Determination of Number-Average and Weight-Average Molecular Weights of Polymer Sample from Diffusion and Sedimentation Velocity Measurements in Theta Solvent

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Synopsis

Several methods to determine number-average molecular weight M_n and weight-average molecular weight M_w, of a polymer sample are proposed from diffusion and sedimentation velocity measurements at the Θ point. According to these methods, M_n and M_w are determined from the diffusion constant vs. molecular weight relationship, and also from the equations of Svedberg and Flory–Mandelkern, using the 2nd-order and the −2nd-order diffusion constants. These methods have been applied to four samples of polydisperse polystyrene in the Θ solvent, cyclohexane at 35°C. It was experimentally ascertained that M_n and M_w of each sample determined by the present methods were in good agreement with the results of column fractionation, light scattering, and calculated values from molecular weight distribution curve within experimental errors. It is concluded that the present methods are useful for determining M_n and M_w, since the reliabilities of M_n and M_w values, which are fundamental quantities of polymer characterization, can be raised by comparing the experimental data observed by conventional methods such as osmotic pressure, light scattering, and the Archibald method with those observed by the present methods.

INTRODUCTION

It is well known that diffusion measurement in dilute polymer solution is a useful method for polymer characterization such as determination of frictional coefficient of a polymer molecule in the solution and the molecular weight combining with sedimentation velocity measurement using the Svedberg equation.[1] Recently, it has also become possible to estimate a molecular weight distribution from diffusion measurement only, since average values of diffusion constants observed for a polydisperse polymer were proved to be moments of various orders of weight distribution function of diffusion constants.[2–4] In order to obtain M_n and M_w from a conventional diffusion method, it is necessary to assume an appropriate distribution function of diffusion constants such as Gralén's function[2] from the observed values, and further to convert it into molecular weight distribution curve using diffusion constant vs. molecular weight relationship. It may be a weak point in the conventional method to assume a distribution function of diffusion constants.

In previous papers, a diffusion apparatus with moiré optics, equipped with a new type of diffusion cell and an apparatus for boundary formation,[5,6] was

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designed and constructed by the present authors in order to precisely obtain diffusion constants of a polymer in solution.[7] It was experimentally ascertained that diffusion constants measured by the moiré method were more precise than those obtained by the Schlieren method.

In this study, several methods of estimating M_n and M_w of a polydisperse polymer are proposed from diffusion measurement at the Θ point using diffusion constant vs. molecular weight relationship without assuming a distribution function of diffusion constants, and also using equations of Svedberg and Flory–Mandelkern combining with sedimentation velocity measurement. Applicabilities of these methods are experimentally tested by using four samples of polydisperse polystyrene in the Θ solvent, cyclohexane at 35°C.

THEORETICAL

In a diffusion measurement of dilute solution for a polydisperse polymer, positive-order diffusion coefficients are calculated from moments around a initial boundary of a diffusion curve at time t as follows[3,8]:

$$m_n/m_0 = 2^n \pi^{-1/2} \Gamma((n + 1)/2) \cdot {}_{n/2}D^{n/2} \cdot t^{n/2} \tag{1}$$

with

$$m_n = \int_{-\infty}^{\infty} |x|^n y \, dx, \qquad m_0 = \int_{-\infty}^{\infty} y \, dx \qquad (n = 1, 2, 3, \cdots) \tag{2}$$

where ${}_{n/2}D$ is the $(n/2)$th-order diffusion coefficient obtained from the nth-order moment m_n of the diffusion curve, Γ the gamma function, m_0 the area under the diffusion curve, and y the height of the diffusion curve at distance x from the initial boundary x_0. Furthermore, negative-order diffusion coefficients are also calculated from the diffusion curve using the following equations[3,8]:

$$S_n = \int_{-\infty}^{\infty} Z_n \, dx = [(-1)^n m_0/2^n] \cdot {}_{-n}D^{-n} \cdot t^{-n} \tag{3}$$

$$(Z_n)_{x=0} = (-1)^n m_0/\pi^{1/2} 2^{n+1} \cdot {}_{-(n+1/2)}D^{-(n+1/2)} \cdot t^{-(n+1/2)} \tag{4}$$

with

$$Z_0 = y = [m_0/2(\pi D t)^{1/2}] \exp(-x^2/4Dt) \tag{5}$$

$$Z_n = (dZ_{n-1}/dx)/x \qquad (n = 1, 2, 3, \cdots) \tag{6}$$

where ${}_{-n}D$ and ${}_{-(n+1/2)}D$ are the $(-n)$th-order and the $-(n + 1/2)$th-order diffusion coefficients, respectively.

A diffusion constant can be determined by extrapolating the diffusion coefficients at initial concentration C_0 to infinite dilution. Among diffusion constants of a polydisperse polymer, the following inequalities are found to hold[8]:

$$_{-(n+1/2)}D \leq {}_{-n}D \leq D_A \leq {}_{n/2}D \qquad (n = 1, 2, 3, \cdots) \tag{7}$$

where D_A is a diffusion constant by the height-area method,[2] which corresponds to a negative-order diffusion constant. In case of a monodisperse polymer, diffusion constants in relation (7) coincide with each other. Positive-order and

negative-order diffusion constants correspond to the $(n/2)$th-, the $(-n)$th-, and the $-(n+1/2)$th-order moments around a origin of weight distribution function of diffusion constant as follows[2,3,8]:

$$_{n/2}D = \left(\sum_i W_i D_i^{n/2} \bigg/ \sum_i W_i \right)^{2/n} \tag{8}$$

$$_{-n}D = \left(\sum_i W_i D_i^{-n} \bigg/ \sum_i W_i \right)^{-1/n} \tag{9}$$

$$_{-(n+1/2)}D = \left(\sum_i W_i D_i^{-(n+1/2)} \bigg/ \sum_i W_i \right)^{-2/(2n+1)} \tag{10}$$

where W_i is the weight fraction of the polymer having a diffusion constant D_i. D_A corresponds to the diffusion constant with $n = 1/2$ in eq. (9), that is, $D_A = _{-1/2}D$.

According to the dilute solution theory for a monodisperse linear polymer at the Θ point, the diffusion constant vs. molecular weight relationship is expressed by the equation[9-13]

$$D_i = K_{D\Theta} \cdot M_i^{-1/2} \tag{11}$$

where M_i is the molecular weight of the polymer having a diffusion constant D_i, and $K_{D\Theta}$ is a constant of the polymer–Θ solvent system. Substituting eq. (11) into eq. (8) with $n = 4$ and into eq. (9) with $n = 2$, respectively, we obtain the following equations which are valid at the Θ point:

$$_2D = \left(\sum_i W_i D_i^2 \bigg/ \sum_i W_i \right)^{1/2} = K_{D\Theta} \left(\sum_i W_i M_i^{-1} \bigg/ \sum_i W_i \right)^{1/2} = K_{D\Theta} \cdot M_n^{-1/2} \tag{12}$$

$$_{-2}D = \left(\sum_i W_i D_i^{-2} \bigg/ \sum_i W_i \right)^{-1/2} = K_{D\Theta} \left(\sum_i W_i M_i \bigg/ \sum_i W_i \right)^{-1/2} = K_{D\Theta} \cdot M_w^{-1/2} \tag{13}$$

where M_n and M_w are number-average and weight-average molecular weights of a polymer, respectively. It is found from eqs. (12) and (13) that in case of a polydisperse polymer, the molecular weights determined by eq. (11) are number-average and weight-average, when $_2D$ and $_{-2}D$ observed at the Θ point are used as diffusion constants in eq. (11), respectively. Accordingly, M_n and M_w of a polydisperse polymer can be directly determined from the diffusion measurement at the Θ point, using eqs. (12) and (13) with the value of $K_{D\Theta}$. Subsequently, we can define a scale of polydispersity of a sample as $(_2D/_{-2}D)^2$, since its value is equal to M_w/M_n from eqs. (12) and (13) at the Θ point. Equation (12) was derived earlier by Kotera and Matsuda.[14] In the methods described above, we must have the relationship of eq. (11), and it is essential that the value of $K_{D\Theta}$ be sufficiently accurate. In the next place, we propose the other methods of estimating M_n and M_w of a polydisperse polymer without using the value of $K_{D\Theta}$ in eq. (11).

According to Svedberg[1] and Flory-Mandelkern[15,16] molecular weights, M_{SD}, M_{SV}, and M_{DV}, of a monodisperse polymer can be determined from measurements of sedimentation constant S, diffusion constant D, and intrinsic viscosity

$[\eta]$ using the following equations:

$$M_{SD} = SRT/D(1 - \bar{v}\rho_0) \tag{14}$$

$$M_{SV} = (P^{-1}\Phi^{1/3})^{-3/2}N_A^{3/2}[S\eta_0/(1 - \bar{v}\rho_0)]^{3/2}[\eta]^{1/2} \tag{15}$$

$$M_{DV} = (P^{-1}\Phi^{1/3})^3(kT/\eta_0)^3D^{-3}[\eta]^{-1} \tag{16}$$

where R is the gas constant, T the absolute temperature, $\bar{v}$ the partial specific volume of a solute in a solvent having density ρ_0, $P^{-1}\Phi^{1/3}$ Flory's constant, N_A Avogadro's number, η_0 the viscosity of the solvent, and k Boltzmann's constant. If eqs. (14), (15), and (16) are applied to a polydisperse polymer, M_{SD}, M_{SV}, and M_{DV} become highly complex averages which are different from M_w and M_n because the sedimentation constant, diffusion constant, and intrinsic viscosity for the sample are certain averages.[12,17,18] It is more remarkable that M_{SD}, M_{SV}, and M_{DV} are not inherent values for a polymer sample but vary with solvent and temperature.[12]

On the contrary, if $_2D$ and $_{-2}D$ observed at the Θ point are used as diffusion constants in eqs. (14) and (16), we can obtain M_n and M_w combining with eq. (15) as follows: At the Θ point, sedimentation constant and intrinsic viscosity of a polydisperse polymer are expressed by the equations[19-21]

$$S = \sum_i W_iS_i \bigg/ \sum_i W_i, \qquad S_i = K_{S\Theta} \cdot M_i^{1/2} \tag{17}$$

$$[\eta] = \sum_i W_i[\eta]_i \bigg/ \sum_i W_i, \qquad [\eta]_i = K_{V\Theta} \cdot M_i^{1/2} \tag{18}$$

where $K_{S\Theta}$ and $K_{V\Theta}$ are constants of the polymer–Θ solvent system. Substituting eqs. (17) and (18) into eq. (15), we obtain the following equation[22]:

$$M_{SV} = K_{SV}^{-3/2}\left(\sum_i W_iM_i^{1/2}\bigg/\sum_i W_i\right)^2 = \left(\sum_i W_iM_i^{1/2}\bigg/\sum_i W_i\right)^2 \tag{19}$$

with

$$K_{SV} = (P^{-1}\Phi^{1/3})[(1 - \bar{v}\rho_0)/\eta_0N_A]K_{S\Theta}^{-1}K_{V\Theta}^{-1/3} = 1. \tag{20}$$

Furthermore, substitutions of eq. (8) with $n = 4$ into eqs. (14) and (16), with relationship of eq. (19), lead to the following equations[22]:

$$M_{S(_2D)} = K_{SD}\left(\sum_i W_iM_i^{1/2}\bigg/\sum_i W_i\right)\left(\sum_i W_iM_i^{-1}\bigg/\sum_i W_i\right)^{-1/2}$$

$$= (M_{SV} \cdot M_n)^{1/2} \tag{21}$$

with

$$K_{SD} = [RT/(1 - \bar{v}\rho_0)]K_{S\Theta}K_{D\Theta}^{-1} = 1, \tag{22}$$

$$M_{(_2D)V} = K_{DV}^3\left(\sum_i W_iM_i^{1/2}\bigg/\sum_i W_i\right)^{-1}\left(\sum_i W_iM_i^{-1}\bigg/\sum_i W_i\right)^{-3/2}$$

$$= (M_{SV}^{-1} \cdot M_n^3)^{1/2} \tag{23}$$

with

$$K_{DV} = (P^{-1}\Phi^{1/3})(kT/\eta_0)K_{D\Theta}^{-1}K_{V\Theta}^{-1/3} = 1. \tag{24}$$

On the other hand, substitutions of eq. (9) with $n = 2$ into eqs. (14) and (16) lead to the following equations:

$$M_{S(-2D)} = K_{SD} \left(\sum_i W_i M_i^{1/2} \Big/ \sum_i W_i \right) \left(\sum_i W_i M_i \Big/ \sum_i W_i \right)^{1/2}$$

$$= (M_{SV} \cdot M_w)^{1/2} \tag{25}$$

$$M_{(-2D)V} = K_{DV}^3 \left(\sum_i W_i M_i^{1/2} \Big/ \sum_i W_i \right)^{-1} \left(\sum_i W_i M_i \Big/ \sum_i W_i \right)^{3/2}$$

$$= (M_{SV}^{-1} \cdot M_w^3)^{1/2}. \tag{26}$$

From eqs. (21) and (23), we finally obtain number-average molecular weights as follows:

$$M_n = M_{S(2D)}^2 \cdot M_{SV}^{-1} \tag{27}$$

$$M_n = (M_{(2D)V}^2 \cdot M_{SV})^{1/3}. \tag{28}$$

Furthermore, from eqs. (25) and (26), weight-average molecular weights are obtained as follows:

$$M_w = M_{S(-2D)}^2 \cdot M_{SV}^{-1} \tag{29}$$

$$M_w = (M_{(-2D)V}^2 \cdot M_{SV})^{1/3} \tag{30}$$

Accordingly, M_n and M_w can be also determined from the 2nd-order and the $-$2nd-order diffusion constants observed at the Θ point, combining with sedimentation constant and intrinsic viscosity without using the value of $K_{D\Theta}$ in eq. (11).

Substituting eq. (11) into eq. (9) with $n = 1$, we can further derive an equation at the Θ point as follows:

$$_{-1}D = \left(\sum_i W_i D_i^{-1} \Big/ \sum_i W_i \right)^{-1} = K_{D\Theta} \left(\sum_i W_i M_i^{1/2} \Big/ \sum_i W_i \right)^{-1}$$

$$= K_{D\Theta} \cdot M_{SV}^{-1/2} \tag{31}$$

Equation (31) means that, in case of a polydisperse polymer, the average molecular weight calculated by eq. (11) is M_{SV}, when $_{-1}D$ observed in the Θ solvent is used as the diffusion constant.

EXPERIMENTAL

Sample

The present methods were experimentally tested by using four samples of polydisperse polystyrene in the Θ solvent, cyclohexane at 35°C. These samples are as follows: ASAHI DOW Styron 683-7, PS-1, PS-2, and PS-3. Styron 683-7 is a commercial unfractionated polystyrene, and PS-1, PS-2, and PS-3 are mixed samples of monodisperse standard polystyrenes (Toyo Soda Manufacturing Co., Ltd., Tokyo), F-10, F-40, and F-80. The weight-average molecular weights of F-10, F-40, and F-80 are 10.7×10^4, 42.2×10^4, and 77.5×10^4, and the ratios of weight-average molecular weight to number-average molecular weight, M_w/M_n, are 1.01, 1.05, and 1.04, respectively. PS-1 and PS-2 are mixtures of equal

weights of F-10 and F-40 and of F-10 and F-80, respectively. PS-3 is a mixture of F-10, F-40, and F-80 in the ratio of 3:2:1 by weight.

Pellets of Styron 683-7 were dissolved in purified methylethylketone (MEK) and precipitated with methanol. After washing with methanol, the sample was dried under reduced pressure at 50°C until a constant weight was reached. Each sample of F-10, F-40, and F-80 was dried under reduced pressure before using.

Solvent

Cyclohexane of the first grade (Kanto Chemical Co., Inc., Tokyo), used as the Θ solvent, was shaken several times with a mixture of concentrated nitric and sulfuric acids, followed by repeated washing with distilled water, then was dried with calcium chloride, and finally was fractionally distilled over sodium metal.

Diffusion Measurement

Diffusion measurements were carried out in cyclohexane at 35 ± 0.02°C using a new type of diffusion apparatus with moiré optics, which was designed and constructed in our laboratory. A light source is a helium–neon laser. According to previous procedures,[6,7] a sharp boundary was formed in the middle of a rectangular quartz cell, and five or six moiré patterns were photographed during each diffusion process.

Sedimentation Velocity Measurement

Sedimentation velocity measurements were carried out in cyclohexane at 35 ± 0.2°C using a Hitachi Model 282 Analytical Ultracentrifuge with Schlieren optics. A single sector cell of 12-mm centerpiece was used, and measurements were made at 55,130 rpm, and at four or five initial concentrations of about 0.09–0.81 g/100 cm^3.

Viscosity Measurement

Measurements of intrinsic viscosity were carried out in cyclohexane at 35 ± 0.02°C using a dilution viscometer of Ubbelohde type. Correction for the kinetic energy was negligible under the experimental conditions. The viscosity data were extrapolated to infinite dilution by using two plots, η_{sp}/C vs. C and $(\ln \eta_r)/C$ vs. C, where η_{sp} and η_r denote specific viscosity and relative viscosity of a solution of concentration C (g/100 cm^3), respectively. These plots are shown in Figure 1. As the data of Styron 683-7 and PS-1 are overlapped, the plots of PS-1 are excluded from Figure 1. The intrinsic viscosity $[\eta]$ and the Huggins constant k' determined are tabulated in Table I. Viscosity and density of cyclohexane, η_0 and ρ_0, are 0.740×10^{-2} P and 0.7634 g/cm^3 at 35 ± 0.02°C, respectively.

RESULTS AND DISCUSSION

Examples of typical diffusion patterns of moiré optics for Styron 683-7 in cyclohexane are shown in Figure 2. Each line of moiré pattern corresponds to
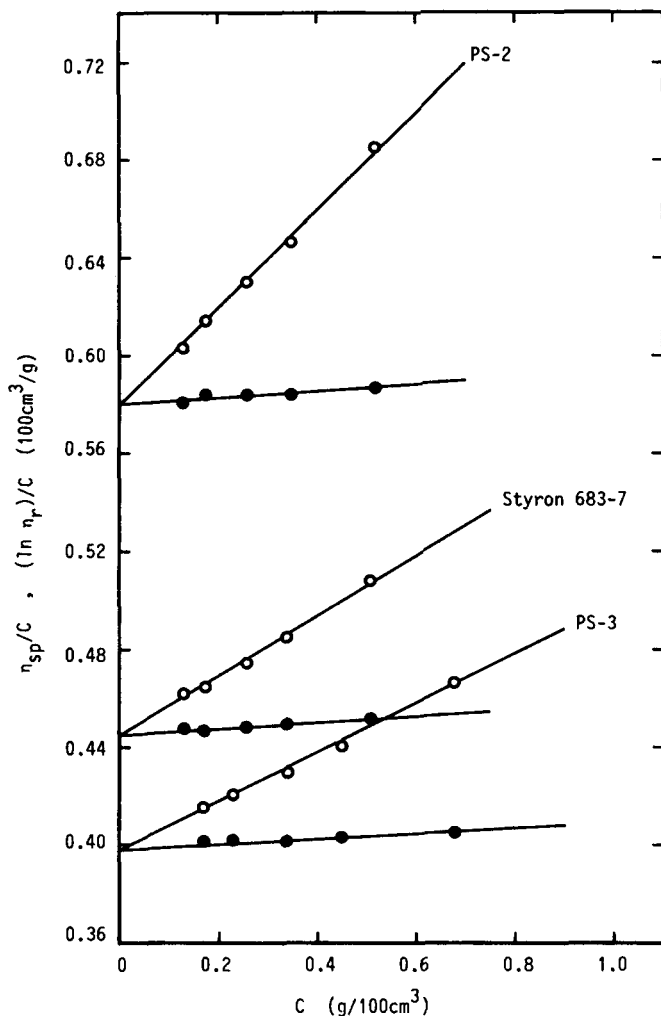
Fig. 1. Concentration dependence of the reduced viscosity (O) and the inherent viscosity (●) for polystyrene samples in cyclohexane at 35°C.

a diffusion curve in a conventional method.   The right-hand side on the photograph of the diffusion curve is a solution side, and it is observed that the diffusion curve is slightly skew toward the solution side at the θ point.   This phenomenon

TABLE I
Intrinsic Viscosities and Sedimentation Constants in Cyclohexane at 35°C

Sample	$[\eta]$ (100 cm^3/g)	k'^a	$S_0 \times 10^{13}$ (s)	k_s^b (100 cm^3/g)
Styron 683-7	0.445	0.62	7.14	0.24
PS-1	0.447	0.60	7.76	—
PS-2	0.580	0.58	9.23	—
PS-3	0.398	0.64	8.25	—

a Huggins constant.
b Concentration dependence coefficient of sedimentation coefficient.
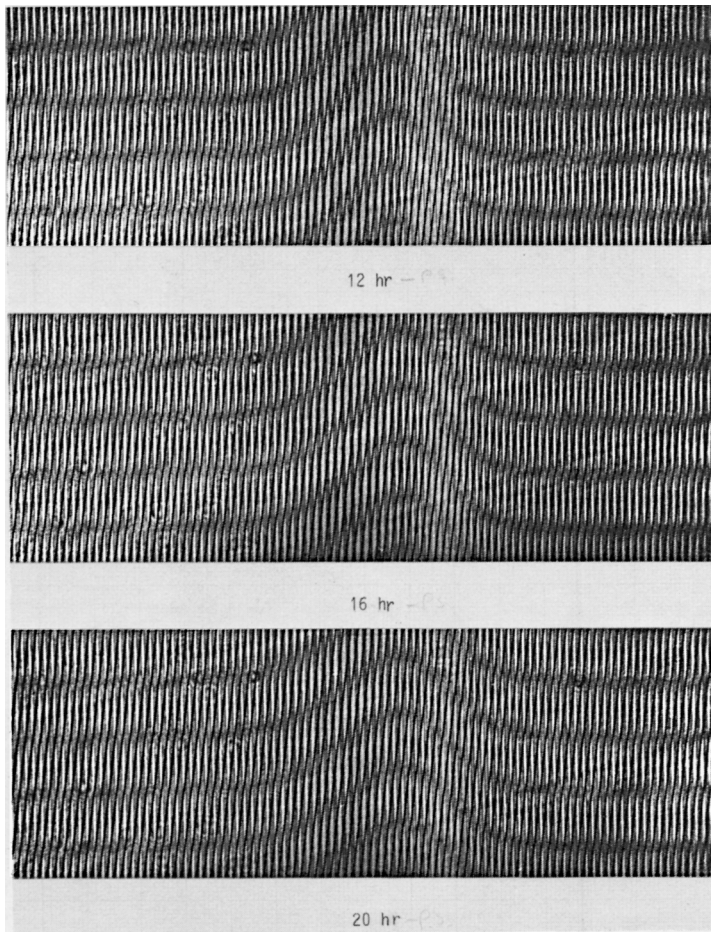
Fig. 2. Typical diffusion patterns by moiré optics for Styron 683-7 in cyclohexane at 35°C: initial concentration $C_0 = 1.30$ g/100 cm^3. The figures show diffusion time t (h).

is attributed to the concentration dependence effect of the diffusion coefficient. Thus, in the system which has concentration dependence of diffusion coefficient, we calculated the nth-order moment around the initial boundary x_0 of the diffusion curve using the following equations,[23] instead of eq. (2):

$$m_n = \int_{-\infty}^{\infty} |x - x_0|^n y \, dx = m'_n - n x_0 m'_{n-1} + O(x_0^2, x_0^3, \cdots) \qquad (32)$$

with

$$x_0 = \int_{-\infty}^{\infty} xy \, dx \Big/ \int_{-\infty}^{\infty} y \, dx \qquad (33)$$

where m'_n and m'_{n-1} are the nth- and the $(n-1)$th-order moments of diffusion curve around the origin at which the height of diffusion curve has its maximum value $H_{\max}$, respectively. Since $x_0 \ll 1$ at the Θ point, higher-order terms than x_0^2 are negligible. To the practical calculations of m_n and m_0 in eqs. (32) and (33),
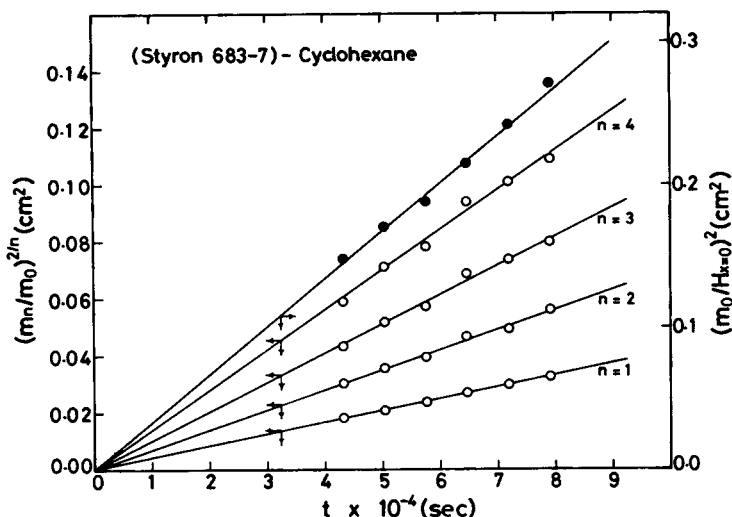
Fig. 3. Determination of positive-order diffusion coefficients according to eq. (1) for Styron 683-7: (O) moment method. n is order of moment of the diffusion curve. The height-area method ($\bullet$) is also plotted in this figure, and the negative-order diffusion coefficient D_A is obtained by the equation $(m_0/H_{x=0})^2 = 4\pi \cdot D_A \cdot t$. $C_0 = 1.30$ g/100 cm^3.

we applied the Simpson's 1/3 rule with a width of division, 0.254 mm, which was a spacing of equispaced parallel lines notched on a glass-made grating of moiré optics.

Positive-order and negative-order diffusion coefficients of each sample were calculated from the slopes of the straight lines, plotting $(m_n/m_0)^{2/n}$ vs. t by eq. (1), $(m_0/H_{x=0})^2$ vs. t, $(m_0/S_n)^{1/n}$ vs. t by eq. (3), and $[m_0/(Z_n)_{x=0}]^{2/(2n+1)}$ vs. t
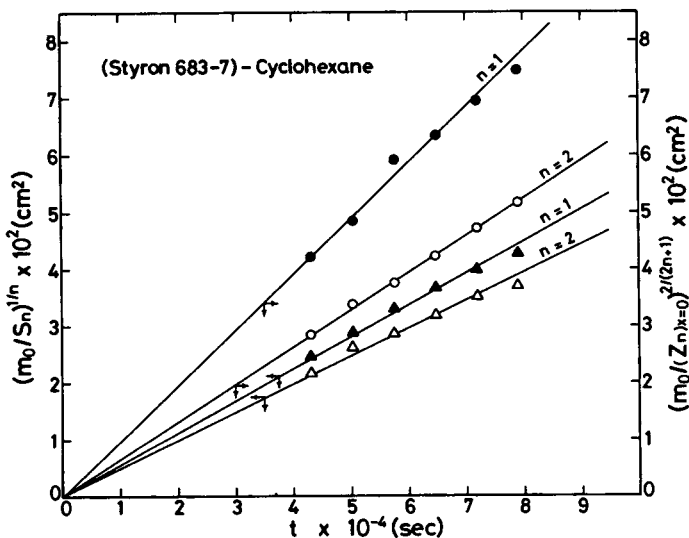

Fig. 4. Determination of negative-order diffusion coefficients according to eqs. (3) and (4) for Styron 683-7: ($\blacktriangle$, $\triangle$) eq. (3); ($\bullet$, O) eq. (4). $C_0 = 1.30$ g/100 cm^3.

TABLE II
Experimental Conditions and Diffusion Constants in Cyclohexane at 35°C

Sample	C_0^a (g/100 cm³)	Δt^b (s)	k_D^c (100 cm³/g)	$-5/2D$	$-2D$	$-3/2D$	$-1D$	D_A	$1/2D$	$1D$	$3/2D$	$2D$
								($D_0 \times 10^7$ cm²/s)				
Styron 683-7	1.30	0	−0.084	2.28	2.46	2.65	2.80	2.81	3.46	3.69	3.95	4.29
PS-1	1.60	0	−0.054	2.79	2.81	2.84	2.88	2.90	3.18	3.23	3.30	3.35
				(2.72)	(2.78)	(2.85)	(2.93)	(3.09)	(3.19)	(3.29)	(3.35)	(3.46)
PS-2	1.00	0	−0.071	2.19	2.20	2.32	2.43	2.52	2.99	3.07	3.11	3.18
				(2.07)	(2.15)	(2.25)	(2.36)	(2.50)	(2.83)	(3.00)	(3.15)	(3.30)
PS-3	1.50	0	−0.094	2.39	2.46	2.55	2.80	2.42	3.33	3.35	3.46	3.49
				(2.43)	(2.51)	(2.61)	(2.71)	(2.83)	(3.06)	(3.19)	(3.28)	(3.41)

a Initial concentration.
b Initial time correction.
c Concentration dependence coefficient of diffusion coefficient. ( ) = Calculated values of diffusion constant.

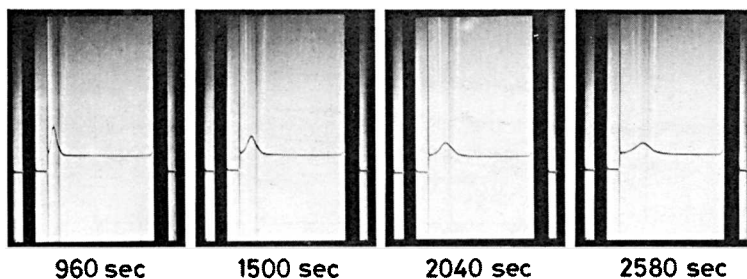960 sec   1500 sec   2040 sec   2580 sec

Fig. 5. Typical sedimentation patterns by Schlieren optics for Styron 683-7 in cyclohexane at 35°C: rotor speed 55,130 rpm; initial concentration $C_0 = 0.762$ g/100 cm³; initial time correction $t_0 = 300$ s; diagonal bar angle $\phi = 80°$. The figures show sedimentation time t (s).

by eq. (4), where $H_{x=0}$ is height of the diffusion curve at the initial boundary x_0. These plots are shown in Figures 3 and 4 for Styron 683-7. Excellent straight lines were obtained, and initial time correction, Δt, was not necessary in the present study. In this respect, a sharp boundary between solvent and solution was formed in our diffusion experiment.

The diffusion coefficients obtained at initial concentration C_0, D_{C_0}, were extrapolated to infinite dilution by Gralén's method[2] using the equations

$$D_{C_0} = D_0[1 + k_D(C_0/2)] \tag{34}$$

with

$$k_D(C_0/2) = (m_0/2\sigma^2)(x_0/H_{\max}), \qquad \sigma^2 = m_2/m_0 \tag{35}$$

where D_0 is the diffusion constant and k_D is the concentration dependence coefficient of diffusion coefficient. The observed values of diffusion constant and k_D of each sample are tabulated in Table II. Calculated values of diffusion constants for PS-1, PS-2, and PS-3 are also summarized these in parentheses. These were calculated by substituting eq. (11) with the value[24] of $K_{D\theta} = 1.43 \times 10^{-4}$ into eqs. (8), (9), and (10), assuming that each component of F-10, F-40, and F-80 was monodisperse. Calculated values of D_A were obtained in the same manner using the equation,[2] $D_A = (\sum_i W_i D_i^{-1/2}/\sum_i W_i)^{-2}$. It may be seen that the diffusion constants measured by the present study are reasonable in comparison with those calculated and satisfy the inequalities of relation (7).
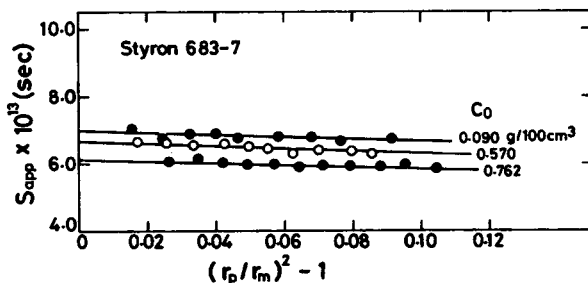

Fig. 6. Examples of extrapolation of apparent sedimentation coefficients S_{app} to meniscus according to eq. (36) for Styron 683-7 in cyclohexane at 35°C.
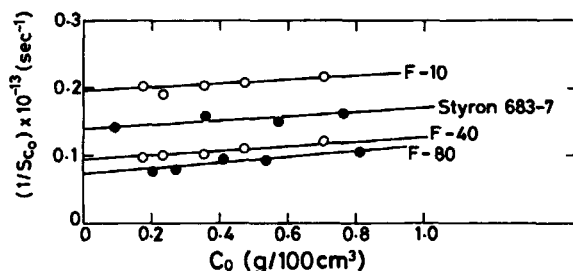
Fig. 7. Concentration dependence of sedimentation coefficients according to eq. (37) for poly-styrene samples in cyclohexane at 35°C.

Examples of sedimentation pattern of Schlieren optics for Styron 683-7 in cyclohexane are shown in Figure 5. Sedimentation coefficients were obtained from the position of the maximum of the refractive index gradient. Pressure effect on the sedimentation coefficient in cyclohexane was eliminated by extrapolating the apparent sedimentation coefficients to the meniscus using Fujita's equation[25,26]

$$S_{app} = [\ln (r_p/r_m)]/\omega^2(t - t_0) = S_{C_0}\{1 - G[(r_p/r_m)^2 - 1]\} \qquad (36)$$

with

$$1/S_{C_0} = (1/S_0)(1 + k_sC_0) \qquad (37)$$

where S_{app} is the apparent sedimentation coefficient, r_p the position of the maximum refractive index gradient, r_m the position of the meniscus, ω the angular velocity, t the sedimentation time measured from the moment when a rotor is set in motion, t_0 the initial time correction, G the parameter which includes the pressure and radial dilution effects, and k_s the concentration dependence
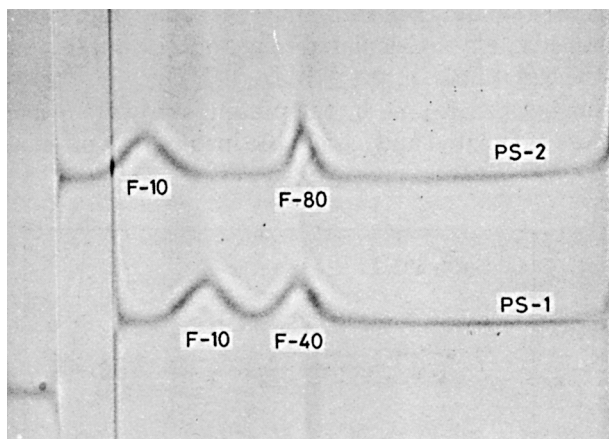

Fig. 8. Sedimentation patterns photographed simultaneously for PS-1 and PS-2 in cyclohexane at 35°C: +1°-wedge window cell was used for PS-2; rotor speed, 55,130 rpm; sedimentation time $t = 2280$ s; initial concentrations of PS-1 and PS-2 are 0.177 and 0.202 g/100 cm³, respectively; diagonal bar angle $\phi = 65°$.

TABLE III
Average Molecular Weights Determined by Svedberg and Flory–Mandelkern Equations

	Styron 683-7	PS-1	PS-2	PS-3
$M_{(-_2D)V} \times 10^{-4}$	44.9	30.0	48.1	50.2
$M_{S(-_2D)} \times 10^{-4}$	25.9	24.7	37.5	29.9
$M_{SV} \times 10^{-4}$	19.7	22.4	33.0	23.1
$M_{S(_2D)} \times 10^{-4}$	14.9	20.7	25.9	21.1
$M_{(_2D)V} \times 10^{-4}$	8.5	17.7	15.9	17.6
$\dfrac{M_{S(_2D)}^3}{M_{(_2D)V} \cdot M_{SV}^2}$	1.00	0.99	1.00	1.00
$\dfrac{M_{S(-_2D)}^3}{M_{(-_2D)V} \cdot M_{SV}^2}$	0.99	1.00	1.01	0.99

coefficient of sedimentation coefficient. S_{C_0} and S_0 are sedimentation coefficients at initial concentration C_0 of a solution and at infinite dilution, respectively.

In this study, initial time correction t_0 was determined by extrapolating the position of the maximum refractive index gradient to that of the meniscus, since a linear relationship was experimentally found to hold between $\ln(r_p/r_m)$ and sedimentation time t when t was small. Accordingly, sedimentation coefficient S_{C_0} in eq. (36) is obtained from the intercept of the straight line when S_{app} is plotted against $[(r_p/r_m)^2 - 1]$. These plots are shown in Figure 6 for Styron 683-7. Sedimentation coefficients S_{C_0} were extrapolated to infinite dilution as shown in Figure 7, and the sedimentation constant S_0 was obtained for each sample according to eq. (37). A mixed sample of PS-1 or PS-2 had two peaks of Schlieren pattern as shown in Figure 8, when PS-1 or PS-2 was centrifuged in cyclohexane. In such a system, it is necessary to correct the Johnston–Ogston effect.[27] In a four-component system (one solvent and three solutes) such as PS-3, this correction is very difficult. Thus, in the present study, sedimentation constants of mixed samples were determined from sedimentation velocity experiments for individual components F-10, F-40, and F-80, using the equation $S_0 = \sum_i W_i S_{0,i}/\sum_i W_i$, where $S_{0,i}$ is the sedimentation constant of the component i. The observed values of sedimentation constant of each sample are tabulated in Table I.

The partial specific volume of polystyrene in cyclohexane was determined in the previous study[28] as $\bar{v} = 0.934$ cm^3/g. Average molecular weights in eqs. (14), (15), and (16) were determined using the following values: $R = 8.314 \times 10^7$ erg·mol^{-1}·K^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}, $k = 1.381 \times 10^{-16}$ erg·K^{-1}, $P^{-1}\Phi^{1/3} = 2.5 \times 10^6$, and $T = 308.2$ K. The results of average molecular weight are tabulated in Table III. According to Kimura, the following relationships were found to hold[29]:

$$M_{S(n/2D)}^3/(M_{(n/2D)V} \cdot M_{SV}^2) = 1 \qquad (38)$$

$$M_{S(-_nD)}^3/(M_{(-_nD)V} \cdot M_{SV}^2) = 1 \qquad (39)$$

The present data were tested by eq. (38) with $n = 4$ and by eq. (39) with $n = 2$, and it was confirmed that left-hand sides of both equations were closely equal to unity as shown in Table III. Thus, average molecular weights determined by eqs. (14), (15), and (16) may be reasonable.

TABLE IV
Number-Average and Weight-Average Molecular Weights

Sample	$M_n \times 10^{-4}$			$M_w \times 10^{-4}$		
	Eq. (12)	Eqs. (27), (28)	Calcd[a]	Eq. (13)	Eqs. (29), (30)	Calcd[a]
Styron 683-7	11.1	11.2	12.5[b]	33.8	34.1	27.7[b], 30.2[c]
			11.5[d]			33.1[d]
PS-1	18.2	19.1	17.1	25.9	27.2	26.5
PS-2	20.2	20.3	18.8	42.3	42.5	44.1
PS-3	16.8	19.2	17.6	33.8	38.8	32.3

[a] Calculated values, assuming that each component is monodisperse, except for Styron 683-7.
[b] Observed by column fractionation.
[c] Observed by light scattering.
[d] Determined by Gralén's distribution function.

Number-average molecular weight and weight-average molecular weight of each sample determined by the present methods are tabulated in Table IV. These values are in good agreement with those observed by column-fractionation and light-scattering measurements[30] for Styron 683-7, and with the calculated values for PS-1, PS-2, and PS-3, within experimental errors. M_n and M_w values of Styron 683-7 determined by Gralén's distribution function[2] are also given in Table IV. In the present study, eqs. (27) and (28), and eqs. (29) and (30) gave the same values of M_n and M_w for each sample, respectively.

Though M_n and M_w of a polymer sample have hitherto been determined by osmotic pressure, light scattering, and the Archibald method, it becomes also possible to estimate M_n and M_w from diffusion and sedimentation velocity measurements using the present methods. Accordingly, the reliabilities of M_n and M_w values, which are fundamental quantities of polymer sample, can be raised by comparing the experimental data observed by osmotic pressure, light scattering, and the Archibald method with those observed by the present methods. In conclusion, our method is considered as a useful one for determining M_n and M_w, although it is valid only at the Θ point.

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