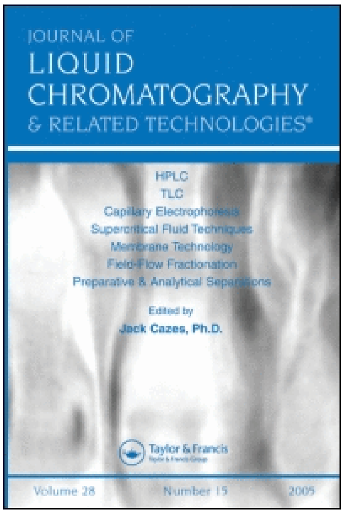

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OBSERVATION OF ABSENCE OF MECHANICAL DEGRADATION OF HIGH MOLECULAR WEIGHT POLYSTYRENES DURING ELUTION THROUGH A COLUMN IN SIZE EXCLUSION CHROMATOGRAPHY

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ABSTRACT

Size exclusion chromatography of several polystyrene (PS) standards of a narrow molecular weight (MW) distribution was performed with an on-line light scattering detector (MALLS) using Shodex SEC column KF 806L packed with PS gel packings. Tetrahydrofuran was used as the mobile phase and the flow rate was 1.0 mL/min. Mechanical degradation of the sample PS was not observed even the PS sample having MW four million daltons. MW averages obtained after elution were comparable to those of vendor's values. Peak width of RI (refractometer) chromatograms increased with increasing sample concentrations and polymer components composed of the chromatograms had approximately the same MW except both

ends of the chromatograms. This observation is attributed to the overloading effect and the preferable sample concentration should be as low as possible. The breakthrough volume was independent on the sample concentration, although the peak retention volume increased with the sample concentration. The decrease in molecular size with increasing sample concentration was not observed and therefore, the increase in the peak retention volume with increasing sample concentration is considered to be attributed to the overloading effect, not to the decrease in the hydrodynamic volume.

INTRODUCTION

High molecular weight polymers are fairly sensitive to shear degradation when the polymer solutions flow through capillary. Barth and Carlin reviewed the polymer shear degradation in size exclusion chromatography (SEC).[1] They listed an injection valve, capillary connecting tubing, column frits, and packed columns as possible sources of polymer degradation in SEC and estimated the shear rates generated in these sources. The shear rates generated in columns as a function of particle diameter for a given flow rate in a given inside diameter (I.D.) column were calculated. They concluded from this calculation that a shear rate below about $1x10^4$ s^{-1}, which would be attained at a flow rate of 3.0 mL/min in a 8-mm I.D. column packed with high performance packings of 5 µm, was probably sufficiently low to avoid shear degradation of most polymers of molecular weight (MW) less than $1x10^6$ and that for ultrahigh MW (over 10^6) polymers, flow rate of 0.2 mL/min in a 8-mm I.D. column might be necessary.

A single pass through the conventional SEC system (polystyrene (PS) gel packings over 40 µm) seriously degraded $4.37x10^7$ MW PS by a twofold factor.[2] Polymer degradation is flow rate dependent and was first noticeable for poly(isobutylene) having MW of $1x10^6$ at flow rates greater than 0.15 mL/min.[3] At a flow rate of 2 mL/min, MW decreased by almost a factor of two. Shear degradation effects of PS of MW of $2.7x10^6$ to $7X10^6$ were studied using high performance columns (8 mm I.D.) packed with PS gel and silica gel at a flow rate of 2 mL/min.[4] No MW decrease was observed for the PS gel column, whereas, some degradation was observed for the silica gel column.

A small pore size and particle diameter of packings enhances the degradation.[5] Solvent compatibility with PS gels is also important. A recommendable SEC procedure was proposed;[5] use the lowest possible flow

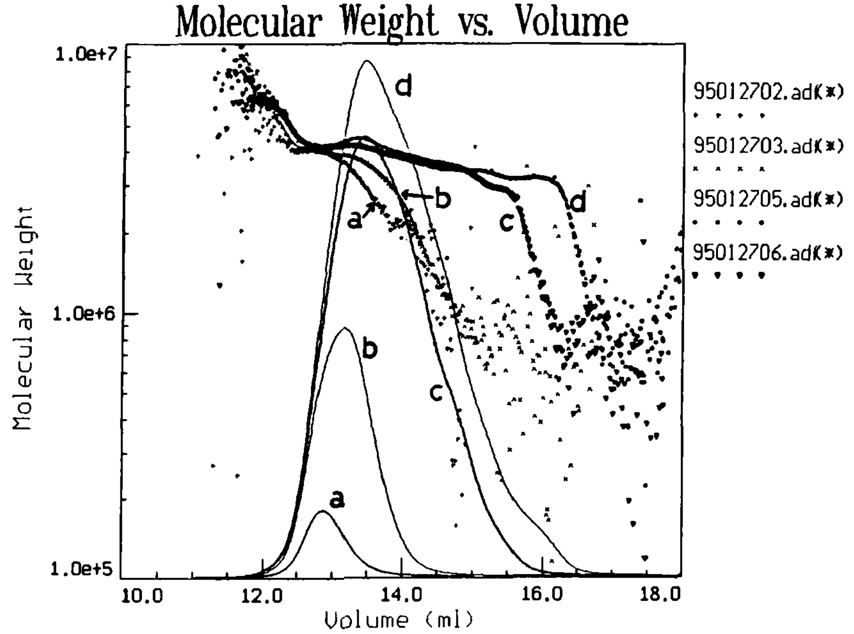

Figure 1. RI chromatograms for PS 4000K at different concentrations and the relationship between V_R and log MW (1). Concentration (%): a 0.0197; b 0.100, c 0.309; d 0.398.

rates and pressures; use the largest interstitial volumes; avoid low pore sizes; use swelling solvents; use concentrations well below the entanglement region and as low as can be detected. The degradation of PS standards of MW of 4.2×10^6 and 2.3×10^6 after elution through SEC columns was observed with calculated MW of 1.0 - 1.1×10^6 and the source of degradation was considered to be attributed to the 2 μm exit frit in a column.[6]

Tendencies in recent high performance SEC are to use column packings of lower particle diameter less than 5 μm and narrower I.D. columns of 6-mm I.D. instead of 8-mm I.D. Recent developments in polymer science require characterization of ultrahigh MW polymers by SEC. Under these circumstances, it is important to ascertain the shear degradation during elution through SEC columns of user's own.

The object of this work was to ascertain whether the degradation of PS standards having high MW was observed or not when the PS standards passed

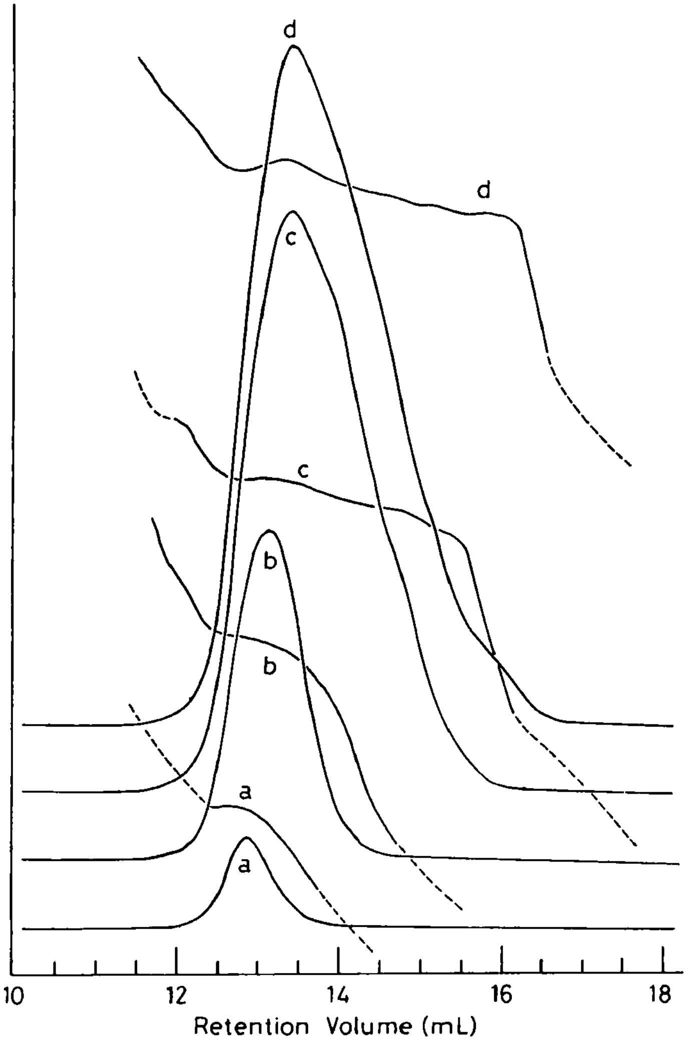

Figure 2. RI chromatograms for PS 4000K at different concentrations and the relationships between V_R and log MW (2). Concentration (%): same for Figure 1.

through commercially available SEC columns used in our laboratory and to study overloading and concentration effects by SEC/on-line light scattering photometry.

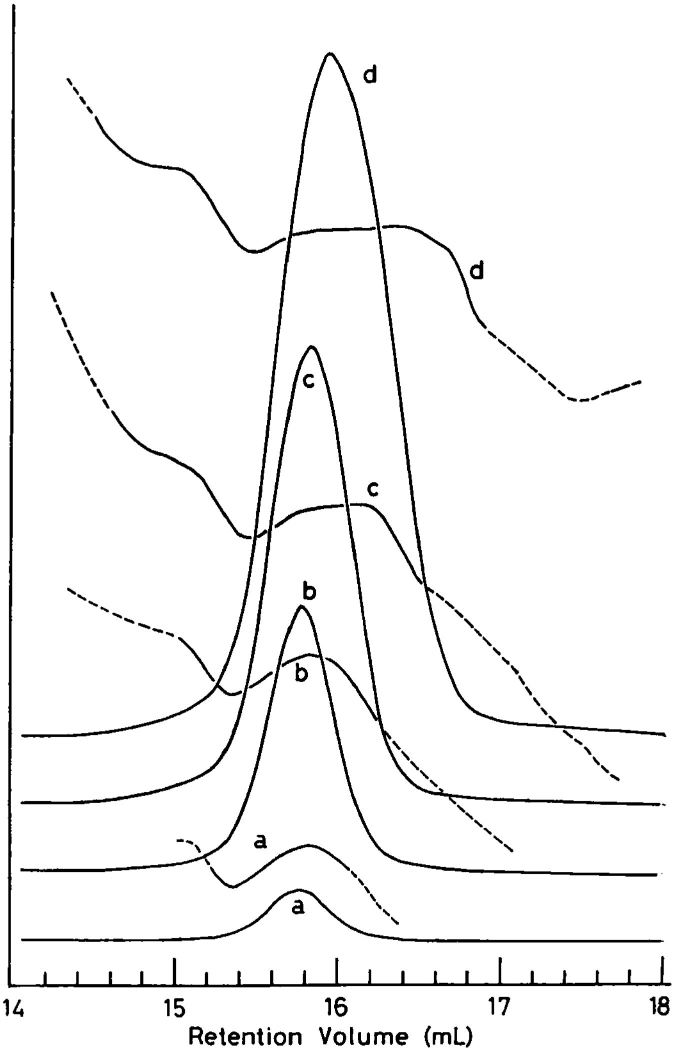

Figure 3. RI chromatograms for PS 200K at different concentrations and the relationships between V_R and log MW. Concentration (%): a 0.0203; b 0.101; c 0.203; d 0.406.

EXPERIMENTAL

Samples

Three PS standards of narrow MW distribution were used: PS 200K and PS 900K obtained from Pressure Chemical Co. (Pittsburgh, PA) and PS 4000K from Showa Denko Co. (Minato-ku, Tokyo, Japan). Vendor's values of MW averages determined by low-angle laser light scattering (LALLS) photometer were 2.16×10^5, 9.29×10^5, and 4.056×10^6, respectively. The PS standards were dissolved in tetrahydrofuran (THF) in the concentrations of 0.02, 0.1, 0.2 (or 0.3) and 0.4 (w/v)%. After being left for one day in a dark place, the sample solutions were filtered with a 0.5 μm membrane filter.

Size Exclusion Chromatography

SEC measurements were performed on a Shodex Size Exclusion Chromatograph Model System-11 (Showa Denko) with a differential refractometer (RI) Model Shodex RI-71 and a multiple angle laser light scattering (MALLS) Model DAWN DSP-F (Wyatt Technology, Santa Barbara, CA). Columns were two Shodex KF806L (30 cm x 8 mm I.D.) which were linear columns packed with PS gel having the exclusion limit of PS MW over 1×10^7.

THF was used as the mobile phase. The flow rate was 1.0 mL/min and measurements were performed at room temperature (25-28°C). Injection volume of the sample solutions was 0.1 mL.

MALLS Parameters and Settings

Sixteen scattering angles ranging from 18.6° to 151.9° were used. ASTRA 3.0 software was used for data collection and further processing was done with the program EASI 6.0. Measurements were made at a wavelength of 632.8 nm. The specific refractive index increment for PS in THF (dn/dc, cm^3/g) was 0.185 measured with an interferometric refractometer Model Wyatt/Optilab 903. The second virial coefficients were 4.72×10^{-4} mL mol/g^2 for PS 200K, 3.33×10^{-4} for PS 900K, and 2.00×10^{-4} for PS 4000K, respectively. These values were taken from the literature.[7]

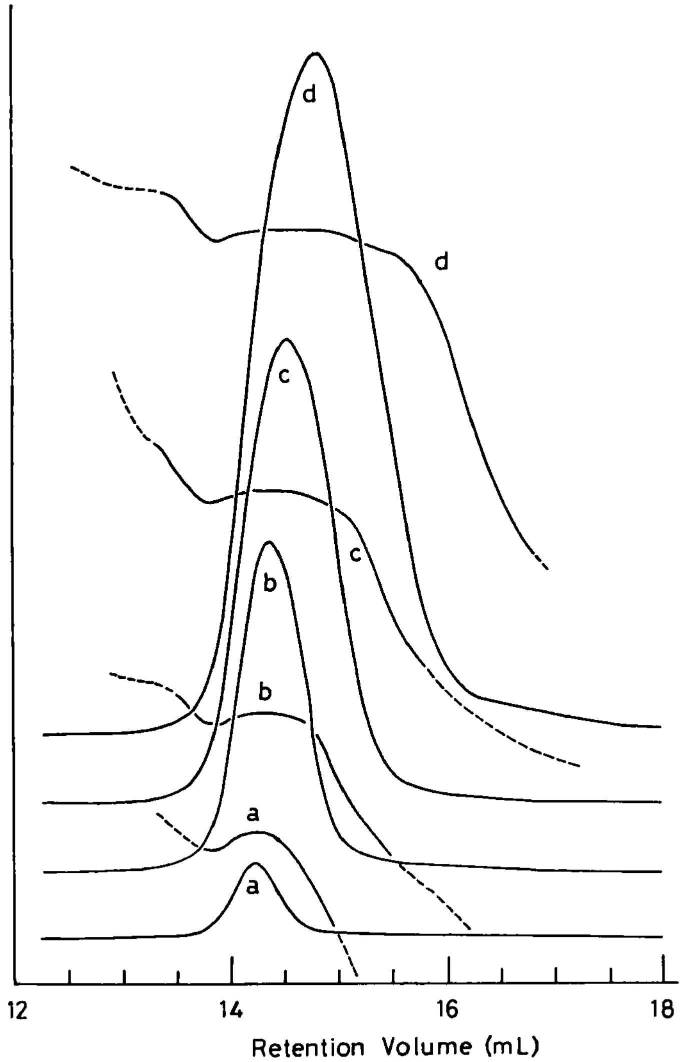

Figure 4. RI chromatograms for PS 900K at different concentrations and the relationships between V_R and log MW. Concentration (%): a 0.0201; b 0.107; c 0.201; d 0.403.

RESULTS

RI chromatograms and the relationships between retention volume (V_R) and log MW for PS 4000K at different concentrations were shown in Figure 1. Maximum MW near peak top was 4.09×10^6 at 12.70 mL for Figure 1 (a), 4.09×10^6 at 12.72 mL for (b), 4.22×10^6 at 13.23 mL for (c), and 4.54×10^6 at 13.3 mL for (d), respectively.

For the ease to see, the plots of the chromatograms and the relationship between log MW and V_R are shifted somewhat, and redisplayed in Figure 2. The abscissa is retention volume and the ordinate is the concentration of PS solutions for the RI chromatograms and log MW for the curves of the V_R - log MW relationship. Data points of log MW against V_R at the both ends of each peaks scattered as shown in Figure 1 and therefore, average points of these scattered data are drawn with a dotted line. Similarly, RI chromatograms and the relationships between retention volume (V_R) and log MW for PS 200K and PS 900K at different concentrations are shown in Figures 3 and 4, respectively, by shifting the plots of the chromatograms and the relationships.

Figures 5, 6 and 7 show RI chromatograms and the relationships between V_R and z-average root-mean square radius (RMS) for these three PS standards at different concentrations, respectively. Designation of the abscissa and the ordinate and the meaning of the dotted line are the same to those for Figures 1 to 3. The plots are also shifted somewhat for the ease to see.

Table 1 lists number- and weight-average MW, RMS in nm, and retention volume, MW, and RMS at peak top of the RI chromatograms for these three PS standards at different concentrations. As already stated, maximum MW for PS 4000K was not obtained at the peak top, but just before the peak top. However, for the case of PS 200K, maximum MW was obtained after the peak top: 2.42×10^5 at 15.87 mL for Figure 3 (a); 2.37×10^5 at 15.97 mL; 2.34×10^5 at 16.13 mL; and 2.31×10^5 at 16.38 mL. Maximum MW for PS 900K was nearly at the peak top in all concentrations tested.

DISCUSSION

Wang and Glasbrenner[6] reported the degradation of PS having MW of 4.25×10^6 and 2.3×10^6 after elution by SEC. MW observed after elution by on-line LALLS was 1.1 - 1.7×10^6 and 0.95- 1.0×10^6, respectively. The source of degradation was attributed to the 2 micron exit frit in the single Jordi mixed bed column.

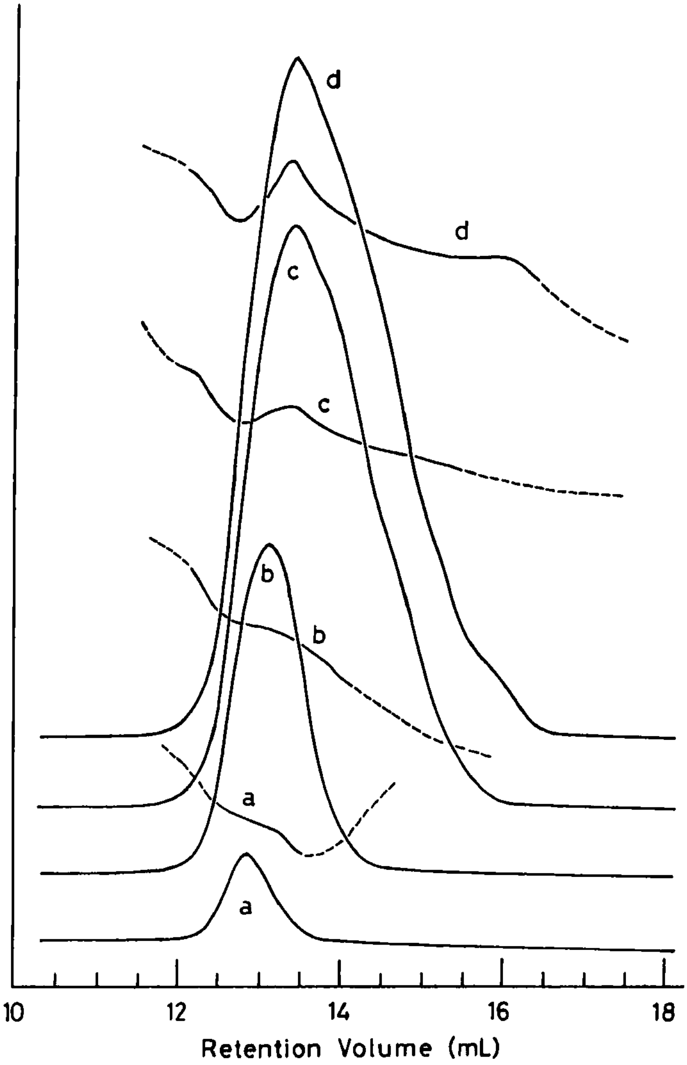

Figure 5. RI chromatograms for PS 4000K at different concentrations and the relationships between V_R and RMS. Concentration (%): a 0.0197; b 0.100; c 0.308: d 0.398.

Table 1

Molecular Weight, Root-Mean Square Radius and Retention Volume of PS Standards after Elution through SEC Columns

Standard	Conc. %	M_n x10^{-5}	M_w x10^{-5}	R_z nm	Vp mL	M_p x10^{-5}	R_p nm
200K	0.0203	2.17	2.20	16.7	15.75	2.28	16.2
	0.101	2.08	2.15	16.7	15.78	2.25	16.3
	0.203	2.11	2.19	17.4	15.85	2.26	17.0
	0.406	2.15	2.20	17.5	15.98	2.25	17.1
900K	0.0201	8.67	9.33	43.1	14.23	10.15	43.4
	0.107	9.16	9.57	44.4	14.38	10.15	44.5
	0.201	9.24	9.61	44.0	14.55	10.08	44.4
	0.403	7.97	9.50	44.7	14.83	10.30	46.0
4000K	0.0197	36.5	37.6	96.2	12.88	39.9	95.8
	0.100	35.7	37.4	96.8	13.15	39.0	97.0
	0.309	38.1	38.9	101.6	13.45	41.4	107.0
	0.398	39.1	39.9	107.1	13.45	44.7	123.0

M_n: number-average MW; M_w: weight-average MW; R_z: Z-average root-mean square radius; Vp retention volume at peak top of the RI chromatogram; M_p: MW at peak top of the RI chromatogram; R_p: RMS at peak top of the RI chromatogram.

However, as listed in Table 1, the degradation of PS after elution by SEC was not observed in our experiments. MW averages for PS 200K and PS 900k obtained after elution by SEC were comparable to those of vendor's values. In the case of PS 4000K, the former was somewhat lower than the latter, but not as much as observed by Wang and Glasbrenner.

The degradation of polymers accompanied by SEC measurements depends on packing materials in SEC columns as well as the exit frit in the column. Our experimental results were identical to those obtained by Ye and Shi.[4] As far as SEC measurements are performed using Shodex SEC column KF 806L packed with PS gel under the experimental conditions written in the **EXPERIMENTAL** section, the mechanical degradation of PS samples at least having MW less than 4x10^6 is beyond the anxiety. Critical MW for other

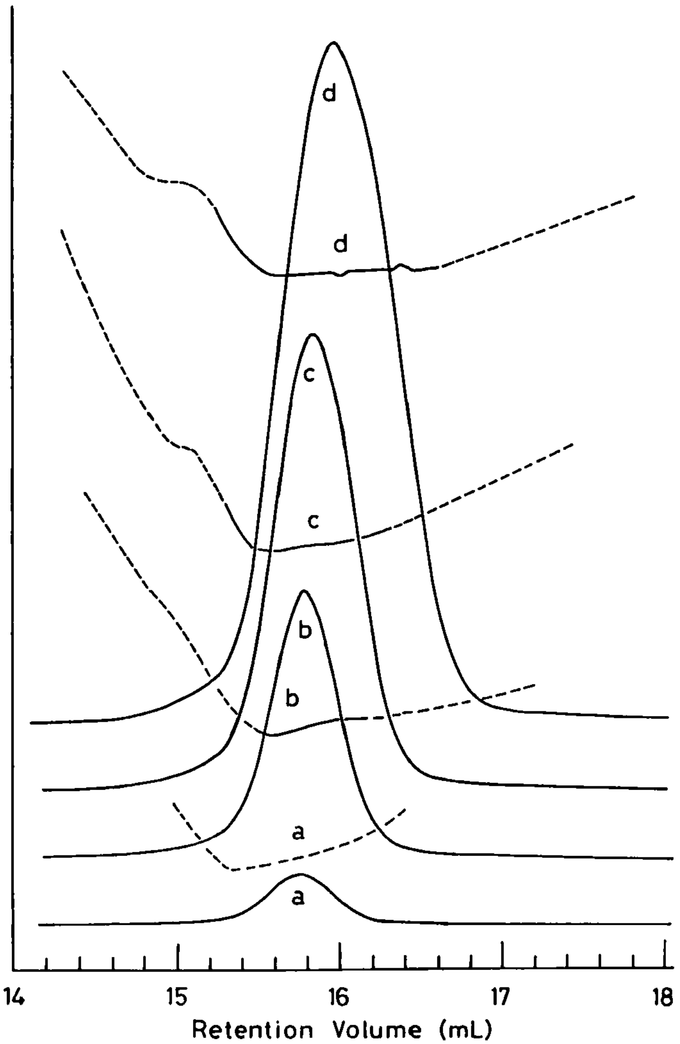

Figure 6. RI chromatograms for PS 200K at different concentrations and the relationships between V_R and RMS. Concentration (%): a 0.0203; b 0.101; c 0.203; d 0.406.

polymers must be determined experimentally.

When shear is applied, the most probable sites of stress concentration on the polymer chain are side chain linkages to main chain (branched points and crosslinked points in network).[8] Therefore, branched polymers may degrade more easily than linear polymers.[9] The degradation of polyolefins having MW less than $1x10^6$ were reported[3,9,10] and the extent of the degradation was flow rate dependent. PS having MW $7x10^6$ was degraded using 8 μm-silica particles as a packing material[11] and therefore, silica particles are not adequate as high performance SEC packing materials.[1,4,12]

From RI chromatograms and the log MW - V_R relationships, it can be seen that polymer components composed of the RI chromatograms had approximately the same MW except both ends of the chromatograms. This phenomenon was independent on the polymer concentration in the sample solutions injected. The peak width of RI chromatograms became broader and also the range of the retention volume where polymer components having the same MW eluted was increased with increasing the sample concentration. The breakthrough volume was independent on the sample concentration. However, the peak retention volume V_P increased with increasing the sample concentration. The decrease in RMS or R_P with increasing the sample concentration was not observed as shown in Figures 5 - 7 and Table 1.

Theoretically, separation by SEC is based on hydrodynamic size and polymer molecules having the same molecular size (and MW for the same type of polymers) should have the same retention volume. Therefore, the increase in the range of the retention volume where polymer components having the same MW eluted can be attributed to the overloading effect in addition to the column broadening effects. The preferable sample concentration would be as low as possible.

The increase in the peak retention volume V_P with increasing the sample concentration has been considered to be attributed to the decrease in the hydrodynamic volume of the polymer in the mobile phase.[1] However, our experimental results could not approve the consideration and from the observation that the breakthrough volume was independent on the sample concentration, the increase in V_P with the increase in the sample concentration should be considered to be attributed to the overloading effect not to the decrease in the hydrodynamic volume. Delayed elution due to the overloading is also considered to be due to the macromolecular compression or viscous fingering effect.

Sample polymers used in this experiment were those having a narrow MW distribution and the elution of the polymers was not a monotonic decrease in MW as retention volume increased. Under the same experimental conditions, the PS NBS 706 which was broad in a MW distribution was

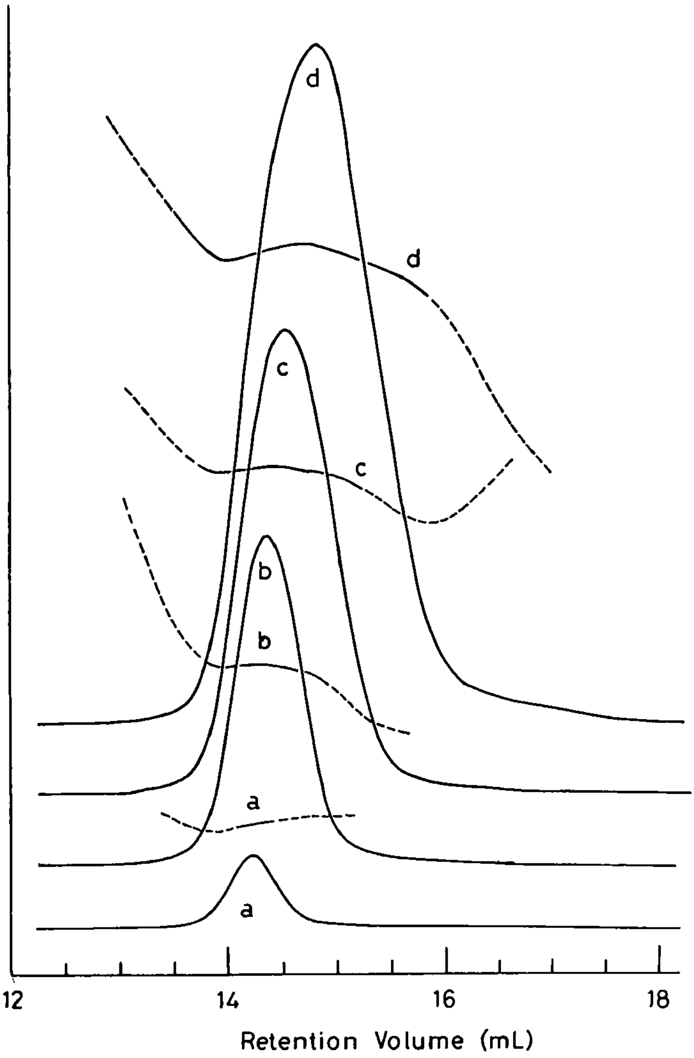

Figure 7. RI chromatograms for PS 900K at different concentrations and the relationships between V_R and RMS. Concentration (%): a 0.0201; b 0.107; c 0.201; d 0.403.

fractionated by the linear fractionation process, i.e., a monotonic decrease in MW as retention volume increased.

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