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Note

High-performance aqueous gel-permeation chromatography of oligomers

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Gel-permeation chromatography (GPC) is a type of liquid chromatography in which the separation is based only on the molecular size of the solute in solution, and hence the setting of the experimental conditions and the interpretation of the results obtained are easy. In general, however, GPC is slow and has a low resolution in comparison with other liquid chromatographic techniques. Therefore, GPC has rarely been applied to the separation of low-molecular-weight compounds and has been mainly employed to separate high-molecular-weight compounds. However, high-resolution columns packed with microparticulate polystyrene gels were developed a few years ago[1], and high-speed GPC with satisfactory resolution was attained[2]. As a result, the possible applications of GPC have been extended to small molecules in organic solvent systems[3,4]. Also in aqueous systems several column packings have been developed for use in high-speed measurements. However, those column packings have adsorptivity, resolution or pore size disadvantages.

Recently, GPC columns packed with microspheres of hydrophilic polymer gels have become commercially available (TSK-GEL, Type-PW; Toyo Soda Manufacturing Co.). These columns can be operated under high pressure in aqueous systems and have a large number of theoretical plates (more than 4000 or more than 6000 plates/ft.). Moreover, several grades of columns with different pore sizes are available. High-speed GPC of ethylene glycol oligomers was performed with two grades of TSK-GEL, Type-PW, with small pore sizes (G2000PW and G3000PW), in order to investigate the resolution and the separation range of these columns. The results are described in this paper.

EXPERIMENTAL AND RESULTS

GPC measurements were carried out at 55° on a commercial gel-permeation chromatograph, HLC-801A (Toyo Soda Manufacturing Co.), with two G2000PW columns or with two G3000PW columns. Each column was 2 ft. long with an I.D. of 0.305 in., all were packed with gel particles of diameter 12–15 μm and had almost the same theoretical plate numbers and pressure drops. In Fig. 1, flow-rate dependences of the theoretical plate number and the pressure drop are shown for G3000PW. Distilled water was used as the solvent, the flow-rate was 1.4 ml/min, the injection volume was 0.18 ml and the sample concentration was varied between 1 and 18 mg/ml depending on the molecular weight distributions of the samples. Narrow molecular

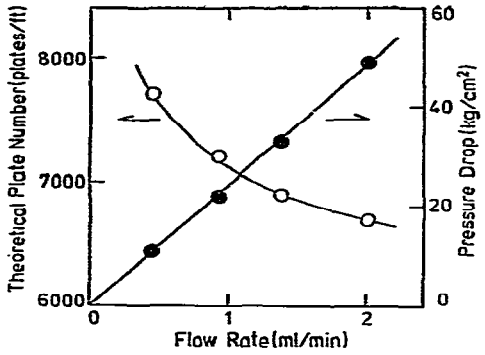

Fig. 1. Flow-rate dependences of the theoretical plate number (○) and the pressure drop (●) for a G3000PW column. The theoretical plate number was measured with ethylene glycol.

weight distribution polyethylene glycols purchased from Wako (Osaka, Japan) shown in Table I, were used as samples.

TABLE I

POLYETHYLENE GLYCOL SAMPLES

Sample No.	*Molecular weight**	*Sample No.*	*Molecular weight**
I	20,000	VI	600
II	7500	VII	400
III	3000	VIII	200
IV	1500	IX	62
V	1000		

* Manufacturer's data.

Figs. 2 and 3 show the elution curves of polyethylene glycols measured with the two-column systems. Samples I, II and III were eluted from the two-G2000PW

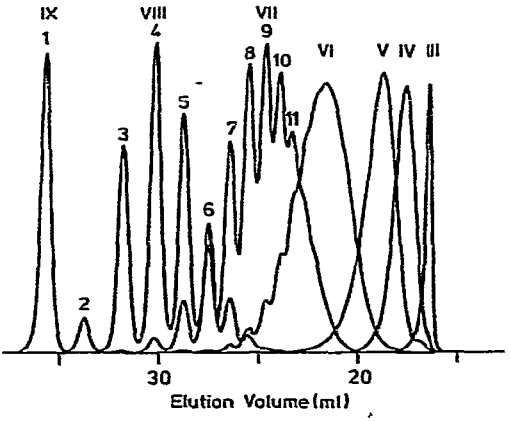

Fig. 2. Elution curves of polyethylene glycols measured with a two-G2000PW column system. Roman numerals (I–IX) are sample numbers and arabic numerals (1–11) are degrees of polymerization of the components.

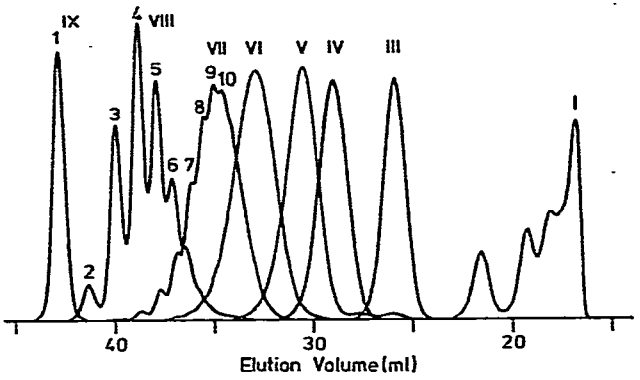

Fig. 3. Elution curves of polyethylene glycols measured with a two-G3000PW column system. Numerals as in Fig. 2.

column system at elution volumes corresponding to the void volume, and the elution curves of samples I and II have been omitted from Fig. 2. Sample II, the elution curve of which is not shown in Fig. 3, was eluted at the same position as the lowest molecular weight component of sample I in the two-G3000PW column system. Although the abscissa is expressed in terms of elution volume, it can be seen that ethylene glycol, which is the sample with the smallest molecular weight, was eluted from the columns within 30 min because the flow-rate was 1.4 ml/min. Peaks of components from the monomer to the decamer or undecamer were observed, which indicates that the resolution in this high-speed GPC is very high. Ethylene glycol oligomers have been measured by aqueous GPC with some other column packings, but resolutions as high as those in Figs. 2 and 3 were not attained even when the analysis time was several hours[5–7]. The specific resolution, R_s, which is useful for comparing the resolutions of different column systems, was calculated from the elution curve of sample VIII in Fig. 2 by using the equation

$$R_s = \frac{2(V_2 - V_1)}{(W_1 + W_2)(\log M_1 - \log M_2)} \quad (1)$$

where V, W and M represent the elution volumes, peak widths at the base and the molecular weights, respectively, of two components. Values of 12.6 and 15.9 were obtained for the dimer and trimer and for the tetramer and pentamer. These values are comparable to or greater than those obtained by high-speed GPC in organic solvent systems in the same molecular weight region[4,8].

Plots of molecular weight against peak elution volume (calibration graphs) are shown in Fig. 4. In the low-molecular-weight region, plots were made for each component separated. The molecular weight of a component with a degree of polymerization n, $(MW)_n$, was calculated by using the equation

$$(MW)_n = 18 + 44n \quad (2)$$

The void volume of the two-G3000PW column system could be determined because high-molecular-weight components in sample I were totally excluded from

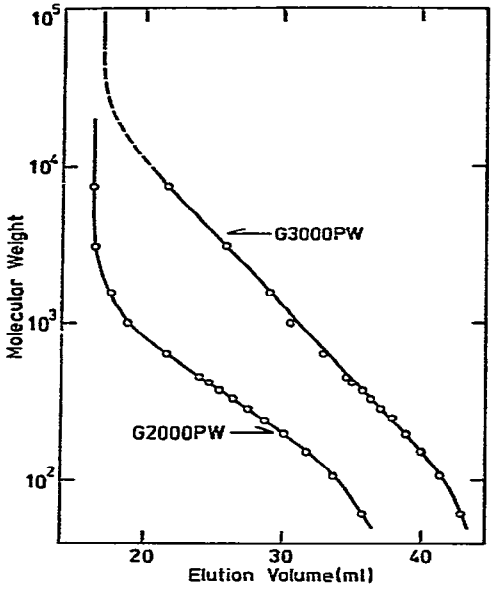

Fig. 4. Semi-logarithmic plots of molecular weight of polyethylene glycol *versus* elution volume for a two-G2000PW and a two-G3000PW column system.

this column system (shown in Fig. 3). Fig. 4 indicates that the molecular weight exclusion limits of G2000PW and G3000PW are 1500 and 20,000, respectively. Although both G2000PW and G3000PW have a resolving power in the region of molecular weights lower than 1000, G2000PW has a higher resolution than G3000PW. This is because the gradient of the calibration graph for G2000PW is smaller than that for G3000PW, and is clearly shown in the elution curves of samples VII and VIII in Figs. 2 and 3.

From the results, it can be concluded that the high-speed aqueous GPC of oligomers and small molecules on TSK-GEL, Type-PW, gives a satisfactory resolution, comparable to that in GPC with organic solvent systems.

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