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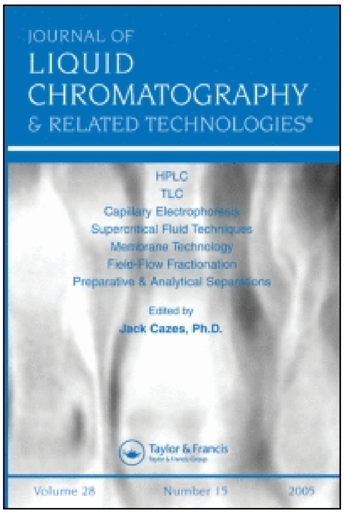

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GEL PERMEATION CHROMATOGRAPHY OF POLYOXYMETHYLENE

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ABSTRACT

The method of universal calibration was applied for polyoxymethylene in gel permeation chromatography. Successful molecular weight distribution curves were obtained for polyoxymethylene from chromatograms. Further, the weight average molecular weights from gel permeation chromatography were in good agreement with those from light scattering.

INTRODUCTION

Determination of molecular weight distribution of polyoxymethylene (POM) had been carried out by column elution method.$^{1,2)}$ After appearance of gel permeation chromatography (GPC), this method has been applied to almost all polymers. Practical use of this method in industries is becoming very popular. This method was also applied to POM.$^{3)}$ However, the study is not sufficient for determining molecular weight and its distribution, because the calibration curve was not prepared for POM. The curve for polystyrene (PS) was conventionally used for POM.

In advancing the study of GPC, an appropriate solvent must be chosen. This polymer is soluble in dimethylformamide (DMF), o-dichlorbenzene, etc. DMF is the most approprite among them for GPC of POM, judging from solubility, the value of refractive index increment, and stability of the polymer. Most POM are stabilized as copolymers, including a small amount of comonomers such as ethylene oxide and trioxocane. The comonomer content is usually equal or less than 2mol% as oxyethylene unit, and furthermore oxyethylene unit is very similar to oxymethylene unit in chemical structure. Most solution properties of these copolymers can be regarded as the same as those of homopolymers.

When we want to determine molecular weight distribution, the calibration curve of polymer in question must be prepared under given conditions. The most useful and practical technique to obtain the calibration curve would be the application of method of universal calibration, which was presented by Grubisic, Rempp and Benoit.4) Namely, if the following equation holds for two polymers in any elution volume, we can obtain the calibration curve of POM from that of a standard polymer, e.g., PS.

$$[\eta]_1M_1 = [\eta]_2M_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where $[\eta]$ means intrinsic viscosity, M molecular weight, and the subscripts 1 and 2 stand for polymers 1 and 2, respectively.
On the basis of this idea, the calibration curve of POM (polymer 1) was determined from that of PS (polymer 2).

EXPERIMENTAL

Molecular weight

The weight average molecular weight $\bar{M}_w$ was calculated according to eq.(2) at a very low angle scattering.

$$\lim_{c\to 0} KC/R = 1/\bar{M}_w \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where K is constant, C concentration of polymer in solution, and R the difference between solvent and solution in Rayleigh ratio. K is a function of differential refractive index increment dn/dc and of refractive index of solvent. POM frcations were obtained by column elution method,[5)] and the molecular weights were determined by a Model KMX-6 low angle light scattering photometer (Chromatix, CA, U.S.A.). Measurements were made using DMF as solvent at the wavelength of 633nm under the conditions of 6 ∿ 7 in apparent degree annulus and the field stop of 0.2. The weight average molecular weight was obtained from the scattered intensity of various concentrations at 135°C. Other experimental procedures are similar to those in the other study.[6)] Refractive index increment of POM was determined in DMF at 135°C by a Shimadzu Model DR-1, where the wavelength of 633nm was adopted and the other conditions were the same as those for light scattering.

Intrinsic viscosity

Intrinsic viscosities of PS standard samples and POM fractions were determined in DMF with an Ubbelohde viscometer at 135°C.

GPC

A Waters Model 150C gel permeation chromatograph equipped with a set of two columns of Shodex A-80M and of a pre-column A-800P were used for obtaining chromatograms and a calibration curve. The set of columns has separation performance ranging from 10^2 to 10^7 in molecular weight of PS. The apparatus was operated with a flow rate of 1.0ml/min at 135°C. The chromatograms were recorded with a RI detector.

RESULTS AND DISCUSSION

Molecular weights of POM and PS

The relation between differential refractive index Δn and polymer concentration is shown in FIGURE 1 for POM and the value of -0.0505ml/g was obtained for dn/dc. An example of molecular weight determination by light scattering is shown in FIGURE 2. Since the value of 1.3745 was experimentally obtained for the

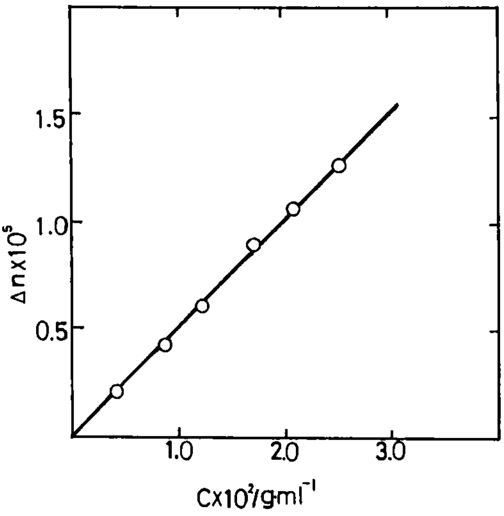

FIGURE 1 Differential refractive index Δn vs. polymer concentration for POM in DMF at 135°C.

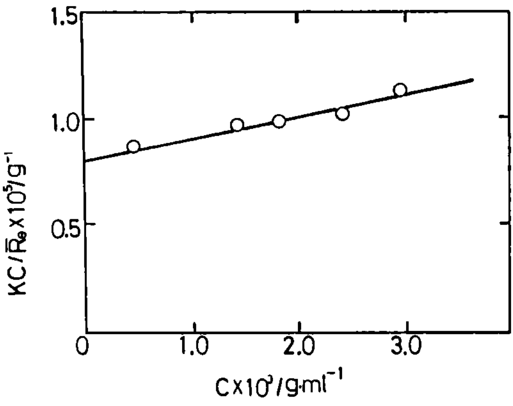

FIGURE 2 Example for light scattering of POM in DMF at 135°C.

TABLE 1 Molecular weights and intrinsic viscosities of POM and PS

Sample POM*	$\bar{M}_w$	$[\eta]$ /dlg^{-1}
POM-1	14600	0.175
POM-2	29500	0.282
POM-3	44100	0.421
POM-4	69900	0.737
POM-5	122000	0.914
POM-6	172400	1.150
PS	$\bar{M}$	$[\eta]$ /dlg^{-1}
PS-1	526	0.014
PS-2	9000	0.061
PS-3	50000	0.181
PS-4	110000	0.327
PS-5	600000	0.933

* : These samples were prepared by fractionation of commercial POM.

refractive index of DMF at 135°C, we obtained the value 1.965×10^{-8} for K in eq.(2), and the weight average molecular weight of 122000 was given for this example. TABLE 1 shows all the values for POM fractions together with those for PS, which were found in a catalogue (Toyosoda, Co., Japan). Intrinsic viscosities of these samples were determined under the same conditions as in GPC, and the results are also shown in TABLE 1.

Universal calibration curve

Logarithmic $[\eta]M$ were plotted against elution counts, as shown in FIGURE 3. This figure clearly indicates that the experimental points fall on one curve; eq.(1) holds between these polymers. The POM fractions have the values from 1.1 to 1.5 in $\bar{M}_w/\bar{M}_n$ when

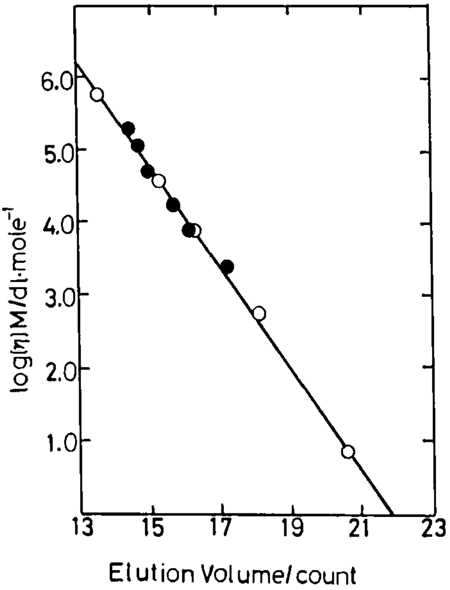

FIGURE 3 Universal calibration curve with POM and PS.
● : POM ○: PS

observed in GPC. These values are relatively large as compared with those of PS standard samples (in PS usually less than 1.1). The effect of these broad molecular weight distribution on the molecular weight corresponding to the peak of the chromatogram was reduced by adopting the corrected values M_p, which is expressed by eq.(3).7)

$$M_p \simeq \bar{M}_w \times D_g^{-1/2} \qquad \text{..............................(3)}$$

where

$$D_g = \bar{M}_{w,g}/\bar{M}_{n,g} \qquad \text{..............................(4)}$$

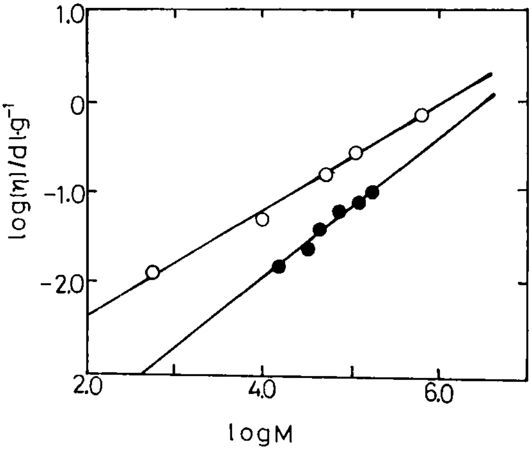

FIGURE 4 Intrinsic viscosity vs. molecular weight for POM and PS in DMF at 135°C.

● : POM, ○ : PS

$\bar{M}_{w,g}$ and $\bar{M}_{n,g}$ indicate the weight and the number average molecular weights, respectively, which are obtained conventionally by GPC.

The Mark-Houwink equation for these polymers was confirmed under the conditions as in GPC. The results are shown in FIGURE 4, and eq.(5) was obtained for POM.

$$[\eta] = 9.082 \times 10^{-5} \times M^{0.7895} \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

POM fractions used for preparing the equation have relatively broad distribution. Therefore, the effect of the distribution on the Mark-Houwink equation must be corrected to obtain accurate universal calibration curve. Generally, the Mark-Houwink equation is expressed by eq.(6).

$$[\eta] = K_t \times M^a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

where K_t and a are constant. This equation is influenced by the molecular weight distribution of samples. If we assume the log normal distribution function for the molecular weight distribution, the relation between $[\eta]$ and $\bar{M}_w$ can be expressed by eq.(7).[8)]

$$[\eta] = K_t \times (\bar{M}_w/\bar{M}_n)^{-0.5a(a-1)} \times \bar{M}_w^a \quad \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

Accordingly, K_t is given as a function of the observed value K_{ob} by the following equation.

$$K_t = K_{ob} \times (\bar{M}_w/\bar{M}_n)^{0.5a(a-1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots(8)$$

By putting the values $K_{ob} = 9.082 \times 10^{-5}$, $\bar{M}_w/\bar{M}_n = 1.366$ and $a = 0.7895$ to eq.(8), we obtained 9.320×10^{-5} for K_t of POM. Finally, the relation between $[\eta]$ and M is given by eq.(9) for POM.

$$[\eta]_1 = 9.320 \times 10^{-5} \times M_1^{0.7895} \quad \ldots\ldots\ldots\ldots\ldots\ldots(9)$$

The relation between $[\eta]$ and M is given by the following equation for PS and is shown in FIGURE 4.

$$[\eta]_2 = 2.795 \times 10^{-4} \times M_2^{0.6056} \quad \ldots\ldots\ldots\ldots\ldots\ldots(10)$$

In this case, no correction is required, because the molecular weight distribution is very narrow. Consequently, the relation between M_1 and M_2 is given by eq.(11).

$$\log M_1 = 0.2665 + 0.8972 \times \log M_2 \quad \ldots\ldots\ldots\ldots(11)$$

Namely, a POM fraction having M_1 and a PS sample having M_2 should give the same elution volume, if these molecular weights are correlated by eq.(11). The calibration curve of POM is easily obtained using eq.(11) from that of PS, if the experiemental conditions such as solvent and temperature are the same as in this study.

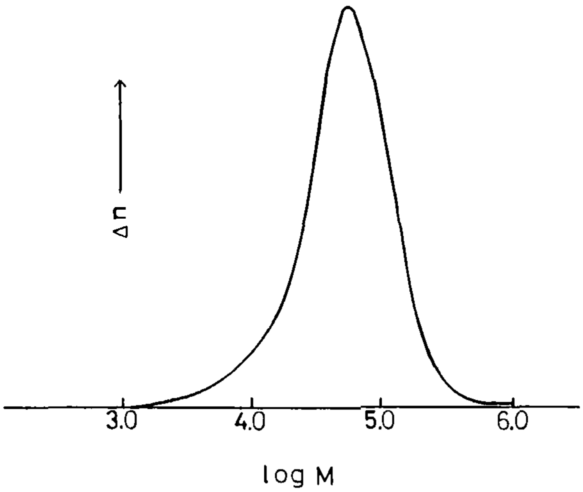

FIGURE 5 Molecular weight distribution curve of POM homopolymer.

Example

The molecular weight distribution curve of commercial POM was obtained using eq.(11) from chromatograms. The polymer sample in FIGURE 5 is a homopolymer, and the one in FIGURE 6 a copolymer containing the comonomer of 2mol% as oxyethylene unit. There is some difference between the two curves in low molecular weight region: a small peak is always present in the chromatogram of POM copolymers. This fact will be discussed elsewhere.

Without saying, the absolute molecular weight can be easily determined from a chromatogram. TABLE 2 shows the results obtained by GPC and light scattering for the weight average molecular weight of commercial POM, where POM-7 ∿ 10 are copolymers and POM-11 is a homopolymer. These results reveal that the calibration curve obtained in this study is very useful for determining the molecular weight and its distribution.

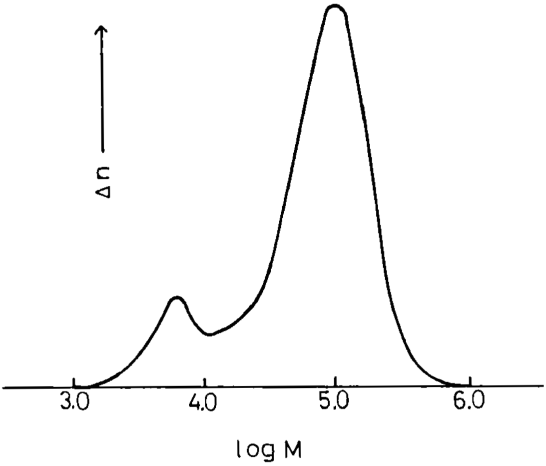

FIGURE 6 Molecular weight distribution curve of POM copolymer.

TABLE 2 Weight average molecular weight of commercial POM obtained by GPC and light scattering

Sample	by GPC	by light scattering
POM-7	104200	104000
POM-8	87300	89800
POM-9	82200	84700
POM-10	96000	94600
POM-11	72000	65700

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