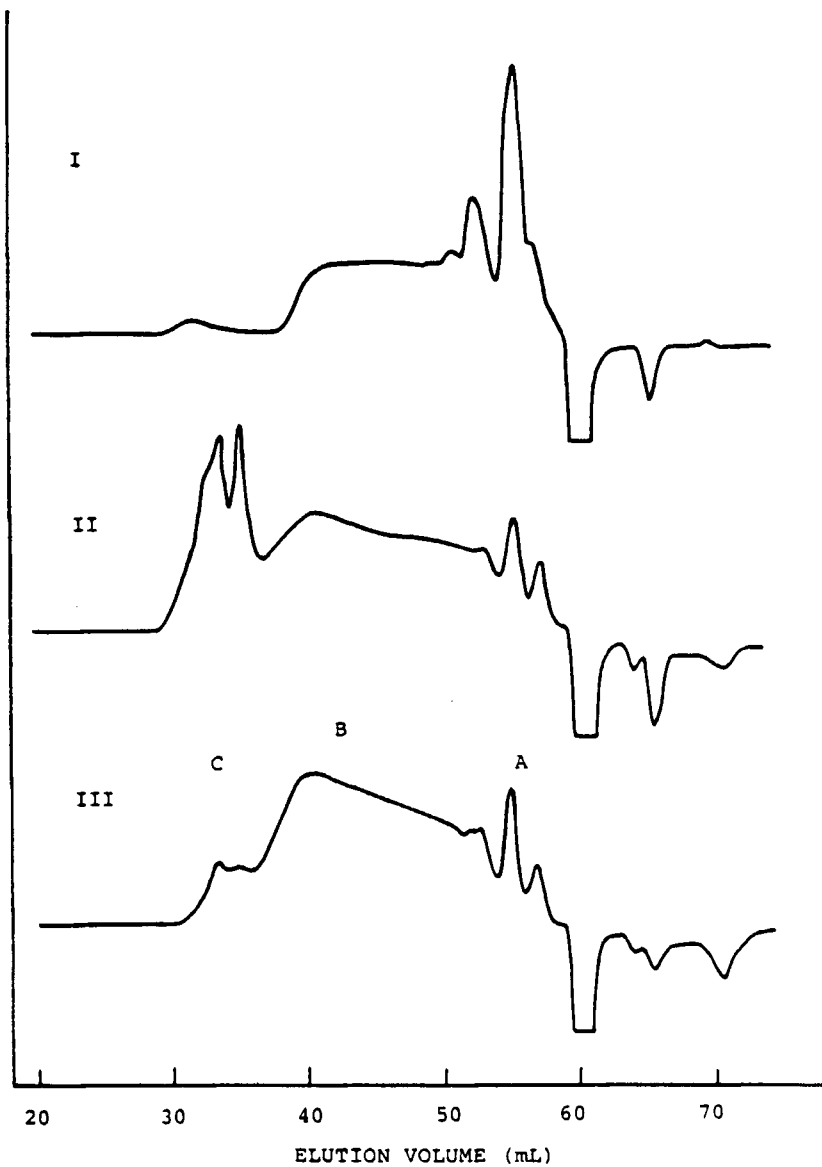


Figure 6. Chromatograms of urea-formaldehyde resins. Sample concentration : 1%. Formaldehyde/Urea mole ratio : (I) 1.4; (II) 2.0; (III) 2.5. For description of A, B, C, see text.

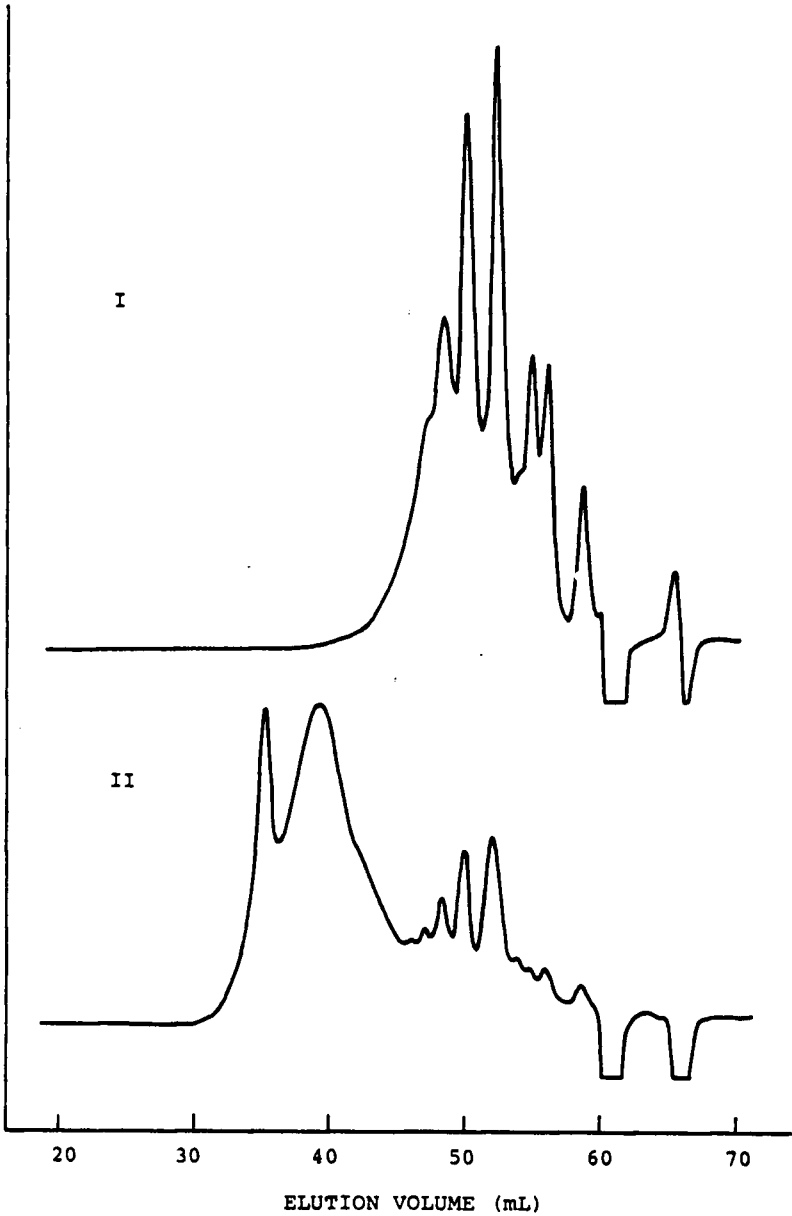


Figure 7. Chromatograms of phenol-formaldehyde resole resins. Sample concentration : 2%. For description of I and III, see text.

### Urea-formaldehyde resins

Figure 6 shows chromatograms of urea-formaldehyde resins reacted in weak alkaline solutions at different formaldehyde-urea mole ratios. Each chromatogram is divided into three groups. Group A is a portion of the resins at an early stage of reaction. Four peaks are observed and they may be mono- and diureas of mono- and dimethylol and similar products. A reaction product estimated to be dimethylol urea as average composition showed the similar chromatogram as group A. Groups B and C may be higher molecular weight resins obtained by condensation reaction. Urea resins hardly soluble in DMF were dissolved in DMSO or a mixture of DMF and DMSO and the solution was injected into the SEC system.

### Phenol-formaldehyde resole resins

Phenol resole resins, the alkali-catalyzed reaction products of phenol with formaldehyde, become insoluble in THF as the reaction proceeds. These resoles can be analyzed by SEC of a PST gel - DMF system as shown in Figure 7. Figure 7, (I) is an early stage reaction product and (II) an advanced stage.

### ACKNOWLEDGEMENTS

The authors wish to thank the member of the Instrument Products Department, Showa Denko Co., Ltd. for collaboration of this work.

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