Estimation of Molecular Weight Distribution of Polystyrene Standard Samples by Diffusion Method

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Molecular weight distributions of polystyrene samples delivered from Dr. H. Mark were estimated by a diffusion method proposed by the present authors. Dependence of diffusion coefficient on concentration in multicomponent solution, dependence of diffusion constant on the molecular weight and relation between the average molecular weights and the orders of moment were discussed in detail.

INTRODUCTION

The possibility to analyse the heterogeneity in molecular weight of polymers by diffusion method has first been suggested by Gralen[1]. Concerning this problem, Sakurada and Hosono have derived a general method to obtain the moment of any order about the diffusion constant from the optically measured diffusion-concentration gradient curve, and proposed a method to estimate the molecular weight distribution with the use of an orthogonal function. Some experimental verifications were carried out successfully with polyvinyl alcohol and polyvinyl acetate.

This paper reports molecular weight distributions estimated by our method for the polystyrene standard sample delivered from Dr. H. Mark.

I. THEORETICAL DESCRIPTION[2]

The molecular weight distribution of polymers may be estimated with our method by the following procedures.

(a) Evaluation of the Moments of Diffusion Coefficient

From the concentration gradient curve which is obtained optically by diffusion measurements on a given multi-component solution, the quantities defined by the following formula can be calculated:

$$
\left.
\begin{aligned}
m_n &= \int_{-\infty}^{\infty} |x|^n y\,dx \\
S_n &= \int_{-\infty}^{\infty} Z_n\,dx \\
(Z_n)_{x=0} & \\
Z_n &= \frac{1}{x}\frac{dZ_{n-1}}{dx} \qquad , \qquad y = Z_0
\end{aligned}
\right\}
\tag{1}
$$

where y is the height of the concentration gradient curve at a distance x from the original boundary. With these quantities, the average diffusion coefficient

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D_c is calculated from:

$$_{n/2}D_c^{n/2} = \frac{\sqrt{\pi}}{\Gamma\left(\dfrac{n-1}{2}\right)} \frac{1}{2^n t^n}\left(\frac{m_n}{m_0}\right)$$

$$_{-n}D_c^{n} = (-1)^n \frac{1}{2^n t^n}\left(\frac{m_0}{S_n}\right)$$

$$_{-(n+1/2)}D_c^{(n+1/2)} = (-1)^n \frac{1}{\sqrt{\pi}\, 2^n t^{n+1/2}}\left(\frac{m_0}{(Z_n)_{x=0}}\right)$$

(2)

where the subscripts $n/2$, $-n$ and $-(n+1/2)$ denote the orders of the moment about diffusion coefficient, the subscript c stands for $C_0/2$ (C_0: original concentration) and t is time. $_pD$ in the left-hand side of eqs (2) can be expressd by

$$_pD^p = \sum_i c_i D^p_i \tag{3}$$

where D_i and c_i is the diffusion coefficient and the weight fraction of the ith-component, respectively. This relation was derived by assuming that Fick's law can be applied to each component and the total flux is equal to the arithmetic sum of the fluxes of the constituent components. Accordingly, the concentration gradient curve of the multi-component system is equal to the sum of those for the components provided that the constituent compoments behave ideally and the interactions between those components are negligible.

If the concentration gradient curve is skewed due to concentration dependence of diffusion coefficient, then y in eq. (1) should be computed from:

$$y = (y_x + y_{-x})/2 \tag{4}$$

where y_x and y_{-x} are the heights of the concentration gradient curve at distances x and $-x$ from the original boundary, respectively.

(b) Concentration Dependence Calibration of Diffusion Coefficients (Evaluation of the Average Diffusion Constants)

The average diffusion coefficent at the infinite dilution is estimated from the average diffusion coefficients obtained in (a), according to the method of Beckmann and Rosenberg[3] or of Gralen[4] by the use of the concentration gradient curve. If the initial concentrations in diffusion measurements are moderately low, then the diffusion coefficients may be given by a linear function of the concentration c:

$$D_c = D_0(1 + k_0 c) \tag{5}$$

where k_0 is a constant. In this paper k_0 was calculated by the method of Beckmann and Rosenberg. Then average diffusion constants are calculated according to the equation:

$$_pD_c = _pD_c\left\{1 + k_0\left(\frac{C_0}{2}\right)\right\} \tag{6}$$

Eq. (6) is an equation held always for the diffusion coefficients given in eq. (2), if the initial concentrations are so chosen as to fulfill eq. (5) and if the heights

are given by eq. (4).

(c) Estimation of the Average Molecular Weights from the Average Diffusion Constants

Adopting the well-known relation between the molecular weight M and diffusion constant D of the constituent component of a polydisperse polymer;

$$D = KM^{-\beta} \tag{7}$$

where K and β are constants, the average molecular weight may be calculated by the following equation:

$$_{-\beta p}\overline{M}^{-\beta p} = \sum_i c_i M_i^{-\beta p} \tag{8}$$

where the quantity is related to the moment of the $-\beta p$ th order of the molecular weight distribution. Average molecular weights thus obtained are plotted against the orders of the moment. From the curve, the moments about a suitably chosen variable (here $M^{1/2}$ was chosen as the variable) are graphically obtained.

(d) Estimation of the Molecular Weight Distributions

The variable ξ used for the estimation of molecular weight distribution should be chosen, with taking the relation between the error in average diffusion constant (accordingly also in average molecular weight) and the moment into account. In line with this view, taking the form

$$\xi = M^{1/2}, \tag{9}$$

we used a moment as a measure of the number of molecules in this report. Thus the moments μ_r' are written as follows.

$$
\left.
\begin{aligned}
\mu_1' &= _{-1/2}\overline{M}^{-1/2}{}_{-1}\overline{M} = _{-1/2}\overline{M}^{-1/2}\overline{M}_N \\
\mu_2' &= \overline{M}_N \\
\mu_3' &= _{1/2}\overline{M}^{1/2} \cdot \overline{M}_N \\
\mu_4' &= _{+1}\overline{M} \cdot \overline{M}_N = \overline{M}_W \cdot \overline{M}_N \\
&\quad \ldots\ldots\ldots, \text{ etc.,}
\end{aligned}
\right\} \tag{10}
$$

where $\overline{M}_W$ and $\overline{M}_N$ denotes the weight average and number average molecular weight, respectively. If we calculate $_pD$ by eq. (2) up to $p \approx 2$ from the concentration gradient curve assuming $\beta = 0.5$, the moments μ_r' up to the 4th order can be obtained.

From the moments, μ_r', calculated by eq. (10), the moments about the mean value, μ_r, is obtained and the molecular weight distribution is estimated by the following equations.

$$f(M) = \frac{1}{2\sqrt{\mu_2}} \frac{1}{\sqrt{M}} g(M) \tag{11}$$

$$g(M) = \phi_0(t) - \frac{C_3}{3!}\phi_3(t) + \frac{C_4}{4!}\phi_4(t) - \ldots.$$

$$\phi_0(t) = \frac{1}{\sqrt{2\pi}}\exp\left(-\frac{t^2}{2}\right), \quad \phi_n(t) = \frac{d^n\phi_0(t)}{dt^n}, \qquad t = \frac{\sqrt{M}-\mu_1}{\sqrt{\mu_2}}$$

$$C_3 = \mu_3/\mu^{3/2}, \qquad C_4 = (\mu_4/\mu^2_2) - 3, \qquad \text{etc.}$$

The molecular weight distribution thus estimated from eq.(11) concerns with the number of molecules. As orthogonal functions to be used, Poisson distribution function or Laguerre function, besides Gaussian distribution function, is considered to be suitable. The values of ϕ_0, ϕ_3 and ϕ are obtained from a numerical table.

II. EXPERIMENTAL

(a) Materials

Three polystyrene standard samples;

$$S102 \ (\overline{M}_W = 82 \times 10^3, \ \overline{M}_N = 78.5 \times 10^3),$$
$$S111 \ (\overline{M}_W = 0.239 \times 10^6, \ \overline{M}_N = 0.221 \times 10^6),$$
$$S114 \ (\overline{M}_W = 3.56 \times 10^6, \ \overline{M}_N = 2.87 \times 10^6),$$

which were delivered from Dr. H. Mark, were investigated without further treatments.

(b) Apparatus

Diffusion measurements were carried out with a Type HT-A Tiselius apparatus manufactured by Hitachi Inc., Tokyo, Japan, at $25 \pm 0.05°$C.

(c) Calculation of Diffusion Coefficients

Some examples of the refractive index gradient curve (concentration gradient curve) are shown in Fig.1. The initial concentration of the measurement is 2.9614, 3.053 and 0.870g/100cc for S102, S111 and S114, respectively. Considerable skew is observed for S114. Methyl ethyl ketone, reagent grade after being dried with sodium sulfate anhydride and redistilled at $79.6 - 79.7°$C, was used for all the measurements.

The average diffusion coefficients were calculated from the following equations:

$$
\left.
\begin{aligned}
&_{1/2}D = 0.785 \times \frac{1}{t}\left(\frac{m_1}{m_0}\right)^2, \quad _{-1/2}D = 0.0796 \times \frac{1}{t}\left(\frac{m_0}{y_{x=0}}\right)^2 \\
&_1D = 0.500 \times \frac{1}{t}\left(\frac{m_2}{m_0}\right), \quad _{-1}D = 0.500 \times \frac{1}{t}\left(\frac{m_0}{\Sigma Z_1 \varDelta x}\right) \\
&_{3/2}D = 0.366 \times \frac{1}{t}\left(\frac{m_3}{m_0}\right)^{2/3}, \quad _{-3/2}D = 0.271 \times \frac{1}{t}\left(\frac{m_0}{(Z_1)_{x=0}}\right)^{3/2} \\
&_2D = 0.289 \times \frac{1}{t}\left(\frac{m^4}{m_0}\right)^{1/2}, \quad _{-2}D = 0.500 \times \frac{1}{t}\left(\frac{m_0}{\Sigma Z_2 \varDelta x}\right)^{1/2}
\end{aligned}
\right\} \qquad (12)
$$

As obvious from eqs. (12), $(m_1/m_0)^2$, (m_2/m_0),.... and $(m_0/\Sigma Z_2 \varDelta x)^{1/2}$ were proportional to time t. An example is given in Fig.2. The diffusion time was corrected using the above mentioned relations. The corrected time was in the range of $1 - 2 \times 10^4$ sec. The errors due to the left-hand side in eqs. (12) were adjusted within at most 5 to 10%. The method of adjustment[2] is not specified here.

(d) Evaluation of $K_0(C_0/2)$ from the Concentration Gradient Curve

The diffusion coefficient D_c at a concentraton c is, in the vicinity of initial

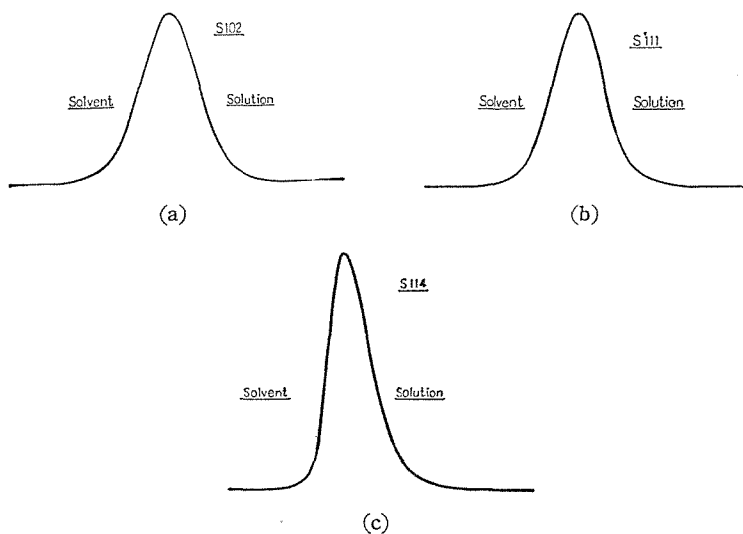concentrations (C_0) used here, obtained from the following equations by the use of the concentration gradient curve.

Fig. 1. Refractive index gradient curves: (a), S102 at $t=2.14\times10^4$ sec; (b), S111 at $t=2.77\times10^4$ sec; (c), S114 at $t=3.50\times10^4$ sec.
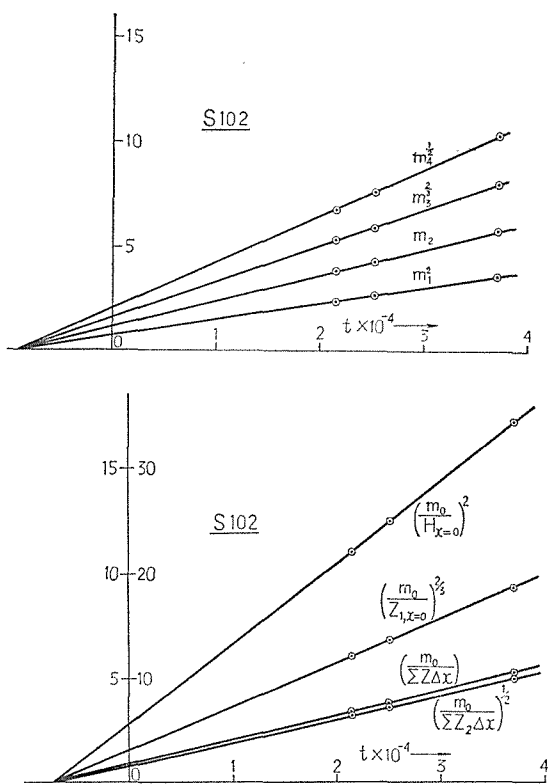

Fig. 2. Zero-time correction plots for S102.

$$D_c = -\frac{1}{2ty} \int_{-\infty}^{x} xy \ dx$$

$$c/C_0 = \frac{1}{m_0} \int_{-\infty}^{x} ydx$$

(13)

The results obtained for three samples were illustrated in Fig. 3. Time t in eq. (13) should be the corrected time which can be obtained for example from Fig. 2. $K_D(C_0/2)$ is easily found from Fig. 3, to be -0.09, -0.02 and 0.55 for S102, S111 and S114, respectively.
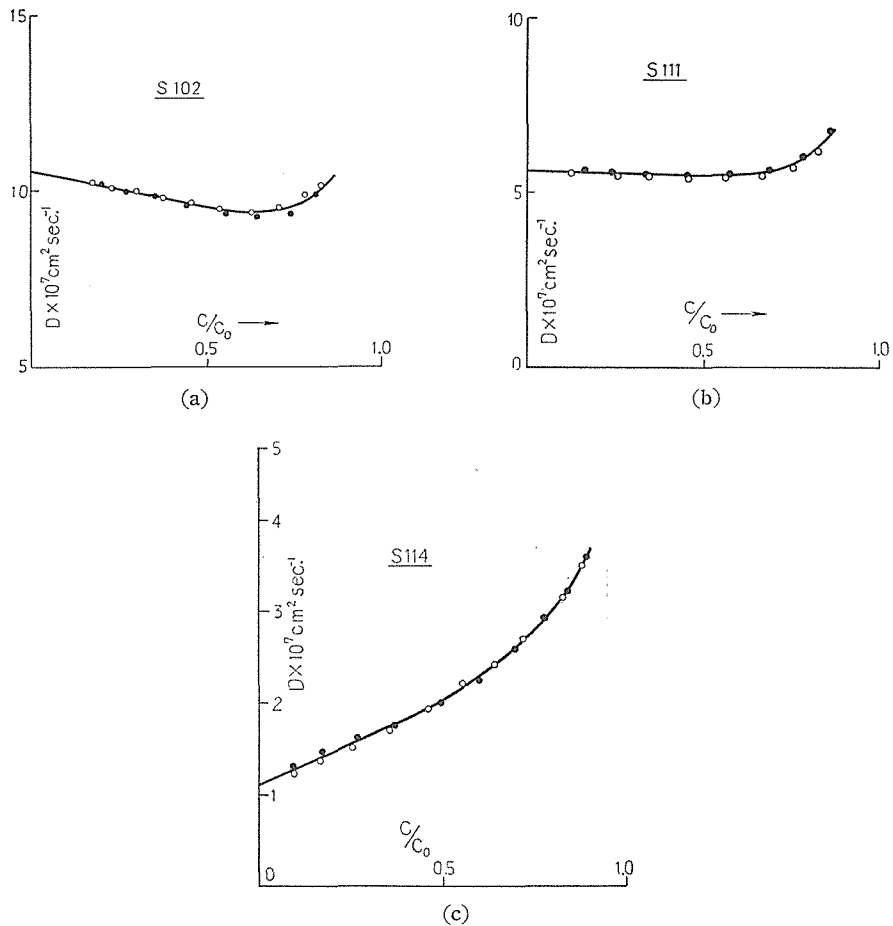

Fig. 3. Concentration dependence of the diffusion coefficient
obtained by the Beckmann-Rosenberg's procedure.

(e) Estimation of the Average Molecular Weight from the Diffusion Data

The results of Schick and Singer[5] on the relation between the molecular weight and diffusion constant at 27°C for the fractionated samples were used for the present calculations at 25°C neglecting the small temperature difference. Fig. 4 is a reproduction of their results, from which we have $\beta = 0.59$ and $K = 7.93 \times 10^{-4}$.
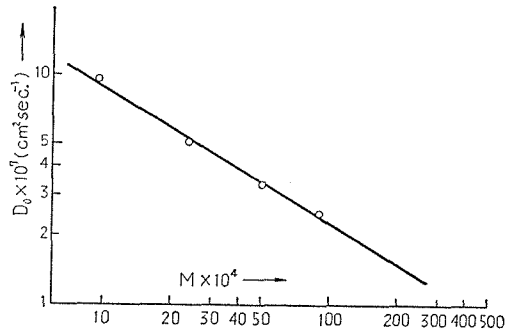
Fig. 4. Dependence of the diffusion constant on molecular weight
for polystyrene fractions in methyl ethyl ketone.

III. RESULTS

In Table 1, the results obtained for the average diffusion constant D_0, the average molecular weight M and the order of moment n were tabulated.

Fig. 5 shows the relation between the average molecular weights and the orders of moment. Two broken lines in the figure show the range of deviations of the experimental results obtained with an error of 10%. Within the calculated range of the orders of moment, experimental results may be represented by a straight line shown in the figure. This relation may be supported by the fact that the average molecular weight is, in most cases, nearly a linear function of the order of corresponding moment for $-1 < n < 1$.

$_{-1}\overline{M}$, $_{-1/2}\overline{M}$, $_{1/2}\overline{M}$ and $_1\overline{M}$, obtained graphically from Fig. 5, were listed in Table 2. From the results in Table 2, C_3 and C_4 in eq. (11) were found to be $C_3 = 0.044$, $C_4 = 0.006$ for S102; $C_3 = 0.041$, $C_4 = 0.003$ for S111; and $C_3 = 0.069$. $C_4 = 0.007$ for S114;

Table 1. The Average diffusion coefficients, estimated average molecular
weights and corresponding orders of moment for polystyrene standard
samples.

Order of Moment	about Diffusion coefficient	2.0	1.5	1.0	0.5	−0.5	−1.0	−1.5	−2.0
	about Mol. weight	−1.18	−0.89	−0.69	−0.30	0.30	0.59	0.89	1.18
S102	$D_c \times 10^7$	9.89	9.74	9.62	9.27	9.45	9.18	8.83	8.71
	$D_0 \times 10^7$	10.78	10.63	10.48	10.10	10.30	10.00	9.62	9.50
	$M \times 10^{-4}$	7.22	7.40	7.58	8.06	7.80	8.20	8.76	8.95
S111	$D_c \times 10^7$	5.48	5.40	5.33	5.23	5.23	5.15	5.06	4.93
	$D_0 \times 10^7$	5.59	5.51	5.44	5.33	5.33	5.25	5.16	5.03
	$M \times 10^{-5}$	2.20	2.25	2.30	2.38	2.38	2.45	2.52	2.63
S114	$D_c \times 10^7$	2.22	2.18	2.10	2.06	2.03	1.93	1.89	1.88
	$D_0 \times 10^7$	1.22	1.20	1.16	1.13	1.12	1.06	1.04	1.03
	$M \times 10^{-6}$	2.90	2.98	3.16	3.30	3.35	3.68	3.80	3.86

Table 2. $_{-1}\overline{M}$, $_{-1/2}\overline{M}$, $_{1/2}\overline{M}$ and $_1\overline{M}$ of polystyrene standard samples.

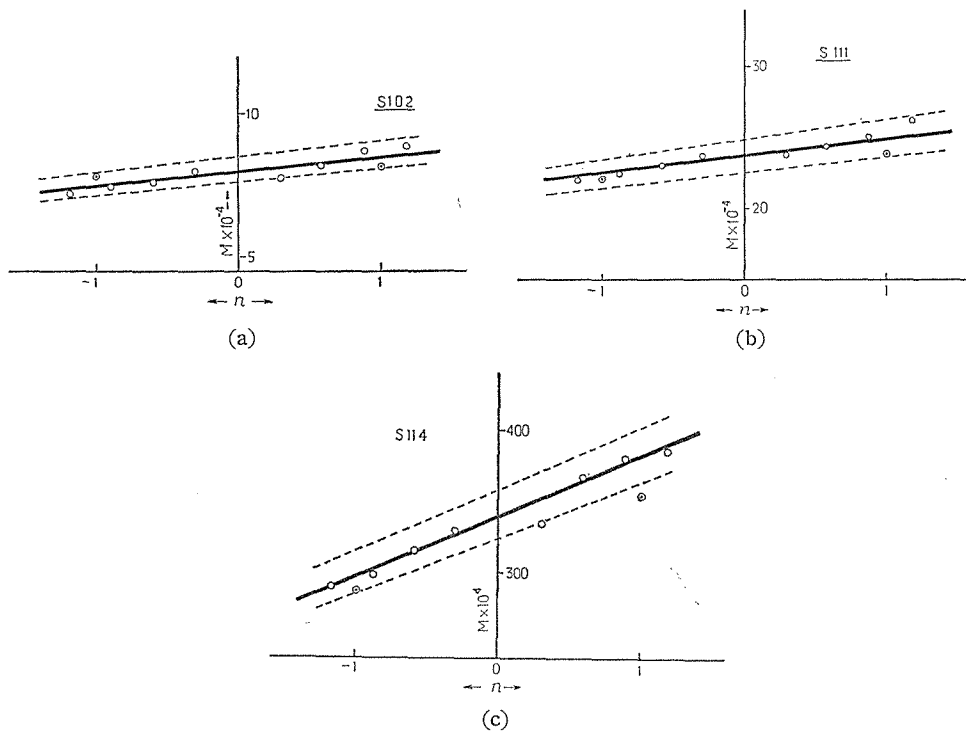| Average	Mol. Weight	$_{-1}\overline{M}=\overline{M}_N$	$_{-1/2}\overline{M}$	$_{1/2}\overline{M}$	$_1\overline{M}=\overline{M}_W$
S102	from Diffusion	7.50×10^4	7.75×10^4	8.25×10^4	8.50×10^4
	Standard Value	7.85×10^4	—	—	8.20×10^4
S111	from Diffusion	2.26×10^5	2.32×10^6	2.44×10^5	2.50×10^5
	Standard Value	2.21×10^5	—	—	2.39×10^5
S114	from Diffusion	2.96×10^6	3.18×10^6	3.62×10^6	3.84×10^6
	Standard Value	2.87×10^6	—	—	3.56×10^6

Fig. 5. Relation between average molecular weight and order of moments.

The molecular weight distribution of polystyrene standard samples is obtained using the numerical values mentioned above and shown in Table 3. and in Fig. 6. The full curves in Fig. 6 are the weight distributions of molecular weight and the broken curves are those suggested by Mark.
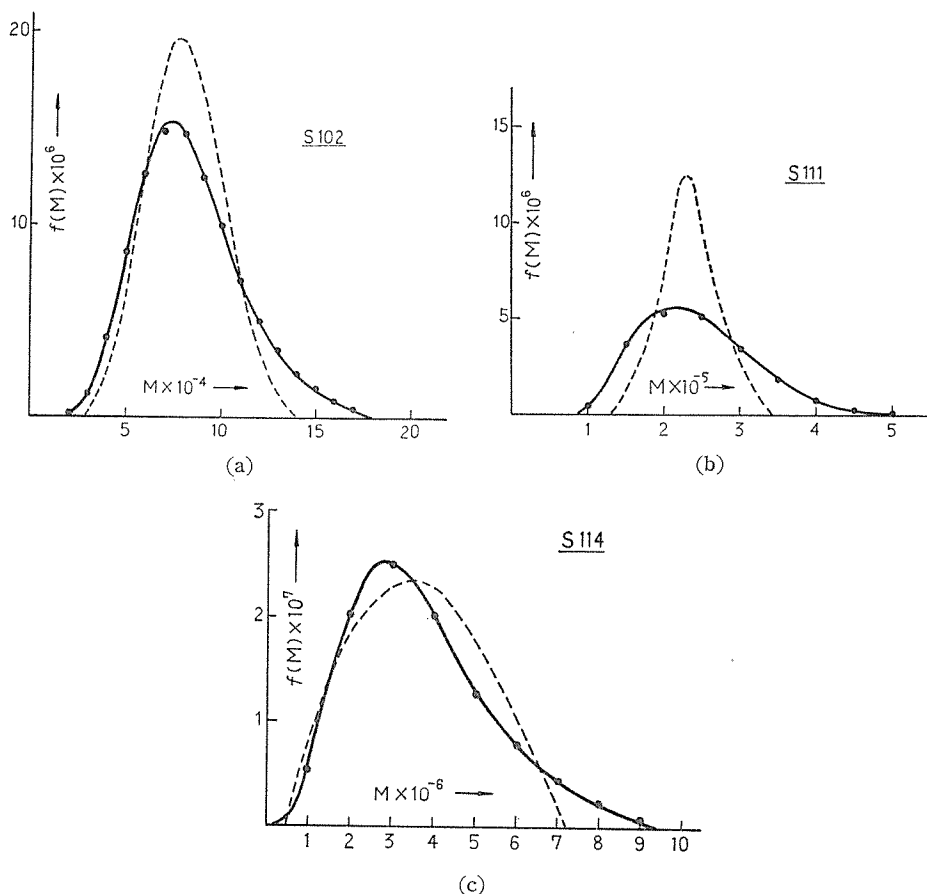
Fig. 6. Molecular weight distribution of polystyrene standard samples estimated by the diffusion method.

——— by the diffusion method.
------ distribution curve suggested by Mark.

IV. DISCUSSION

(a) Dependence of Diffusion Coefficient on Concentration in the Multi-component Solution

For multi-component solution, K_D obtained from eq. (13) should be a mean value depending on the method of calculation. Accordingly it may be questionable to use this value regardless of the order of moments. Nevertheless, a definite value was used in this report. Moreover, if K_D is different for each component, then the mean value of K_D, which has to be used in eq. (6), should be the one depending on the method of calculation of the average diffusion constant. In such a case, in order to estimate the average diffusion constant strictly, it may be necessary to correspond $_pD$ to the initial concentration and to calculate a value extrapolated to the infinite dilution. But these are very complicated problems.

However, through simple calculations of the mean values of K_D, the relative

Table 3. Number and weight frequencies for the molecular weights of polystyrene standard samples estimated by the diffusion method.

S102			S111			S114		
$M\times10^{-4}$	$f_N\times10^6$	$f_W\times10^6$	$M\times10^{-5}$	$f_N\times10^6$	$f_W\times10^6$	$M\times10^{-6}$	$f_N\times10^7$	$f_W\times10^7$
2	0.61	0.16	0.5	—	—	1	1.50	0.54
3	3.07	1.24	1.0	1.01	0.45	2	2.99	2.02
4	7.75	4.18	1.5	4.10	2.74	3	2.48	2.51
5	12.70	8.55	2.0	5.82	5.18	4	1.45	2.01
6	15.60	12.60	2.5	4.64	5.17	5	0.75	1.26
7	15.70	14.80	3.0	2.55	3.40	6	0.38	0.77
8	13.60	14.70	3.5	1.17	1.82	7	0.19	0.45
9	10.30	12.50	4.0	0.47	0.83	8	0.10	0.26
10	7.37	9.93	4.5	0.17	0.34	9	0.04	0.14
11	4.90	7.37	5.0	0.06	0.14	10	0.02	0.06
12	3.17	5.12						
13	2.00	3.50						
14	1.25	2.37						
15	0.76	1.54						
16	0.46	0.99						
17	0.27	0.59						

f_N : Number frequency.
f_W : Weight frequency.

difference in K_D's was known[2] to be not so large for samples, which are not extremely heterogeneous, in the range of the orders of moment used here. Therefore the difference in K_D's was neglected in the present paper.

(b) **Dependence of Diffusion on the Molecular Weight**

β recalculated by us from the eperimental data by Schick and Singer was slightly higher than their value 0.53. The difference in β has its origin in a fact that the experimental result of their low molecular weight sample D-8 was taken into our consideration.

Furthermore the following problem may arise about the use of their results for the present purpose. Their samples are sharp fractions indeed but not monodisperse. So, strictly speaking, there may remain some questions in using such data for analysis of dishomogeneity. If we really want to know the relation of molecular weight and diffusion constant for monodisperse components we may succeed by relating corresponding the zeroth order average diffusion constants to the zeroth order average molecular weights. For such treatment, samples are not required to be fractionated. This may be possible by combined experiments of diffusion and ultracentrifuge.

However, in this paperas a matter of practical problem, we have adopted their results.

(c) **Relation between the Average Molecular Weights and the Orders of Moment**

In this report, the average molecular weights were approximated by a linear function of the orders of corresponding moment. This assumption may approximately be acceptable within the range of orders usually ued for various distribution functions, but strictly not correct. In other words, by such assumption we may deal with only limited groups which can be approximated by the linear function. To investigate the characteristics of unknown distribution functions in more detail, we may need to evaluate the moments of higher orders. For such purpose, the apparatus should be improved to reduce the experimental errors.

In this report, analytical investigations were performed within allowable calculation errors by considering the experimental errors of our present apparatus.

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