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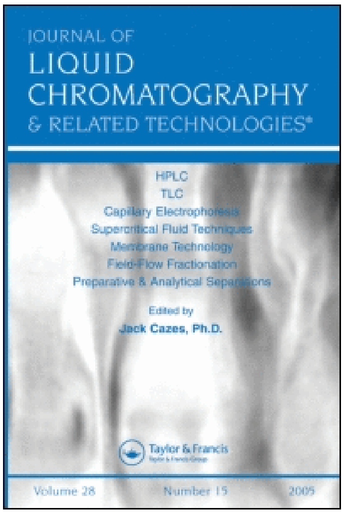

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MOLECULAR WEIGHT-RETENTION VOLUME RELATION FOR NARROW AND BROAD POLYSTYRENES BY SIZE EXCLUSION CHROMATOGRAPHY EQUIPPED WITH A LIGHT SCATTERING DETECTOR

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ABSTRACT

The difference of the relation of molecular weight (MW) and retention volume of narrow polystyrene (PS) samples from broad ones in the size exclusion chromatography - light scattering (LS)/refractive index (RI) detectors is discussed. Effects of interdetector delay volume on the relation was serious and the approach to adjust the interdetector delay volume so as to get a plateau relation of MW and retention volume for PS samples with a narrow MW distribution was proposed. The interdetector delay volume was found to be a function of MW. PS samples with a broad MW distribution had the similar relation of MW and retention volume to the calibration curve constructed with PS standards with narrow MW distributions; and the MW averages obtained by the LS/RI approach gave the comparable values to those calculated by a calibration curve method.

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On the other hand, PS samples with a narrow MW distribution had the plateau relation of MW and retention volume and the calculation of MW averages for such polymers using a calibration curve was found to be invalid unless a proper band-broadening correction is applied.

INTRODUCTION

Measurement of molecular weight (MW) averages of synthetic polymers by size exclusion chromatography (SEC) equipped with a concentration detector such as a differential refractive index (RI) detector requires the construction of a calibration curve of log MW vs. retention volume using polystyrene (PS) standards of a narrow molecular weight distribution (MWD). Employment of MW-sensitive detectors such as light scattering (LS) and viscosity detectors with a concentration detector increases the power of SEC analysis and can yield information on MW directly without SEC column calibration in advance. There are several types of commercially available LS instruments for SEC: the low-angle laser LS photometer (LALLS), the multi-angle one (MALLS), the triple-angle one (TALLS), the dual-angle one (DALLS), and the right-angle one (RALLS).

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The MALLS detector can provide information on both MW and the root-mean square radius of gyration, while the LALLS detector can give only the information on MW. Complicating the matter is the fact that MALLS produces much more data than does LALLS and involves many more computational options in data interpretation than does LALLS.[1] In order to interpret the LS signal, parameters of dn/dc (the refractive index increment of the polymer solution), the RI constant, and the interdetector delay volume in the connecting tubing between the measurement points of the LS cell and the RI cell must be determined at first. These parameters affect the calculated MW averages. Among these parameters, the interdetector delay volume must be known experimentally and precisely, because the geometric estimate of the interdetector delay volume is not suitable, and the experimentally obtained one is greater than the geometric one but it gives the best results.[2]

The deviation from a monodispersed size distribution for a solute in the column and in the detector cell is referred to as band broadening, peak broadening, axial dispersion, and many other terms.[3] Band broadening in SEC is adequately described by Tung's integral equation and the interpretation of data from SEC of polymers to obtain MW averages and MWD requires calibration of separation and corrections for band broadening using this equation.[4]

Recent advances of column technology make us ignore band broadening corrections. However, band broadening leads to an overestimate of sample polydispersity and weight-average MW, M_w, and to an underestimate of number-average MW, M_n, because of broadening of the eluting peak with the result that it appears to cover a wide MW range. Band broadening is particularly important when studying narrow MWD polymers and the presence of band broadening makes calculating the polydispersity of very narrow MWD samples difficult.

In the present paper, the difference of the relation of MW and retention volume of narrow PS samples from broad ones in the SEC-LS/RI system is discussed. Effects of interdetector delay volume on the relation was serious and band-broadening correction was very important for polymer samples of narrow MWD.

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EXPERIMENTAL

The SEC-MALLS/RI instrument system consisted of a Model TRIROTAR® -V pump (JASCO, Tokyo, Japan), two Shodex KF 806L SEC columns (300 mm x 8 mm i.d., Showa Denko, Tokyo, Japan), a Model RID-300 RI detector (JASCO), and a Dawn-F MALLS (Wyatt Tech., CA, USA). Data collection and handling were carried out using ASTRA® and EASY® software (Wyatt). Data points were collected every 1.0 s. The value for dn/dc used in the present work was 0.184 mL/g. Normalization of the MALLS instrument was performed using a solution SRM1478 and the RI constant was 3.4780×10^{-5} by adjusting the mass injected and the mass calculated. The mobile phase was tetrahydrofuran (THF) at the flow rate of 1 mL/min.

Samples were several PS standards of known MW averages: SRM1478, SRM 1479, SRM705a, and SRM706 purchased from National Institute of Standards and Technology (NIST)(MD, USA). The former three standards are narrow MWD PS samples and the last one is a broad MWD PS. The certified values of these polymers are listed in Table 1. Several other narrow MWD PS standards used for the calibration of the SEC system were obtained from Polymer Laboratories (Shropshire, UK).

All PS samples were dissolved in 0.1% concentration in THF except SRM706 which was dissolved in THF in 0.2% concentration. All sample solutions were filtrated with a membrane filter of 0.45μm and degassed under a vacuum. Sample injection volume was 0.1 mL.

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Table 1

Molecular Weight Average of SRM Polystyrene Standards Certified by NIST

Polymer	M_n		σ	M_w		σ	M_w/M_n
SRM1478	35,800	MO	0.4%	37,400	SE	0.7%	1.045
SRM1479				1,050,000	LS	4%	
SRM705a	170,900	MO	580	179,300	LS	740	1.049
				189,800	SE	2100	1.111
SRM706	136,500	MO		257,800	LS	930	1.889
				288,100	SE	9600	2.111

Note: MO = membrane osmometry; LS = light scattering; SE = sedimentaiton equilibrium.

RESULTS AND DISCUSSION

The determination of the interdetector delay volume between MALLS and RI detectors is the inherent matter of problem as for any other multidetector arrangements. The SEC system used in the present experiment connected an RI detector after MALLS with stainless-steel tubing of 67.3 cm in length and 0.25 mm i.d. (the volume was 0.033 mL).

Besides the volume of this tubing, the volume of two detector cells (0.03 mL for MALLS and 0.01 mL for RI) and of the tubing from the inlet at the RI detector panel to the inlet of the RI cell makes the delay volume and the total geometric delay volume may be approximately 0.10 mL. However, it is known that the geometric delay volume is much lower than the experimentally observed apparent delay volume and an optimal value for the apparent delay volume can be determined by experiment only.[2, 5]

A number of approaches can be used to determine the interdetector delay volume. The most commonly used approach for the determination of the delay volume for SEC-LS is to measure the difference of peak retention volumes of a narrow MWD polymer standard which is transported from the LS detector to the RI detector.[1]

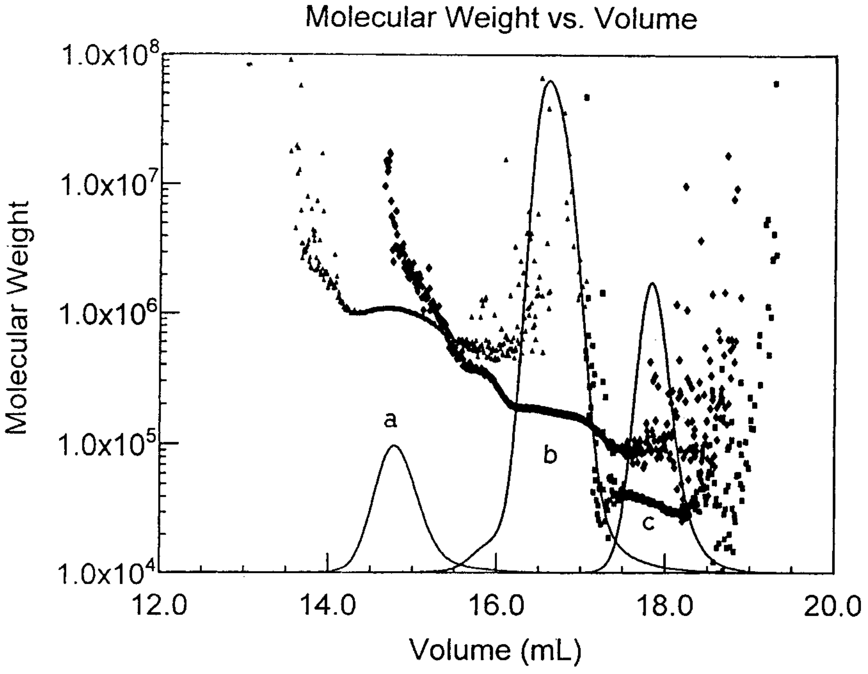

Figure 1. RI chromatograms and plots of measured molecular weight vs. retention volume for three narrow molecular weight distribution polystyrenes at the interdetector delay volume 0.216 mL. (a) SRM1479, (b) SRM705a, (c) SRM1478.

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In our experiment, the difference was 0.216 mL for SRM1478 and SRM1479 (the 90° LS signal was chosen for this purpose) and this value was first used as the interdetector delay volume. Figure 1 shows RI chromatograms of three PS samples, SRM1478, SRM1479, and SRM705a and the relationship of MW and retention volume obtained by using the interdetector volume of 0.216 mL.

The interdetector delay volume of 0.216 mL yielded a plot of decreasing MW with the increase of retention volume for SRM1478 and SRM705a. However, the PS standard SRM1479 showed a plot of a bent curve and maximum MW was at the peak top. These polymer standards are nearly monodisperse and they should have the same MW over a certain range of retention volume due to column broadening effects, or a plot of decreasing MW with the increase of retention volume. The interdetector delay volume was then adjusted to have a constant plateau relation of MW and retention volume for

SRM1479 and it was 0.185 mL. However, with this value, a plot of increasing MW with the increase of retention volume was obtained for SRM1478. This inconsistency in the relation of MW and retention volume was reported as being due to secondary instrumental broadening of the polymers which occurs primarily in the RI detector which follows the LS detector.[6]

If the RI signal was broadened more than the LS signal, then the normalized RI chromatogram must be broader than the normalized LS chromatogram, at 90°, for example. The experimental results were not like that, but the normalized RI chromatogram was almost superimposed on the LS chromatogram. The similar observation was also reported in the literature.[7] As MALLS cell volume is much larger than the RI cell volume, it can be assumed that the secondary instrumental broadening is negligibly small and it is possible to consider the peak undergoes no additional broadening in passing from one instrument to the other.

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Although several different procedures were reported for the determination of the interdetector delay volume,[8-11] there were no reports on the interdetector delay volume as a function of retention volume or MW. However, it seems to change slightly with MW of polymer samples.[12] As these three PS standards are those of narrow MWD,one possible approach to get the correct interdetector delay volume for these polymers is to search the interdetector delay volume so as to get a plateau relation of MW and retention volume. The interdetector delay volume calculated by this approach was 0.185 mL for SRM1479, 0.198 mL for SRM705a, and 0.205 mL for SRM1478. The results are shown in Figure 2.

The relation for the PS standards of narrow MWS as shown in Figure 2 exhibited a plateau form, which means that molecules with the same MW and molecular size eluted over a certain range of retention volume due to column band broadening effects. Figure 2 also demonstrates the importance of the correct determination of interdetector delay volume and the serious influence of column band broadening on the calculation of MW averages for polymers of narrow MWD (see below).

Figure 3 shows RI chromatograms and plots of measured MW as a function of retention volume for SRM705a and SRM706, and a calibration curve of log MW vs. retention volume constructed with narrow MWD PS standards. A PS sample SRM706 is a broad MWD polymers and the plot of measured MW against retention volume is in good agreement with that for narrow MWD PS standards, though there is a small divergence. If there is any

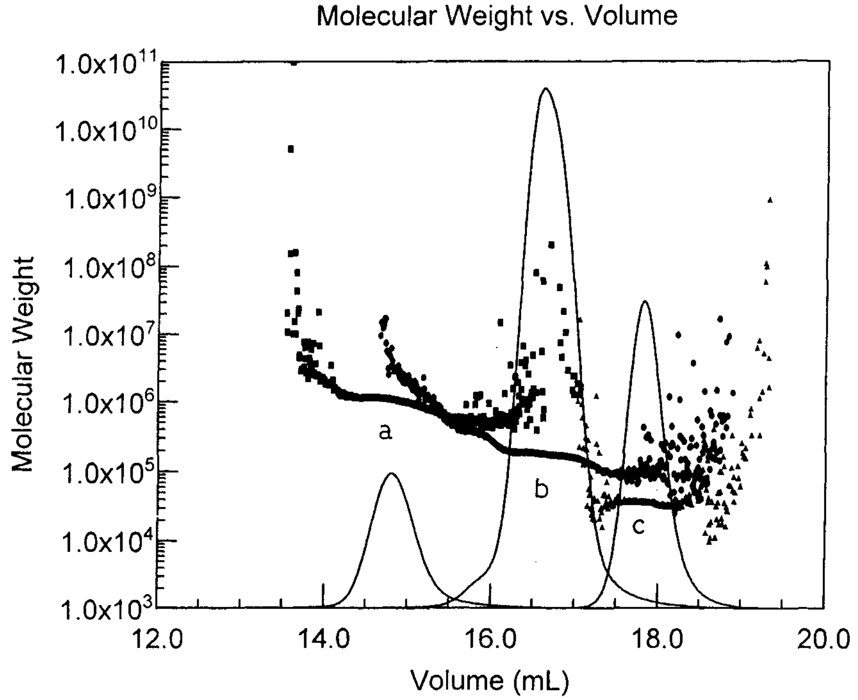

Figure 2. RI chromatograms and plots of measured molecular weight vs. retention volume for three narrow molecular weight distribution polystyrenes at the different interdetector delay volumes. (a) SRM1479, 0.185 mL, (b) SRM705a, 0.198 mL, (c) SRM1478, 0.205 mL.

broadening for broad MWD polymers, each retention volume is polydisperse in MW, and the measured quantity is a weight average. The slope of the measured M_w against retention volume is flatter than the calibration curve obtained by narrow MWD PS standards.[13] Figure 3 clearly shows this concept.

On the contrary, the MW-retention volume relation for narrow MWD PS, SRM705a, was different from that for broad one and the relation was different from the calibration curve. It means that the calculation of MW averages of polymers with narrow MWD such as SRM705a and SRM1478 using a calibration curve constructed with narrow MWD PS standards is invalid unless a proper band-broadening correction is applied to the RI chromatogram.

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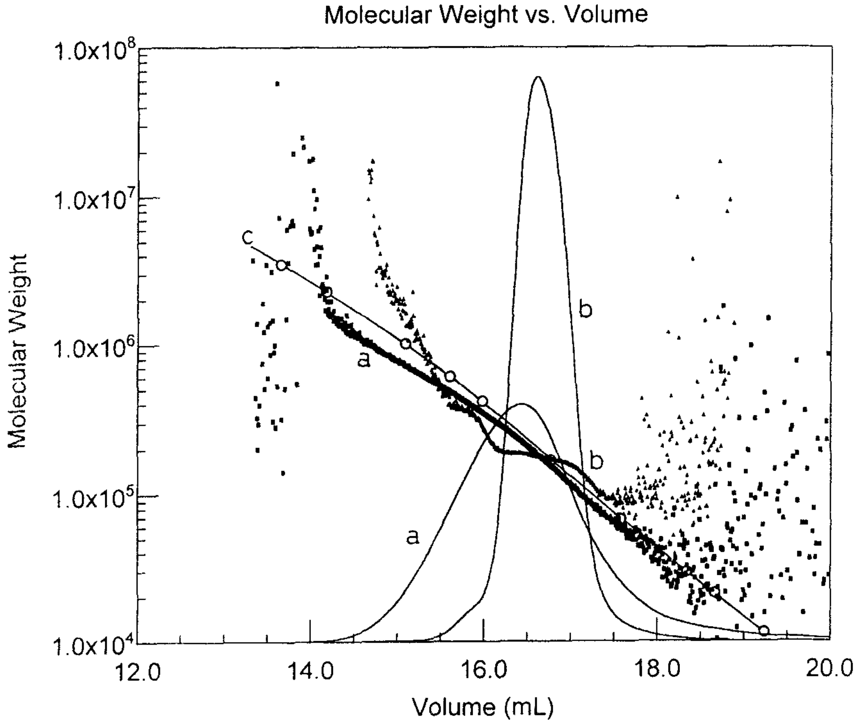

Figure 3. RI chromatograms and plots of measured molecular weight vs. retention volume for polystyrene standards. (a) SRM706, (b) SRM705a, (c) a calibration curve of log MW vs. retention volume constructed with narrow MWD PS standards. Interdetector delay volume is 0.198 mL.

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MW averages for PS samples can be calculated by SEC, in general, using a calibration curve prepared with narrow MWD PS standards. This procedure is referred to as "CC method" in this paper. The use of a LS detector with the SEC system can measure the true MW at each retention volume directly and can calculate MW averages without the construction of a calibration curve. This procedure is referred to as "SEC-LS method" in this paper. Table 2 lists MW averages for PS samples, SRM705a, SRM706, SRM1478, and SRM1479 calculated by "CC method" and by "SEC-LS method". Any band broadening correction was not applied. The calculated MW averages for SRM706 by "SEC-LS method" are nearly the same as those by "CC method", though the values of M_n by "CC method" was somewhat smaller.

Table 2

Comparison of Molecular Weight Averages Obtained by a SEC-LS Method and by a Conventional Method with a Calibration Curve

Polymer	Method	M_nX10^{-5}	M_wX10^{-5}	M_w/M_n
SRM705a	SEC-LS[a]	1.705	1.788	1.048
	CC[b]	1.356	1.659	1.223
SRM706	SEC-LS	1.395	2.723	1.952
	CC	1.247	2.700	2.165
SRM1478	SEC-LS	0.3498	0.3764	1.076
	CC	0.3653	0.4158	1.138
SRM1479	SEC-LS	9.600	10.15	1.043
	CC	8.255	10.48	1.092

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[a] Size exclusions chromatography coupled with light scattering detection.
[b] Calibration curve.

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These values are also comparable to the literature values.[1] It means that the both methods give similar results and that band-broadening corrections may not be necessary. The reason that M_n value calculated by "CC method" was lower than that obtained by "SEC-LS method" was mostly due to the problem of the baseline construction[14] and the lack of the response of the LS detector at the region of low MW.

MW averages, M_n and M_w, calculated by "SEC-LS method" for SRM705a and SRM1478 were in agreement with the certified values and, especially, those for SRM705a were almost the same. These results reveal the usefulness of "SEC-LS method" and,also, the "SEC-LS method" does not need the consideration of band-broadening corrections. On the other hand, MW averages for SRM705a calculated by "CC method" were lower and those for SRM1478 were higher than the certified values. This means that the calculation of MW averages for polymers with narrow MWD using a calibration curve, gives incorrect values and that the "SEC-LS method" has to be applied for the calculation of MW averages for these narrow MWD polymers.

The calculated value of M_w for SRM1479 by "SEC-LS method" was smaller than the certified value and the values by "CC method" was comparable to the certified value. This may be due to the degradation of the sample during the passing the column and, therefore, we don't discuss this resutlt.

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