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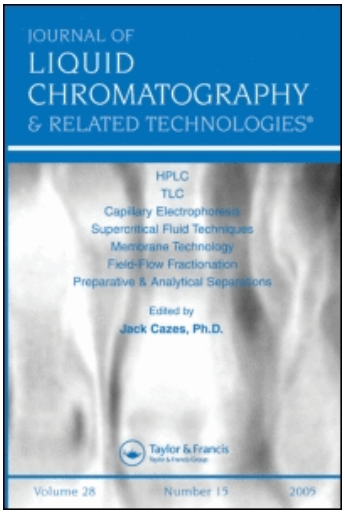

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Semimicro Size Exclusion Chromato-Graphy For Oligomers. II. Separation of Oligomers and Comparison With Conventional Columns

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SEMIMICRO SIZE EXCLUSION CHROMATOGRAPHY FOR OLIGOMERS. II. SEPARATION OF OLIGOMERS AND COMPARISON WITH CONVENTIONAL COLUMNS

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ABSTRACT

Sixteen columns of 1.5 mm i.d. x 25 cm length packed with polystyrene gels of a particle diameter 10 ± 2 μm and having the exclusion limit of 8000 molecular weight as polystyrene were connected in series and used for the separation of oligomers such as oligostyrenes, epoxy resins, methylated melamine-formaldehyde resins, and phenol-formaldehyde resins of novolac and resol types. The observed overall value of the number of theoretical plates was 103000 plates/4 m. Separation results were compared with the conventional SEC which used two SEC columns of 8 mm i.d. x 30 cm length packed with PS gels of a particle diameter 6 ± 2 μm and having the same exclusion limit of the semimicro SEC. The value of N of this column was 17500 plates/30 cm. Oligostyrenes up to n = 11 (undecamer) were separated. Methyl ether derivatives of polynuclear methylol melamines up to penta-nuclear methylol melamine were separated. The possibility for separation of overlapping peaks by SEC having clearly higher efficiency was discussed.

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INTRODUCTION

In part I of this series [1], packing procedure of polystyrene (PS) gels of a particle diameter 10 ± 2 μm into 1.5 mm i.d. x 25 cm length columns to obtain high-quality columns such as 8600 plates/25 cm has been demonstrated. This value was comparable to the conventional size exclusion chromatography (SEC) columns, which contained PS gels of the same particle diameter (10 ± 2 μm) and were packed by a manufacturer. Sixteen columns which have the value of the number of theoretical plates (N) between 5800 and 10000 were connected in series. The calculated overall value of N was 107000 plates/4 m and the observed one was 103000 plates/4 m.

In this paper, the separation of several oligomers with this combined column assembly is reported. The results are also compared with those for conventional SEC.

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EXPERIMENTAL

The SEC measurements were performed on a Jasco TRIROTAR-V high-performance liquid chromatograph (Japan Spectroscopic Co., Hachioji, Tokyo 192, Japan), which can deliver solvent at a 10-μL interval in the semimicro mode and at a 0.1-mL interval in the normal LC mode. A detector was an ultraviolet (UV) absorption detector Model UVIDEC-100II in which a semimicro flow cell (0.5 mm i.d. x 5 mm length; cell volume, 1 μL) or a normal flow cell (1 mm i.d. x 10 mm length; cell volume, 8 μL) can be installed. The sample-injection volume was regulated by time by using a loop injector Model VL-611.

Sixteen columns of semimicro size (1.5 mm i.d. x 25 cm length each) were connected in series. PS gels of a particle diameter 10 ± 2 μm were packed according to the previous report [1]. These gels have the exclusion limit of 8000 molecular weight as PS (comparable to the SEC column Shodex A802). Two Shodex SEC columns KF802 (8 mm i.d. x 30 cm length each; a particle diameter 6 ± 2 μm) were used for comparison purpose. The value of N of this column

was 17500 plates/30 cm (HETP = 17.1 μm) when a portion of 20 μL of 0.5% benzene solution was injected at flow rate of 1.0 mL/min THF.

Sample oligomers were oligostyrenes, epoxy resins, prepolymers of methylated melamine-formaldehyde resins and phenol-formaldehyde resins (novolac and resol resins). Oligostyrenes and epoxy resins are commercially available. Prepolymers of melamine resins and phenol resins were prepared in our laboratory. The mobile phase was tetrahydrofuran (THF) at a flow rate of 40 μL/min. The UV detector was set to 254 nm. SEC was performed at room temperature. Sample solutions were each 0.5% and a 4-μL portion of the solutions was injected. For conventional SEC, the flow rate was 1 mL/min and the injection volume of sample solutions was 30 μL.

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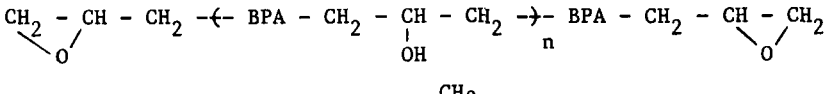
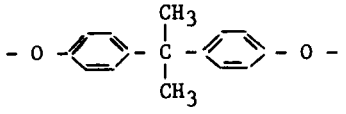
RESULTS AND DISCUSSION

SEC chromatograms of oligostyrenes (A-300 and 600) are shown in Figures 1 and 2. In Figure 1(a), eight peaks from n = 1 (equivalent to n-hexylbenzene) to n = 8 (octamer) can be seen. However, separation on KF802 columns (Figure 1 (b)) was not enough to observe oligostyrenes of n = 7 (heptamer) and n = 8. In Figure 2(a), ten peaks from n = 2 (dimer) to n = 11 (undecamer) can be counted, though only eight peaks can be seen in Figure 2(b). A peak on Figure 1 (a) at retention time 96 minutes was a ghost peak.

Figures 3 and 4 show the SEC chromatograms of commercial epoxy resins EPIKOTE 828 and EPIKOTE 1001. Similar results have been obtained between semimicro and conventional SEC in these cases. No special improvement in separation was observed even in semimicro SEC. The structure of epoxy resins in this work is illustrated as follows:



where BPA is



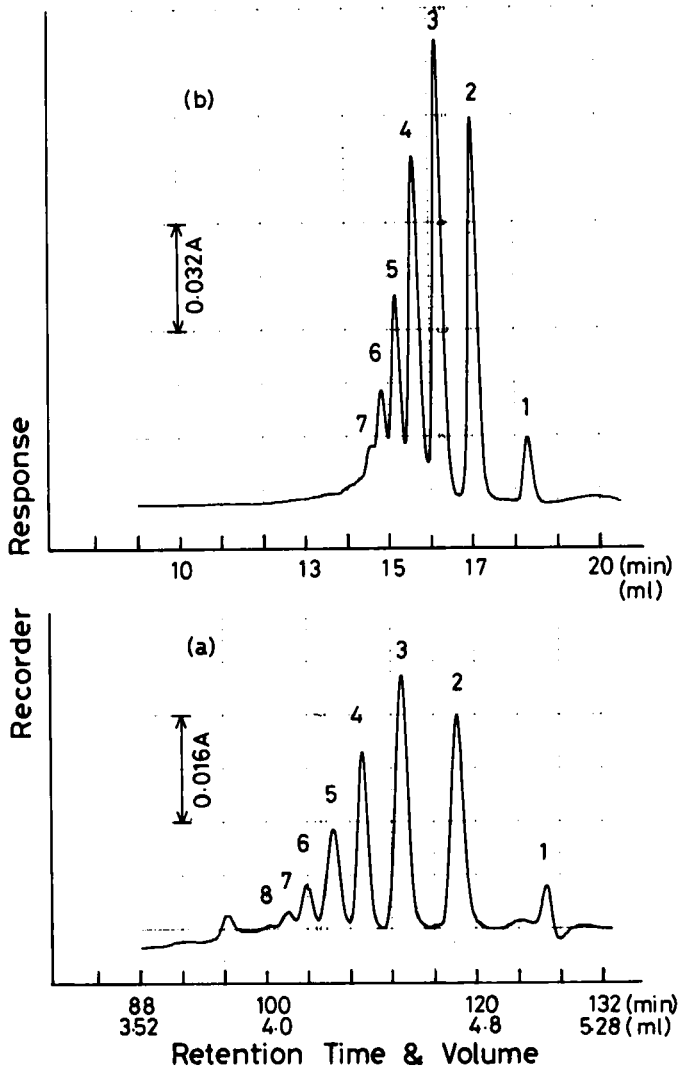


FIGURE 1. SEC chromatograms of oligostyrene A-300(average molecular weight 300).

(a) Semimicro SEC. Sample: 0.5%, 4 μL; flow rate: 40 μL/min; pressure: 50 - 60 Kg/cm^2; detector: UV at 254 nm, 0.16 AU FS; column: 1.5 mm i.d. x 25 cm x 16

(b) Conventional SEC. Sample: 0.5%, 30 μL; flow rate: 1 mL/min; pressure: 30 Kg/cm^2; detector: UV at 254 nm, 0.32 AUFS; column: 8 mm i.d. x 30 cm x 2

Numerals in the drawing represent the degree of polymerization.

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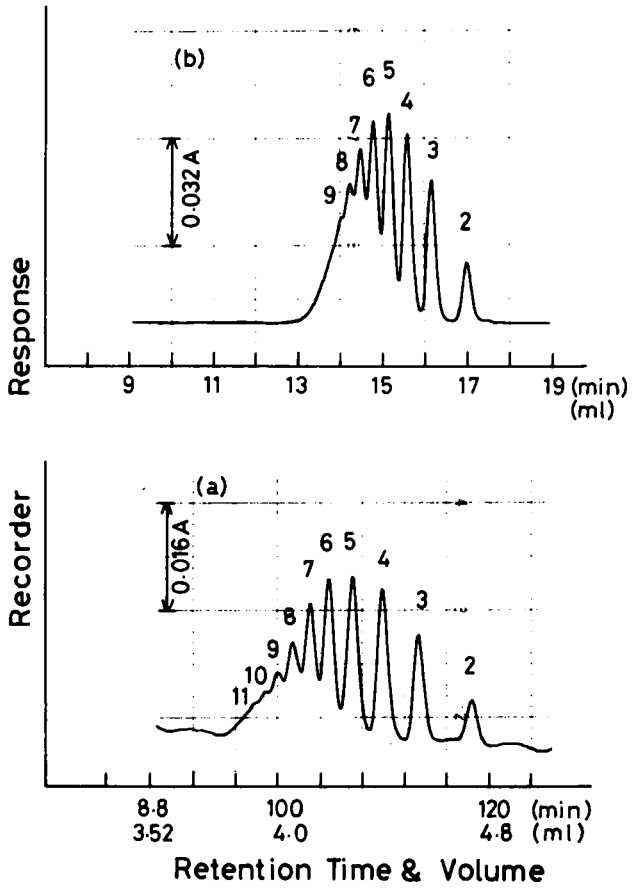

FIGURE 2. SEC chromatograms of oligostyrene 600 (average molecular weight 600).

Conditions are same as those in FIGURE 1.

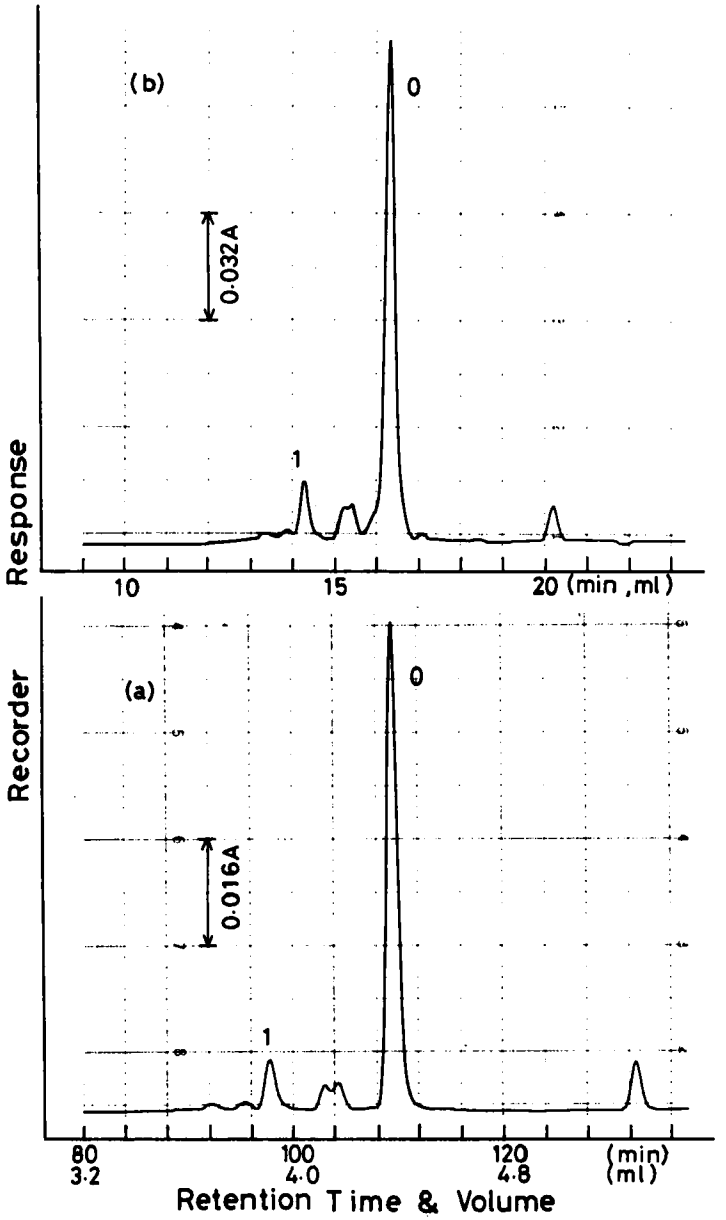

FIGURE 3. SEC chromatograms of epoxy resin EPIKOTE 828. Conditions are same as those in FIGURE 1.

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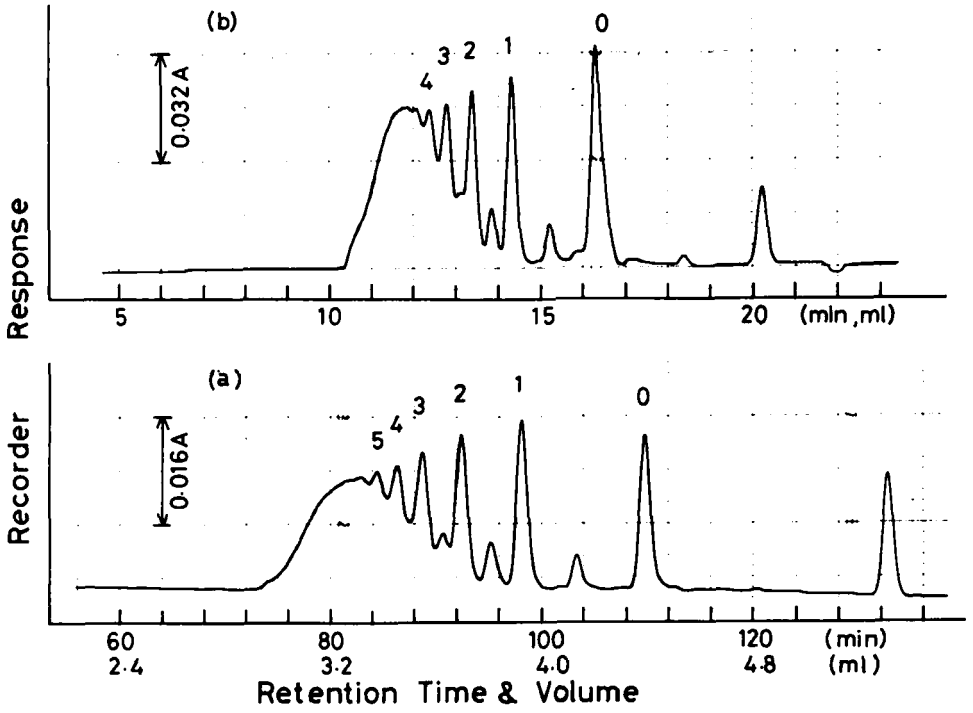

FIGURE 4. SEC chromatograms of epoxy resin EPIKOTE 1001. Conditions are same as those in FIGURE 1.

Methyl ether derivatives of polynuclear methylol melamines obtained by the reaction of the methylol group with methanol were separated and the SEC chromatograms are shown in Figure 5. Peak 1 is mononuclear methylol melamine which contains one melamine and is separated into three fine peaks. These peaks might be concerned with some of six mononuclear methylol melamines (mono-, di-, tri-, tetra-, penta-, and hexa-methylol melamines)[2]. Peak 2 is dinuclear one which contains two melamines bridged by methylene ether or methylene linkages. Peaks 3, 4, and 5 are estimated to be tri-, tetra-, and penta-nuclear methylol melamines.

Figure 6 is the SEC chromatogram of phenol-formaldehyde resines of novolac type which were prepared with an acid catalyst.

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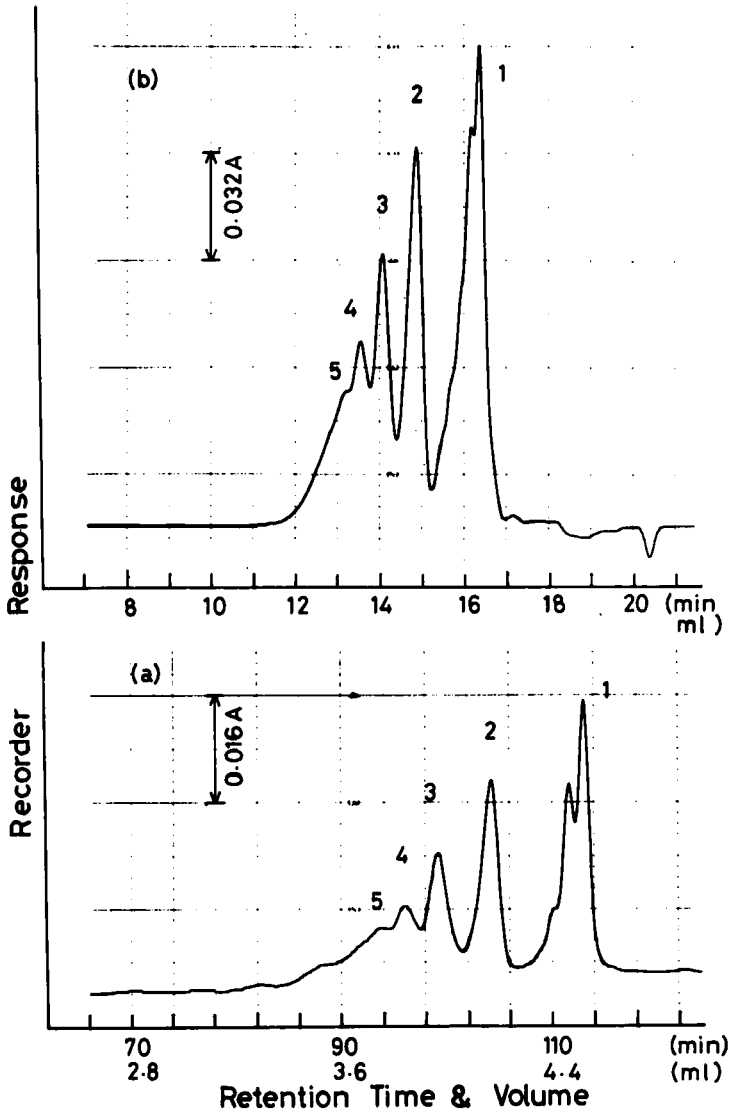

FIGURE 5. SEC chromatograms of methylated melamine-formaldehyde resin prepolymer.
Conditions are same as those in FIGURE 1.

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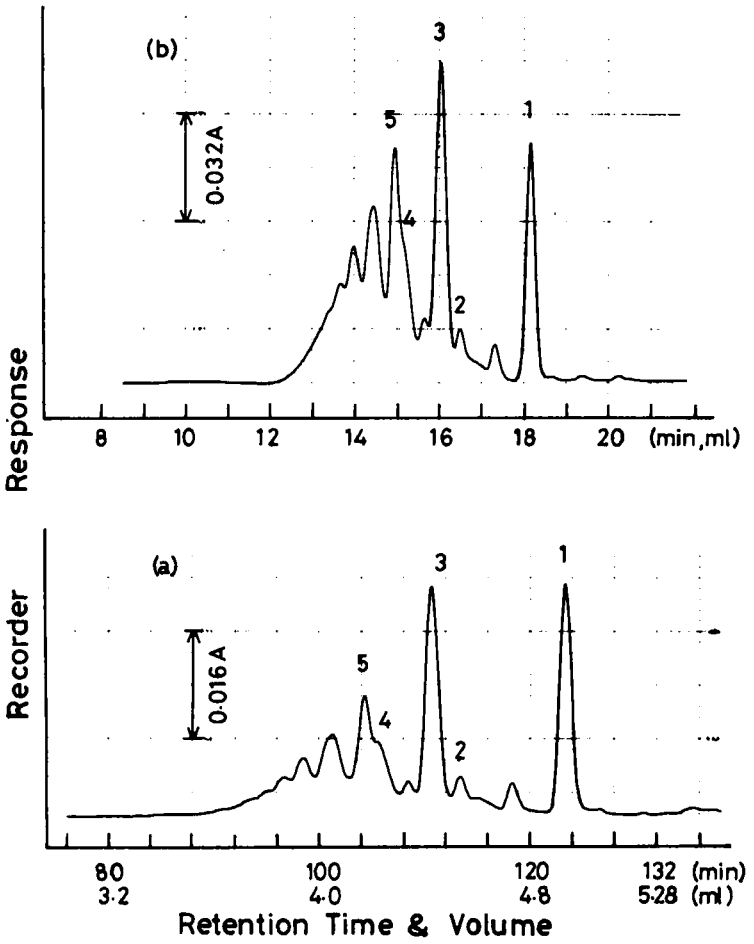

FIGURE 6. SEC chromatograms of phenol-formaldehyde resin prepolymer (novolac type). 1. Phenol, 2. 2,2'-DPM, 3. 2,4'- & 4,4'-DPM, 4. 2,2',6',4"-, 2,2',4',2"- and 2,2',6',2"-trimer, 5. 4,2',4',4"- and 4,2',6',4"-trimer.

Other conditions are same as those in FIGURE 1.

Phenols are linked each other with a methylene group to form the linear polynuclear novolac. Peak 1 is phenol. Peak 2 is 2,2'-DPM (dihydroxy diphenyl methane) and peak 3 is a mixture of 2,4'- and 4,4'-DPM [3,4]. Peak 4 is a complex of 2,2',6',4"-, 2,2',4', 2"- and 2,2',6',2"-trimer of phenol bound by the methylene linkage and peak 5 is that of 4,2',4',4"- and 4,2',6',4"-trimer [3]. A peak between peaks 1 and 2 is probably 2-methylol phenol (MP).

Figure 7 is the SEC chromatogram of phenol-formaldehyde resols. Peak 2 is 2-MP. Peak 3 is a mixture of 4-MP and 2,6-dimethylol phenol (DMP) [3,4]. Peaks 4 and 5 are 2,4-DMP and 2,4,6-TMP, respectively.

In SEC, it is possible to assume that peak width is constant over the elution range. Then, the resolution R_s of two adjacent bands 1 and 2 is defined as

$$R_s = \frac{V_2 - V_1}{1/2(W_1 + W_2)} \fallingdotseq \frac{V_2 - V_1}{W} \qquad (1)$$

$$W = W_1 \fallingdotseq W_2$$

where V_1 and V_2 are the retention volumes of bands 1 and 2 and W_1 and W_2 are the peak widths of them, respectively. The number of theoretical plates N for the peak which has the highest retention volume V_R is expressed as

$$N = 16\left(\frac{V_R}{W}\right)^2 \qquad (2)$$

In order for two adjacent bands 3 and 4 to obtain the same resolution of the adjacent bands 1 and 2, that is,

$$R_s = \frac{V_2 - V_1}{W} = \frac{V_4 - V_3}{W'} \qquad (3)$$

the value of N' should be

$$N' = 16\left(\frac{V_R}{W'}\right)^2 \qquad (4)$$

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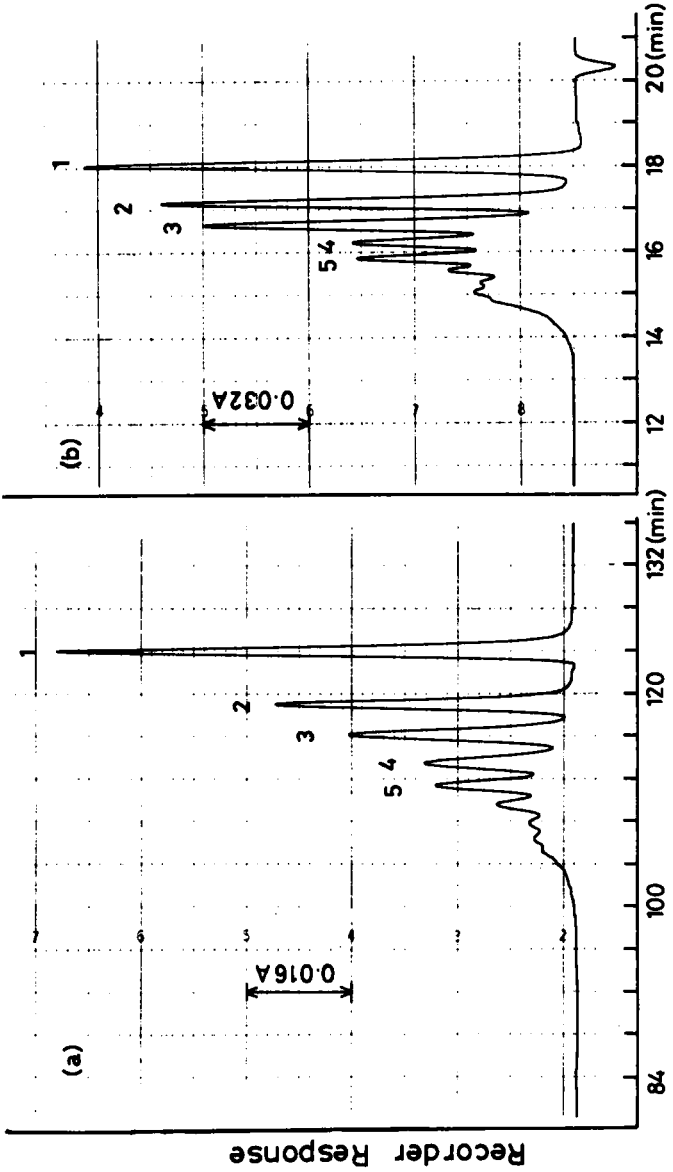

FIGURE 7. SEC chromatograms of phenol-formaldehyde resol resins。
1. Phenol, 2。2-MP, 3。4-MP (2,6-DMP), 4. 2,4-DMP, 5。2,4,6-TMP.
Other conditions are same as those in FIGURE 1.

Therefore,

$$\frac{N'}{N} = \left(\frac{W}{W'}\right)^2 \quad (5)$$

$$= \left(\frac{V_2 - V_1}{V_4 - V_3}\right)^2 \quad (6)$$

For example, if two adjacent peaks 7 and 8 in Figure 2 (a) should bave the same resolution of the adjacent peaks 4 and 5, two and a half times the value of N, i.e., 250,000 plates, is required. In order to separate other two adjacent peaks more closely spaced, much more values of N is needed. Recent knowledge of separation tells us that these overlapping peaks for oligomers can be resolved better by reversed-phase liquid chromatography than SEC.

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