NOTES

Solvent Dependences of Concentration Effect in Gel Permeation Chromatography

In gel permeation chromatography (GPC), an increase in sample concentration causes a shifting of the chromatogram peak to a higher elution volume; and at sufficiently high concentration levels, a distortion and tailing in the sample chromatogram occurs. There-fore, to obtain accurate molecular weight distributions and average molecular weights, column loading must be kept small enough for the concentration effect to be unimpor-tant, or data at several concentrations must be extrapolated to infinite dilution.[1-5] We have previously measured the concentration dependences of the elution volume and the resolution for several solvents with narrow distribution samples, and have found that the concentration effect is decreased as a poorer solvent for the polymer is used and that the elution volume becomes independent of sample concentration when a theta solvent is used.[6,7] Now, concentration dependences of number-average molecular weight (M_n) and weight-average molecular weight (M_w) calculated from GPC data with a theta
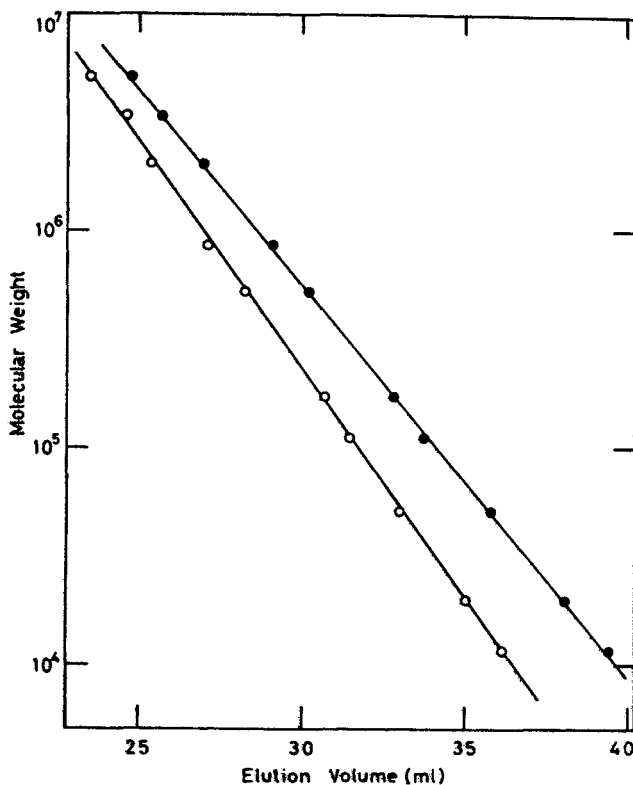

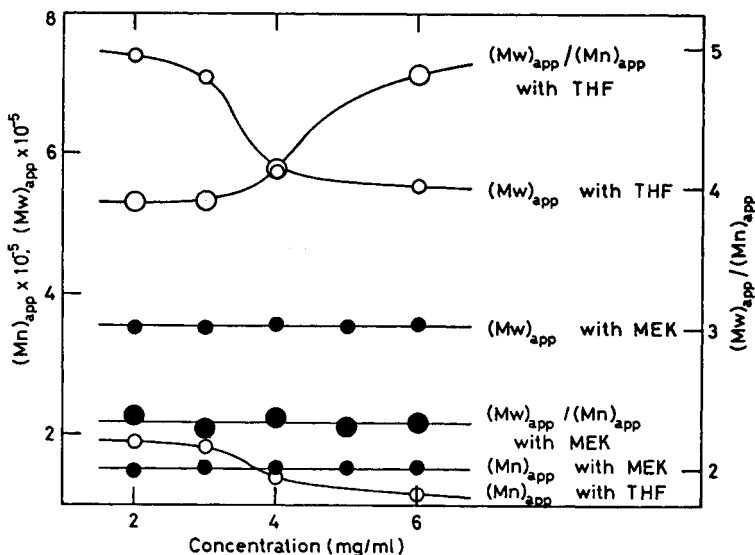Fig. 1. Calibration curves for polystyrene in MEK (-●-) and in THF (-○-).

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Fig. 2.   Dependances of apparent M_n, M_w, and M_w/M_n on sample concentration.

solvent and a good solvent were investigated with respect to a commercial broad-dis-tribution polychloroprene sample.

All measurements were carried out using a commercially available gel permeation chromatograph (Toyo Soda Manufacturing Co., Ltd., Yamaguchi-ken, Japan) at 25°C. Two commercial TSK-GEL H-type columns(Toyo Soda) were used.   Each column was 2 ft in length and 0.305 in. in inner diameter.   These were packed with a mixture of polystyrene gel particles with nominal porosities, respectively of 10^6, 10^4, and 10^3 Å (61:18:21 by volume).   Calibration curves measured with monodisperse polystyrene samples purchased from Pressure Chemical Co. and Toyo Soda at a sample concentra-tion of 0.3 mg/ml are shown in Figure 1.   The theoretical plate count measured with benzene solution in tetrahydrofuran was about 5,000 plates/ft.   Flow rate was 1 ml/ min.   The injection volume of solution was 1 ml.   Solvents were methyl ethyl ketone (MEK), which is a theta solvent at 25°C, and tetrahydrofuran (THF), which is a good solvent.   Sample concentration was varied from 2 to 6 mg/ml.   This concentration range includes those concentrations normally used for GPC measurements.   Inasmuch as calibration curves for polystyrene in Figure 1 were used for computations of M_n and M_w, the M_n and M_w values obtained are not true values but apparent values.   Therefore, these values obtained with MEK and with THF could not be compared.

The dependences of apparent M_n, M_w, and M_w/M_n values on sample concentration are shown in Figure 2.   No effect of sample concentration is seen with MEK, as expected, and the values of apparent M_n, M_w, and M_w/M_n are constant within the limit of experi-mental error.   Accordingly, it could be concluded that accurate average molecular weight can be obtained without correction for sample concentration when a theta solvent is used.   On the contrary, large concentration effects appear at the concentration range from 3 to 6 mg/ml with THF.   Apparent molecular weight distributions converted from chromatograms measured at concentrations of 3, 4, and 6 mg/ml with THF are shown in Figure 3.   This also shows that concentration effects are considerable in a good solvent and that it is necessary to eliminate the concentration effects by extrapolation. However, the added time and effort involved in injecting the sample at several concentra-tions and extrapolating would reduce the advantage of rapid analysis time.   Moreover, the extrapolation procedure has not yet been confirmed although several methods for
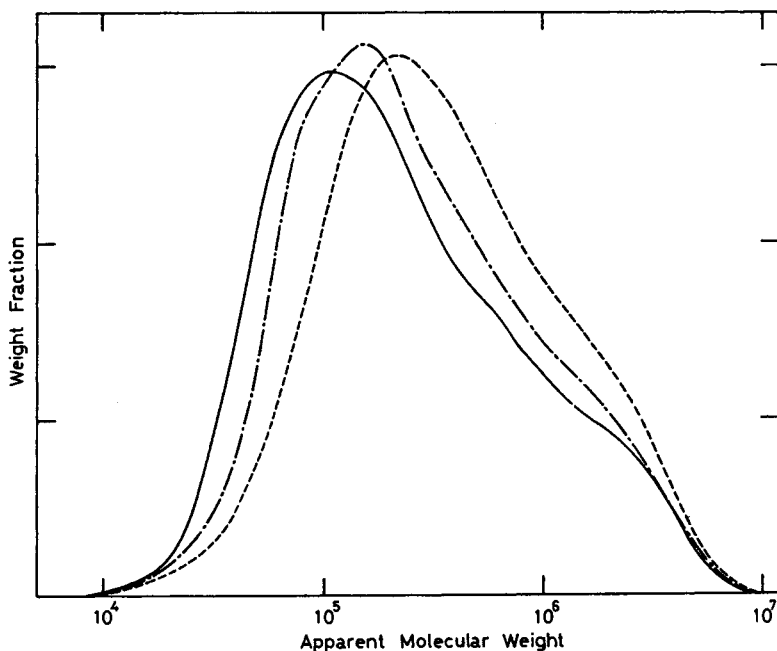
Fig. 3. Effect of sample concentration on apparent molecular weight distributions measured with THF: (- - - - -) 3 mg/ml; (—·—) 4 mg/ml; (——) 6 mg/ml.

plots for linear extrapolation have been reported. For example, Cantow and co-workers suggested the plots of inverse of average molecular weight against sample concentration.[1] However, Lambert showed that Cantow-type plots do not lie on straight lines for high molecular weight samples and recommended plots of average molecular weight against sample concentration.[4] Berger and Schulz recommended plots of M_w/M_n against the square of sample concentration.[5] At present, it is not known which procedure is better. Therefore, it is desirable to use a theta solvent in GPC.

References

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