Methods to Determine Average Molecular Weights by Sedimentation Velocity and Diffusion Measurements in Θ Solvent

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Abstract

Methods to determine number-average molecular weight M_n and weight-average molecular weight M_w of a polymer sample are proposed by sedimentation velocity and diffusion measurements at the Θ point. According to these methods, M_n and M_w are directly determined by sedimentation constant *vs.* molecular weight relationship, diffusion constant *vs.* molecular weight relationship, and also Svedberg's equation without using molecular weight distribution curve.

These methods have been applied to seven polystyrenes in the Θ solvent, cyclohexane at 35℃. It was experimentally ascertained that M_n and M_w of each sample determined by the present methods were reasonable values in comparison with those observed by column fractionation and light scattering measurements. It is concluded that our method is considered as a simple and useful one to determine M_n and M_w.

Introduction

It is well recognized that sedimentation and diffusion measurements of dilute polymer solution are useful methods to determine molecular weight and its distribution of a polymer using the following equations[1)~7)] :

$$S_i = K_S \cdot M_i^\beta \tag{1}$$

$$D_i = K_D \cdot M_i^{-\gamma} \tag{2}$$

where M_i is the molecular weight of the polymer having sedimentation constant S_i and diffusion constant D_i, and K_S, K_D, β, and γ are constants which depend upon the polymer-solvent systems. Eqs. (1) and (2) are called sedimentation constant *vs.* molecular weight relationship and diffusion constant *vs.* molecular weight relationship, respectively. If eqs. (1) and (2) are applied to a polydisperse polymer, molecular weights calculated by these equations become hydrodynamical average molecular weights[6)] which are different from number-average molecular weight M_n and weight-average molecular weight M_w. In order to obtain M_n and M_w from conventional sedimentation and diffusion methods, molecular weight distribution curves must be determined previously from distribution curves of sedimentation and diffusion constants using eqs. (1) and (2). It is, however, very laborious in diffusion method to obtain the distribution curve of diffusion constant because an appropriate distribution function of diffusion constant such as Gralén's function[8)] must be assumed from observed values of diffusion constant.

In this study, several methods to determine M_n and M_w of the polymer sample are proposed by sedimentation velocity and diffusion measurements at the Θ point using eqs. (1) and (2), and also using Svedberg's equation.[9] According to these methods, M_n and M_w are determined directly by eqs. (1) and (2) without using molecular weight distribution curve.

Theoretical

We can define the nth-order molecular weight $_nM$ of the polydisperse polymer as follows:

$$_nM = (\sum_i W_i M_i^n / \sum_i W_i)^{1/n} \tag{3}$$

where W_i is the weight fraction of the polymer having molecular weight M_i. According to Hosono and Sakurada,[7,10] the nth-order diffusion constant $_nD$ is expressed by the equation

$$_nD = (\sum_i W_i D_i^n / \sum_i W_i)^{1/n}. \tag{4}$$

In case of sedimentation constant, we can also define the nth-order sedimentation constant $_nS$ by the equation

$$_nS = (\sum_i W_i S_i^n / \sum_i W_i)^{1/n}. \tag{5}$$

$_nS$ can be calculated by the weight distribution curve of sedimentation constant obtained from sedimentation velocity experiment.

Substituting eqs. (1) and (2) into eqs. (5) and (4), respectively, the following equations are found to hold:

$$_nS = K_S(\sum_i W_i M_i^{n\beta} / \sum_i W_i)^{1/n} = K_S(_{n\beta}M^{n\beta})^{1/n} = K_S \cdot _{n\beta}M^\beta \tag{6}$$

$$_nD = K_D(\sum_i W_i M_i^{-n\gamma} / \sum_i W_i)^{1/n} = K_D(_{-n\gamma}M^{-n\gamma})^{1/n} = K_D \cdot _{-n\gamma}M^{-\gamma} \tag{7}$$

where $_{n\beta}M$ and $_{-n\gamma}M$ are the $(n\beta)$th-order and the $(-n\gamma)$th-order molecular weights defined by eq. (3), respectively. It is remarkable that the average molecular weights determined by the nth-order sedimentation constant $_nS$ and the nth-order diffusion constant $_nD$ correspond to the $(n\beta)$th-order and the $(-n\gamma)$th-order molecular weights, respectively.

Since both exponents β and γ in eqs. (1) and (2) are equal to $1/2$ in the Θ solvents, we obtain the following relations from eqs. (6) and (7) with $\beta = \gamma = 1/2$:

$$_nS = K_{S\Theta} \cdot _{n/2}M^{1/2} \tag{8}$$

$$_nD = K_{D\Theta} \cdot _{-n/2}M^{-1/2} \tag{9}$$

where $K_{S\Theta}$ and $K_{D\Theta}$ are constants which depend upon the polymer-Θ solvent system. Accordingly, M_n are obtained from eq. (8) with $n = -2$ and from eq. (9) with $n = 2$ as follows:

$$_{-2}S = (\sum_i W_i S_i^{-2} / \sum_i W_i)^{-1/2} = K_{S\Theta} \cdot _{-1}M^{1/2} = K_{S\Theta} \cdot M_n^{1/2} \tag{10}$$

$$_2D = (\sum_i W_i D_i^2 / \sum_i W_i)^{1/2} = K_{D\Theta} \cdot _{-1}M^{-1/2} = K_{D\Theta} \cdot M_n^{-1/2}, \tag{11}$$

since $_{-1}M$ corresponds to M_n from eq. (3). On the other hand, M_w are also obtained from eq. (8) with $n = 2$ and from eq. (9) with $n = -2$ as follows:

$$_2S = (\sum_i W_i S_i^2 / \sum_i W_i)^{1/2} = K_{S\Theta} \cdot _1M^{1/2} = K_{S\Theta} \cdot M_w^{1/2} \tag{12}$$

$$_{-2}D = (\sum_i W_i D_i^{-2} / \sum_i W_i)^{-1/2} = K_{D\Theta} \cdot _1M^{-1/2} = K_{D\Theta} \cdot M_w^{-1/2}, \tag{13}$$

since $_1M$ corresponds to M_w from eq. (3). Thus, M_n and M_w are determined directly by eqs. (10), (11), (12), and (13) with the values of $K_{S\theta}$ and $K_{D\theta}$. Eqs. (11) and (13) were derived earlier by Kotera and Matsuda,[11] and Okabe and Matsuda,[12),13)] respectively.

In the next place, we propose the other equations to determine M_n and M_w from Svedberg's equation without using $K_{S\theta}$ and $K_{D\theta}$ in eqs. (8) and (9). According to Svedberg, molecular weight M_{SD} of the polymer can be determined by the equation[9]

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

where R is the gas constant, T the absolute temperature, $\bar{v}$ the partial specific volume of the solute, and ρ_0 the density of the solvent. If eq. (14) is applied to the polydisperse polymer, molecular weight M_{SD} becomes highly complex average because sedimentation constant S and diffusion constant D observed for the sample are certain averages such as eqs. (4) and (5).[6),14),15)] On the contrary, if $_{-2}S$ and $_2D$, and $_2S$ and $_{-2}D$ observed at the Θ point are used in eq. (14), we can obtain M_n and M_w as follows:

Substitutions of eqs. (8) and (9) into eq. (14) lead to the following equation which is valid at the Θ point:

$$M_{(nS)(nD)} = K_{SD}(_{n/2}M \cdot _{-n/2}M)^{1/2} = (_{n/2}M \cdot _{-n/2}M)^{1/2} \tag{15}$$

with[16]

$$K_{SD} = (K_{S\theta}/K_{D\theta})[RT/(1-\bar{v}\rho_0)] = 1. \tag{16}$$

Then, M_n can be derived by substituting eq. (8) with $n=-2$ and eq. (9) with $n=2$ into eq. (15) as follows:

$$M_{(-2S)(2D)} = (_{-1}M^2)^{1/2} = M_n. \tag{17}$$

M_w is also derived by substituting eq. (8) with $n=2$ and eq. (9) with $n=-2$ into eq. (15) as follows:

$$M_{(2S)(-2D)} = (_1M^2)^{1/2} = M_w. \tag{18}$$

Thus, M_n and M_w can be determined by Svedberg's equation without using $K_{S\theta}$ and $K_{D\theta}$.

Experimental

Sample

The present methods were tested experimentally by using four samples of polydisperse polystyrene and three samples of monodisperse polystyrene in the Θ solvent, cyclohexane at 35℃. These samples are shown in Table 1. Styron 683-7 is a commercial 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. M_w-values 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 M_w to M_n, 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℃ 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, and then was dried with calcium chloride, and finally was fractionally distilled over sodium metal.

Sedimentation Velocity Measurement

Sedimentation velocity measurements were carried out in cyclohexane at 35 ± 0.2℃ 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 to 0.81 g/100 cm^3.

Diffusion Measurement

Diffusion measurements were carried out in cyclohexane at 35 ± 0.02℃ using a new type of diffusion apparatus with moiré optics, which was designed and constructed in our laboratory.[17]~[19]   A light source is a helium-neon laser.   According to previous procedures, a sharp boundary was formed in the middle of a rectangular quartz cell[17] and five or six moiré patterns were photographed during each diffusion process.

Results and Discussions

Determination of Sedimentation Constant

Photographs of sedimentation pattern of Schlieren optics for Styron 683-7 in cyclohexane are shown in Figure 1.   From these patterns, an apparent weight distribution curve of sedimentation coefficients is obtained using the equations[3],[20],[21]

$t_1 = 960$sec $t_2 = 1,140$sec $t_3 = 1,320$sec $t_4 = 1,500$sec $t_5 = 1,680$sec
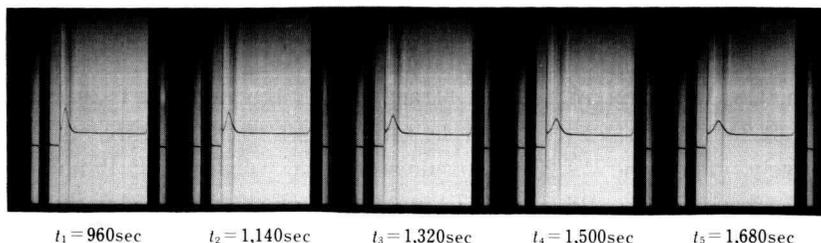
Fig. 1.   Photographs of sedimentation pattern with time t by Schlieren optics for Styron 683-7 in cyclohexane at 35℃ : Rotor speed, 55, 130 rpm ; Initial concentration $C_0 = 0.762$ g/100 cm^3 ; Initial time correction $t_0 = 300$ sec ; Diagonal bar angle $\phi = 80°$.   The figures show sedimentation time t in second.

$$S^* = \frac{ln(r/r_m)}{\omega^2(t-t_0)}\left\{1-\frac{m}{2}[(r/r_m)^2-1]\right\}^{-1} \tag{19}$$

$$g^*(S^*) = \frac{(dn/dr)(r/r_m)^2 r\omega^2(t-t_0)\{1-m[(r/r_m)^2-1]\}^2}{\int_{r_m}^{r_b}(dn/dr)(r/r_m)^2\{1-m[(r/r_m)^2-1]\}dr} \tag{20}$$

with

$$m = \frac{1}{2}\mu\omega^2 r_m^2\rho_0 \tag{21}$$

where S^* is the sedimentation coefficient at initial concentration C_0, $g^*(S^*)$ the apparent distribution function of the sedimentation coefficients with correction for pressure effect, r the radial distance from the axis of rotation, r_m the radial distance from the axis of rotation to the meniscus, r_b the radial distance of the cell bottom, 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, dn/dr the refractive index gradient, μ the pressure dependence coefficient, and ρ_0 the density of the solvent.

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, where r_p the position of the maximum refractive index gradient. $g^*(S^*)$ was determined with a value[22),23)] of $\mu=2\times10^{-9}$ cm^2/dyne and the weight distribution curve of sedimentation constant $g(S)$ was obtained by the ordinary method[3)] with corrections for diffusion and concentration. Integral weight distribution curve of sedimentation constant $G(S)$, which is defined by the equation

$$G(S)=\int_0^S g(S)ds, \tag{22}$$

and $g(S)$ of Styron 683-7 are shown in Figure 2. The 2nd-order and the $(-2nd)$-order sedimentation constants were calculated from these curves using eq. (5) and the values of the present samples were tabulated in Table 1.
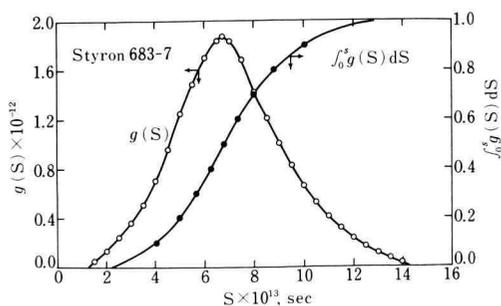

Fig. 2.   Weight distribution curves of sedimentation constant for Styron 683-7.

Table 1. Sedimentation constants and diffusion constants in cyclohexane at 35°C

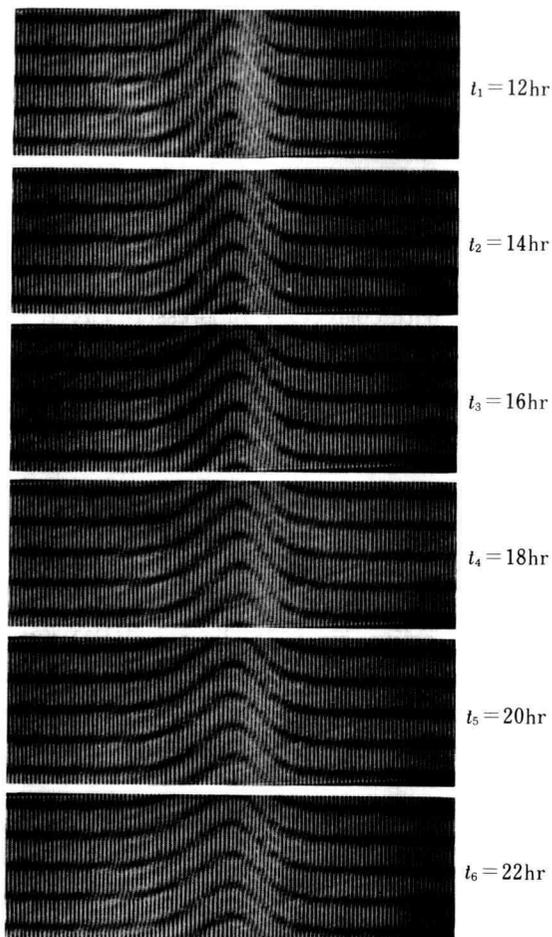| Sample	$_{-2}S$	$_2S$	$_{-2}D$	$_2D$
	($S\times10^{13}$, sec)		($D\times10^7$, cm^2/sec)	
Styron 683-7	4.83	7.58	2.46	4.29
PS-1	6.47	8.19	2.81	3.35
PS-2	6.73	10.10	2.20	3.18
PS-3	6.56	8.87	2.46	3.49
F-10	—	5.10	—	4.33
F-40	—	10.41	—	—
F-80	—	13.35	—	—

Fig. 3. Photographs of diffusion pattern with time
t 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
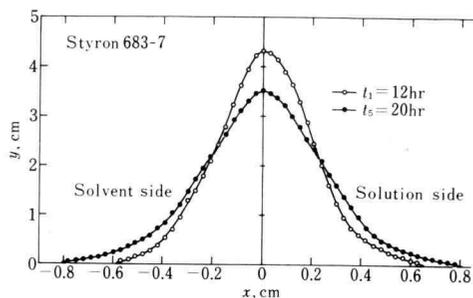diffusion time t in hour.

Fig. 4. Examples of refractive index gradient
curve obtained from Figure 3. y is the
height of the diffusion curve at distance x
in the diffusion cell.

Determination of Diffusion Constant

Photographs of diffusion pattern of the moiré optics for Styron 683-7 in cyclohexane are shown in Figure 3.   The left-hand side of this photograph is solvent (cyclohexane) side and each line of the moiré pattern corresponds to the diffusion curve obtained by Schlieren optics. Examples of refractive index gradient curve obtained from the moiré pattern are shown in Figure 4.   The 2nd-order diffusion coefficient $_2D$ was calculated from the slope of the straight line, plotting $(m_4/m_0)^{1/2}$ vs. t by the equation[7),24)]

$$(m_4/m_0)^{1/2} = \sqrt{12} \cdot _2D \cdot t \qquad (23)$$

with

$$m_4 = \int_{-\infty}^{\infty} |x - x_0|^4 y dx$$

$$= \int_{-\infty}^{\infty} |x|^4 y dx - 4x_0 \int_{-\infty}^{\infty} |x|^3 y dx + 0(x_0^2, x_0^3, \cdots)$$

$$= m_4' - 4x_0 m_3' \tag{24}$$

$$m_0 = \int_{-\infty}^{\infty} y dx \tag{25}$$

$$x_0 = \int_{-\infty}^{\infty} xy dx / \int_{-\infty}^{\infty} y dx \tag{26}$$

where m_4 is the 4th-order moment around the initial boundary x_0 of the diffusion curve, m_0 the area under the diffusion curve, t the diffusion time, and y the height of the diffusion curve at distance x from the origin where y has maximum value. m_4' and m_3' are the 4th-order and the 3rd-order moments around the origin of the diffusion curve, respectively. Higher order terms than x_0^2 in eq. (24) are negligible, since $x_0 \ll 1$ at the Θ point.

The $(-2nd)$-order diffusion coefficient $_{-2}D$ was calculated from the slope of the straight line, plotting $(m_0/S_2)^{1/2}$ vs. t by the equation [7],[10]

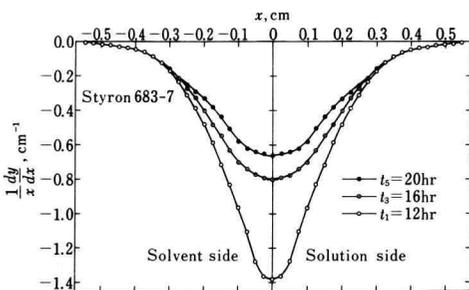$$(m_0/S_2)^{1/2} = 2 \cdot _{-2}D \cdot t \tag{27}$$

with

Fig. 5.   Plots of $\frac{1}{x}\frac{dy}{dx}$ vs. x for Styron 683-7 obtained from Figure 4.

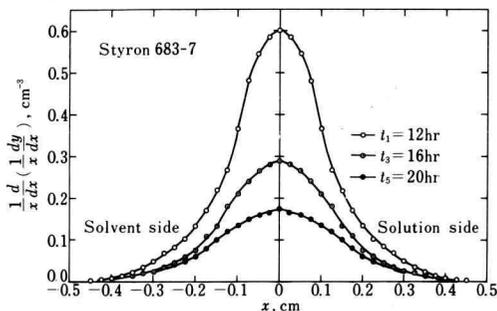Fig. 6.   Plots of $\frac{1}{x}\frac{d}{dx}\left(\frac{1}{x}\frac{dy}{dx}\right)$ vs. x for Styron 683-7 obtained from Figure 5.
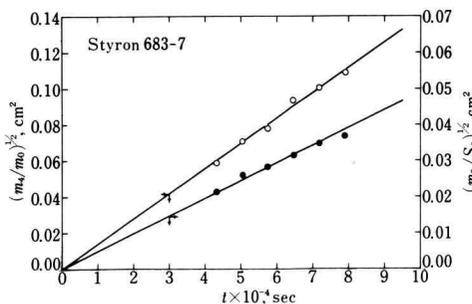

Fig. 7.   Determination of diffusion coefficients for Styron 683-7 according to eqs. (23) and (27): $\bigcirc$, eq. (23); $\bullet$, eq. (27).

Table 2. Number-average and weight-average molecular weights

Sample	$M_n \times 10^{-4}$				$M_w \times 10^{-4}$			
	Eq. (10)	Eq. (11)	Eq. (17)	Calcd[a]	Eq. (12)	Eq. (13)	Eq. (18)	Observed
Styron 683-7	10.7	11.1	10.1	12.5[b]	26.2	33.8	27.5	27.7[b], 30.2[c]
PS-1	19.1	18.2	17.2	17.1	30.6	25.9	26.0	26.5[a]
PS-2	20.6	20.2	18.9	18.8	46.5	42.3	41.0	44.1[a]
PS-3	19.6	16.8	16.8	17.6	35.9	33.8	32.2	32.3[a]
F-10	—	10.9	—	10.5	11.9	—	—	10.7[c]
F-40	—	—	—	40.2	49.5	—	—	42.2[c]
F-80	—	—	—	74.5	81.4	—	—	77.5[c]

[a] Calculated values, assuming that each component is monodisperse.
[b] Observed by column fractionation.[25]
[c] Observed by light scattering.

$$S_2 = \int_{-\infty}^{\infty} \frac{1}{x} \frac{d}{dx} \left(\frac{1}{x} \frac{dy}{dx} \right) dx. \tag{28}$$

S_2 was calculated by differentiating the diffusion curve of Figure 4 as shown in Figures 5 and 6. To the integral calculations in eqs. (25), (26), and (28), 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 the glass-made grating of the moiré optics. Plots of eqs. (23) and (27) are shown in Figure 7 for Styron 683-7. Diffusion coefficients obtained above were extrapolated to infinite dilution and diffusion constants of each sample were tabulated in Table 1.

Number-average molecular weight M_n and weight-average molecular weight M_w were determined using the following numerical values: $K_{S\theta} = 1.48 \times 10^{-15}$, $K_{D\theta} = 1.43 \times 10^{-4}$, $R = 8.314 \times 10^7$ erg mol^{-1}K^{-1}, $T = 308.2$ K, $\bar{v} = 0.934$ cm^3/g, and $\rho_0 = 0.7634$ g/cm^3. The results are tabulated in Table 2. M_n and M_w obtained by the present methods are reasonable values in comparison with those observed by column fractionation and light scattering measurements[25] on Styron 683-7, and with the calculated values[13] on PS-1, PS-2, and PS-3. In conclusion, our method is considered as a useful one to determine M_n and M_w, although it is valid only at the Θ point.

In eqs. (8) and (9), we must know the numerical values of $K_{S\theta}$ and $K_{D\theta}$, and it is essential that these values are sufficiently accurate. It is, however, very laborious to determine these values about a series of monodisperse systems with different molecular weights at the Θ point. On the contrary, the following procedures may be able to determine $K_{S\theta}$ and $K_{D\theta}$ even if the sample is polydisperse. It is found from eqs. (8) and (9) that the nth-order sedimentation constant $_nS$ and the nth-order diffusion constant $_nD$ correspond to the $(n/2)$th-order and the $(-n/2)$th-order molecular weights, respectively. The $(n/2)$th-order molecular weight $_{n/2}M$ and the $(-n/2)$th-order molecular weight $_{-n/2}M$ are for instance determined by the sedimentation equilibrium method. Then, $K_{S\theta}$ and $K_{D\theta}$ can be determined without any effect of molecular weight distribution of the sample from the intercepts of the straight lines with gradients 1/2 and $-1/2$, plotting $\log(_nS)$ vs. $\log(_{n/2}M)$ by eq. (8) and $\log(_nD)$ vs. $\log(_{-n/2}M)$ by eq. (9), respectively.
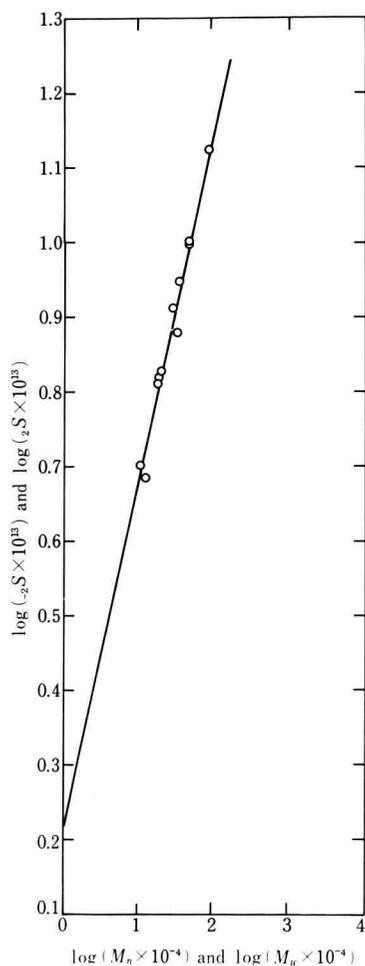
Fig. 8. Plots of log $(_{-2}S \times 10^{13})$ *vs.* log $(M_n \times 10^{-4})$ and log $(_2S \times 10^{13})$ *vs.* log $(M_w \times 10^{-4})$: ○, this work ; solid line, Tung, *et al.*[26]
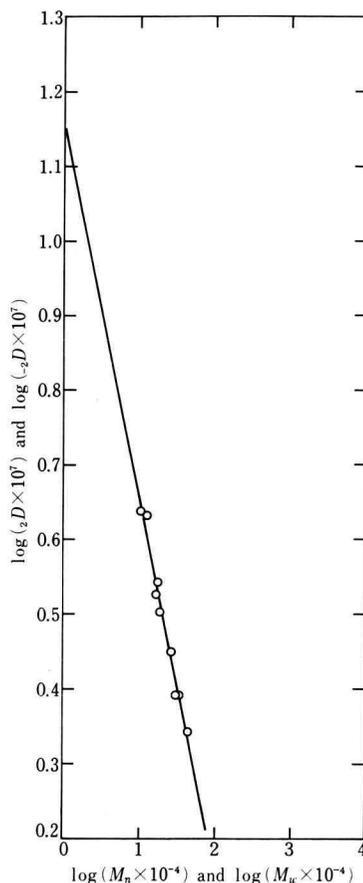
Fig. 9. Plots of log $(_2D \times 10^7)$ *vs.* log $(M_n \times 10^{-4})$ and log $(_{-2}D \times 10^7)$ *vs.* log $(M_w \times 10^{-4})$: ○, this work ; solid line, Kotera, *et al.*[27]

The number-average molecular weight $M_n(=_{-1}M)$ and the weight-average molecular weight $M_w(=_1M)$ were used in this study and these plots were shown in Figures 8 and 9. It can be seen from these Figures that the present data are in close agreement with those reported by Tung, et al.[26] and Kotera, et al.[27] In this study, however, there are no data for lower molecular weight region than 10^5. This problem shall be reported in a subsequent paper.

Conclusions

(1) In dilute polymer solution at the Θ point, the following equations are found to hold :

$$_{-2}S = K_{S\Theta} \cdot M_n^{1/2} \qquad\qquad (10)$$
$$_{2}D = K_{D\Theta} \cdot M_n^{-1/2} \qquad\qquad (11)^{11)}$$
$$_{2}S = K_{S\Theta} \cdot M_w^{1/2} \qquad\qquad (12)$$
$$_{-2}D = K_{D\Theta} \cdot M_w^{-1/2} \qquad\qquad (13)^{12),13)}$$
$$M_n = M_{(-2S)(2D)} = {}_{-2}SRT/[{}_{2}D(1 - \bar{v}\rho_0)] \qquad\qquad (17)$$
$$M_w = M_{(2S)(-2D)} = {}_{2}SRT/[{}_{-2}D(1 - \bar{v}\rho_0)], \qquad\qquad (18)$$

and number-average molecular weight M_n and weight-average molecular weight M_w are directly determined by sedimentation and diffusion constants without using molecular weight distribution curve.

(2) Methods to determine $K_{S\Theta}$ and $K_{D\Theta}$ in the Θ solvent system were proposed without any effect of molecular weight distribution.

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