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# VISCOSITY AND LIGHT SCATTERING STUDIES OF POLYMETHYLMETHACRYLATE IN METHYL ACETATE-ETHANOL*

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ABSTRACT

A polymethylmethacrylate fraction of molecular weight $2.63 \times 10^6$ has been studied by viscosity and by light scattering in an iso-refractive solvent-non-solvent system, methylacetate-ethanol. The results show that $d \log [\eta] / d \log \sqrt{\overline{h^2}} = 3$ as demanded by Flory-Fox's theoretical interpretation of intrinsic viscosity. It is shown that the solution viscosity has reached the region of Newtonian flow at low shear rates under the conditions of ordinary viscometric determinations. The composition of $\theta$-solvent of the system at 25.0° has been found to be $\gamma_w$(ethanol) $= 0.509$. The molecular weight distribution of the sample was determined by the method of sedimentation velocity in ultracentrifuge at the vicinity of $\theta$-temperature in acetone-ethanol. Thus a reliable polydispersity correction could be applied to the evaluation of Flory's universal constant, which gave $\Phi = 1.6_1 \times 10^{23}$, somewhat lower than generally accepted. From the integral distribution of sedimentation coefficients of the sample and the experimental values of $\langle M \rangle_w$ and $[\eta]_\theta$, it is possible to evaluate $\overset{*}{K}_s$ and $\overset{*}{K}_\theta$ in the relations

$$s = \overset{*}{K}_s M^{1/2} \quad \text{and} \quad [\eta]_\theta = \overset{*}{K}_\theta M^{1/2}$$

for a hypothetical monodisperse system. The values found for polymethylmethacrylate in $\theta$-solvent at 25.0° are $\overset{*}{K}_s = 3.02 \times 10^{-15}$ and $\overset{*}{K}_\theta = 4.59 \times 10^{-2}$.

According to the theoretical interpretation by Flory[1], the relationship between intrinsic viscosity and molecular weight is given as

$$[\eta] = \Phi \frac{(\overline{h^2})^{3/2}}{M} = \Phi \frac{(\overline{h_0^2})^{3/2}}{M} \cdot \chi^3, \tag{1}$$

where $\Phi$ is a universal constant independent of the nature of the polymer-solvent system and of temperature; $\overline{h^2}$, $\overline{h_0^2}$ are the mean square end-to-end distance of the polymer chain in a good solvent and in an ideal solvent respectively; $M$ is the molecular weight of the polymer; and $\chi = (\overline{h^2}/\overline{h_0^2})^{1/2}$ is

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a linear expansion factor. The best value of $\Phi$ as obtained experimentally is $2.1 \times 10^{23}$. If equation (1) could be verified quantitatively, it offers a ready means of determining the end-to-end distance of a polymer chain through simple viscometric measurements. There are, however, two questions remained to be elucidated: (1) Is $[\eta]$ really in direct proportion to $(\overline{h^2})^{3/2}$? (2) What is the correct numerical value of the universal constant $\Phi$ and to what extent it is true in the sense of a universal constant? With regard to the first question, Kunst[2] obtained $\nu = d \log [\eta] / d \log \sqrt{\overline{h^2}} = 2.5$ from viscosity and light scattering measurements on a polystyrene fraction ($M = 1.1 \times 10^6$) in a series of benzene-$n$-hexane mixed solvent of different compositions at 25° and 60°C. The experimental data of a polyisobutylene fraction ($M = 1.9 \times 10^5$) in the $n$-heptane-propanol mixed solvent, however, gave $\nu = 2.2$. Krigbaum and Carpenter[3] measured the light scattering of a polystyrene fraction ($M = 3.2 \times 10^6$) in cyclohexane in the temperature range 32.5° to 55° ($T_\theta = 35.2$°C). They obtained $\nu = 2.2$. All these results deviate somewhat from $\nu = 3$ as demanded by equation (1). Cantow and Bodmann[4] measured the light scattering of a polymethylmethacrylate fraction ($M = 1.25 \times 10^6$) in six different solvents including butyl acetate, ethyl acetate, acetone, tetrahydrofuran, dioxane, and chloroform. Their result indicated that $\nu$ has a value of 3 approximately[5]. In all these works the shear rate dependence of intrinsic viscosity had not been considered properly. With samples of high molecular weight, the precision of the light scattering measurement of $\overline{h^2}$ is comparatively higher, but the shear rate dependence of $[\eta]$ will be of considerable importance. As the theory of intrinsic viscosity gives the intrinsic viscosity at zero shear rate, $[\eta]_0$, while the difference between $[\eta]_0$ and $[\eta]$ increases as $\chi$ increases, we should expect a lower value of $\nu$ from these experiments. In our laboratory, we had the experience that the solution viscosity of a polystyrene fraction ($M = 2.4 \times 10^6$) in cyclohexane still exhibited shear rate dependence at the $\theta$-temperature. The solvent and non-solvent used in Kunst's work differ greatly in refractive indices, rendering the results of light scattering not so reliable. Newman *et al.*[6] plotted the experimental data of $\log [\eta]$ versus $\log [(\overline{h^2})^{3/2}/M]$ for five polymer-solvent systems which have quite different intermolecular interactions and obtained a straight line with a slope of unity. But the molecular weight distributions of these samples were not known which would surely affect the value of $(\overline{h^2})^{3/2}/M$ significantly. Hence the result obtained is of doubtful value.

In the present work, viscosity and light scattering measurements were made on a polymethylmethacrylate fraction ($M = 2.63 \times 10^6$) in a series of methyl acetate-ethanol mixed solvents of different proportions at 25°C. The solvent and non-solvent used have nearly equal refractive indices (methyl acetate $n_D^{20} = 1.3619$; ethanol $n_D^{20} = 1.3614$)[7]. Moreover, solution viscosities of the sample in methyl acetate showed no shear rate dependence under the experimental conditions. The experimental results give $\nu = 3$ which is in accord with equation (1). The molecular weight distribution of the sample was determined by sedimentation velocity method in an ultracentrifuge, and consequently a more reliable correction for polydispersity could be applied for the evaluation of $\Phi$ and $(\overline{h_0^2}/M)^{1/2}$.

## Viscosity and Light Scattering

Viscosities of the sample in methyl acetate solution were determined in a horizontal capillary viscometer with external pressure of 3—1200 cm water column applied. The apparatus used and the method of treatment of experimental data were reported previously[8]. The results obtained for solutions at four different concentrations ($c$=3.12, 2.62, 1.75, and 1.19 $\times$ $10^{-3}$ g/ml) are shown in Fig. 1. It is evident that for $c$ less than 3 $\times$ $10^{-3}$ g/ml and the

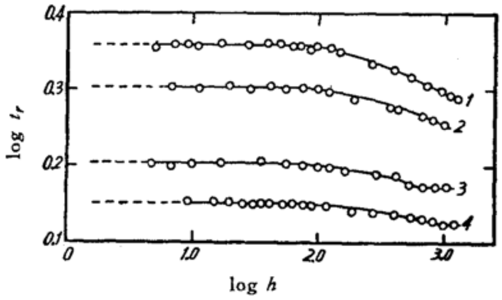


Fig. 1. Shear rate dependence of viscosity of polymethylmethacrylate fraction in methyl acetate solution.

$t_r$ —— ratio of flow times of solution and solvent;
$h$ —— driving pressure, height of water column in cm;
Curve 1 to 4, $C$ = 0.312, 0.262, 0.175, 0.119 $\times$ $10^{-2}$ g/ml.

driving pressure less than 50 cm water column ($\log h$<1.7) the solution viscosity reached the region of Newtonian flow at low shear rates. Hence it is assured that the $[\eta]$ values obtained for the sample in methyl acetate-ethanol mixed solvents in a suitable Ubbelohde dilution viscometer should approach the zero shear rate values.

The results of viscosity and light scattering measurements of the sample in seven methyl acetate-ethanol mixed solvents of various compositions (weight fraction of ethanol $\gamma_w$=0 − 0.509) are shown in Table 1 and Figs. 2 and 3. The solution properties are typical for flexible polymer molecules. The changes of $[\eta]$ and $A_2$ with the change of composition of the mixed solvent are parallel. At $\gamma_w \simeq 0.15$, both $[\eta]$ and $A_2$ show a maximum and decrease with further increase in $\gamma_w$. This is reasonable as the solubility parameter of polymethylmethacrylate ($\delta \simeq 10.0$)[9] lies between those of ethanol ($\delta$=12.8)[10] and of methyl acetate ($\delta$=9.7)[10]. A linear relation between $[\eta]$ and $A_2$ is obtained as predicted by the theoretical equation of Krigbaum[11],

$$[\eta] = [\eta]_\theta + 3 \cdot \frac{134}{105}\left(\frac{3}{4\pi}\right)^{3/2} \frac{\Phi}{\tilde{N}} A_2 M + \cdots \simeq [\eta]_\theta + 0.44 A_2 M. \qquad (2)$$

**Table 1**

Results of Viscosity and Light Scattering Measurements of Polymethylmethacrylate Fraction A in Methyl Acetate-Ethanol Mixed Solvents, 25°C

| $\gamma_w$ | $[\eta]$ | $k'$ | $\langle M\rangle_w\cdot 10^{-6}$ | $A_2\cdot 10^4$ | $[z]$ | $\langle \overline{h^2}\rangle_z^{1/2}\cdot 10^{-3}$, Å | $\Phi\cdot 10^{-23}$ |
|---|---|---|---|---|---|---|---|
| 0.000 | 266.6 | 0.51 | 2.50 | 1.51 | 2.96 | 1.85 | (1.65) |
| 0.117 | 271.0 | 0.50 | 2.62 | 1.81 | 3.00 | 1.87 | (1.65) |
| 0.350 | 196.7 | 0.57 | 2.26 | 1.03 | 2.79 | 1.74 | (1.45) |
| 0.389 | 174.7 | 0.64 | 2.63 | 0.78 | 2.61 | 1.64 | (1.55) |
| 0.432 | 142.0 | 0.78 | 2.52 | 0.54 | 2.43 | 1.52 | (1.57) |
| 0.469 | 110.2 | 1.24 | 2.68 | 0.36 | 2.27 | 1.42 | (1.50) |
| 0.509 | 72.0 | 1.90 | 2.63 | 0 | 1.91 | 1.21 | 1.61 |

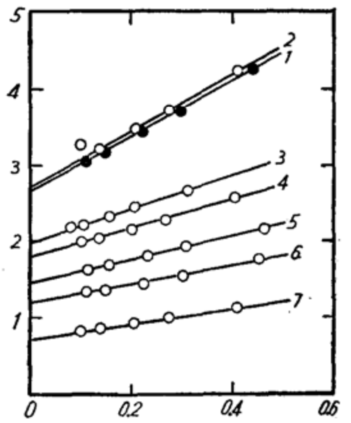


Fig. 2. Viscosities of Fraction A in mixed solvents of different compositions.

Curve 1 to 7, $\gamma_w = 0$, 0.117, 0.350, 0.389, 0.432, 0.469, 0.509.

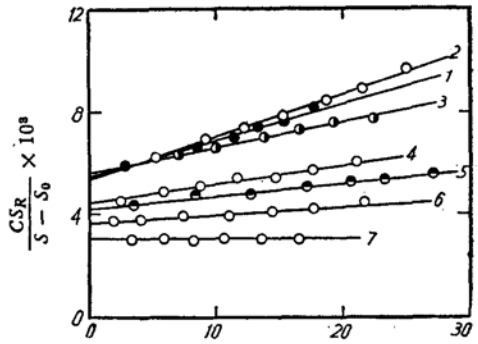


Fig. 3. Light scattering of Fraction A in mixed solvents of different compositions.

$S_0$, $S$, $S_R$ are the relative intensities of light scattered at 90° by solvent, solution and working standard respectively.

Curve 1 to 7, $\gamma_w = 0$, 0.117, 0.350, 0.389, 0.432, 0.469, 0.509.

**Table 2**

$[\eta]_\theta$, $\langle M\rangle_w$, $\langle S\rangle_w$ Values of 4 Polymethylmethacrylate Fractions

| Fraction | $[\eta]_\theta$ | $\langle M\rangle_w\cdot 10^{-6}$ | $\langle S\rangle_w\cdot 10^{13}$* |
|---|---|---|---|
| A | 72.0 | 2.63 | 47.5 |
| B | 62.4 | 2.03 | ...... |
| C | 47.0 | 1.03 | 29.6 |
| D | 24.6 | 0.31 | 16.0 |

* Fraction C and Fraction D used here are Sample 3 and Sample 2 respectively reported in reference [16]; sedimentation experiments were carried out in acetone-ethanol (1:1 by volume) mixed solvent near $\theta$-temperature.

The slope of the straight line in Fig. 4 is $1.20 \times 10^6$ in close agreement with $1.16 \times 10^6$ calculated from equation (2).

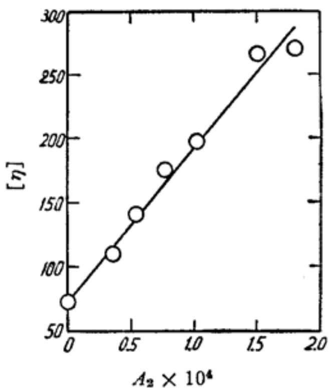


Fig. 4. $[\eta]$-$A_2$ relationship for Fraction A in mixed solvents of different compositions.

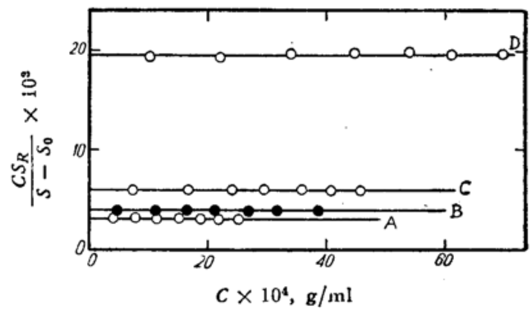


Fig. 5. 90° scattering of Fractions A, B, C, D in $\theta$-solvent.

From the light scattering data, the composition of the $\theta$-solvent for polymethylmethacrylate at 25°C is found to be $\gamma_w$=0.509 or $\gamma$ (volume fraction) =0.55. For further verification of this point, three other fractions of polymethylmethacrylate of lower molecular weights were investigated (Table 2). The intensities of 90° scattering of all these fractions in the $\theta$-solvent are independent of concentrations, i.e. $A_2$=0 (Fig. 5). The $[\eta]$-$M$ relationship for these four fractions in $\theta$-solvent fits the following equation:

$$[\eta]_\theta = K_\theta \langle M \rangle_w^{1/2}. \tag{3}$$

The log $[\eta]$-log $\langle M \rangle_w$ plot gives a straight line with a slope of 0.5 (Fig. 6). If $[\eta]_\theta$ is plotted against $\langle M \rangle_w^{1/2}$, a straight line passing through the origin

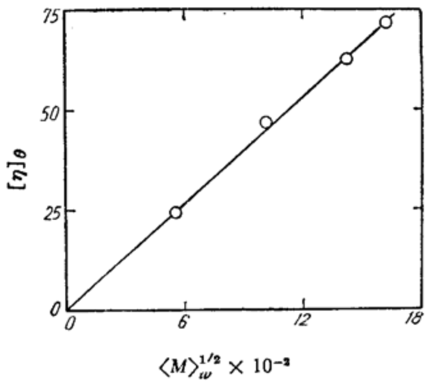


Fig. 6. $[\eta]$-$\langle M \rangle_w^{1/2}$ relation of Fraction A, B, C, D in $\theta$-solvent.

is obtained. From its slope, we get $K_\theta = 4.45 \times 10^{-2}$. The values of $K_\theta$ for polymethylmethacrylate in various $\theta$-solvents as reported by different authors are listed in Table 3. The value obtained in this work is ca. 20% lower than that reported by Chinai[13], and is in good accord with that of Hakozaki[15] reported quite recently.

**Table 3**

$K_\theta$ Values of Polymethylmethacrylate in $\theta$-Solvents

| Year | Author | $T$, °C | Solvent | Criterion for $\theta$-Condition | $K_\theta \cdot 10^2$ | Ref. |
|---|---|---|---|---|---|---|
| 1956 | Chinai, Bondurant | 25.0 | Butanone-isopropanol ($\gamma = 0.500$) | $A_2 = 0$ | 5.92 | 12 |
| 1959 | Chinai, Valles | 26.2 | Toluene-methanol ($\gamma = 0.642$) | $T_C(M = \infty)$ | 5.59 | 13 |
| 1959 | Chang Song Chien | 25.0 | Acetone-water ($\gamma_w = 0.167$) | $a = 1/2$ | 4.7 | 14 |
| 1961 | Hakozaki | 25.0 | Butanone-isopropanol ($\gamma = 0.50$) | $A_2 = 0$ | 4.28 | 15 |
| 1962 | This work | 25.0 | Methylacetate-ethanol ($\gamma_w = 0.509$) | $A_2 = 0$ | 4.45<br>4.59 (monodisperse) | |

The value of the Huggins' constant $k'$ increases with the increase of non-solvent content in the mixed solvent. In $\theta$-solvent, $k'=1.90$, approaching the value for a rigid sphere. Similar trends were observed by Chinai[13].

The straight line obtained from the plot of log $[\eta]$ versus $\log\langle\overline{h^2}\rangle_z^{1/2}$ (Fig. 7) has a slope $\nu=3$ as demanded by equation (1). In this work $[\eta]$

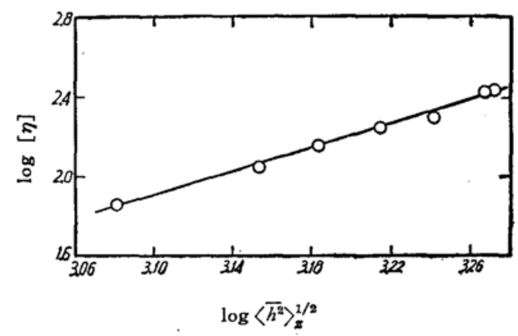


Fig. 7. $\log[\eta]$-$\log\langle\overline{h^2}\rangle_z^{1/2}$ relation of Fraction A in mixed solvents of different compositions.

values for the samples were varied approximately four-fold through the change of solvent compositions. The variation is about twice that obtained by Krigbaum *et al.* for a polystyrene fraction in cyclohexane through the change of temperature. Moreover, the mixed solvent system chosen in this work exhibited no shear rate dependence of the viscosity under the experimental conditions and the difference of refractive indices between solvent and non-solvent is extremely small. Consequently the result reported here should be regarded as more reliable and $\nu=3$ is hereby experimentally verified.

## Polydispersity of the Sample

To calculate the value of $\Phi$ of equation (1) from viscosity and light scattering data, it is necessary to know the exact molecular weight distribution of the sample which was determined by sedimentation velocity measurements in an ultracentrifuge. The measurement was performed in acetone-ethanol ($\gamma=0.50$) mixed solvent at a concentration of $0.17\times10^{-2}$ g/ml near $\theta$-temperature (experimental temperature $22.0\pm0.1°$, $T_\theta=19.0°$) with a rotor velocity of 29,440 r.p.m. Method of treatment of data was reported previously[16]. The integral distribution of sedimentation coefficients $I(s)$ of the sample is shown in Fig. 8.

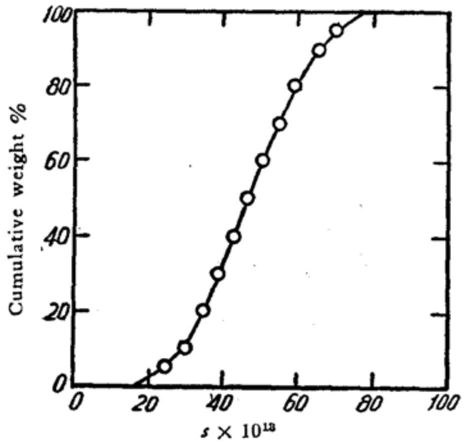


Fig. 8. Integral distribution curve of sedimentation coefficients for Fraction A.

Calculation of the integral molecular weight distribution $I(M)$ from $I(s)$ needs a relationship $S(M)$ for monodisperse solutions, but what obtained from experiment is always the relation between some statistical averages of $S$ and $M$, as the method of obtaining truly monodisperse samples is not available at present. Values of $\langle M\rangle_w$ calculated from $I(M)$ which in turn is calculated from $I(S)$ through the polydisperse relationship of $S$ and $M$ often show slight discrepancy with the experimental values[17], demonstrating internal inconsistency of this procedure. Freund and Daune[18] has proposed a method to obtain the monodisperse $S(M)$ and $D(M)$ relationships from sedimentation and diffusion measurements on polydisperse solutions, so as to make the molecular weight distributions calculated from $I(S)$ and $I(D)$ coincide. When the sedimentation measurements were carried out in a $\theta$-solvent, $S(M)$ relationship is particularly simple and can be represented by an expression involving one parameter only, i.e.

$$s = \overset{*}{K}_s M^{1/2} \tag{4}$$

where $\overset{*}{K}_s$| designates the parameter for monodisperse relation to be differentiated from the polydisperse relation $\langle S\rangle = K_s\langle M\rangle^{1/2}$. It is possible to determine the value of $\overset{*}{K}_s$ by try and error method. Different values of $\overset{*}{K}_s$ are tried in equation (4) and the proper value of $\overset{*}{K}_s$ should be so chosen as the conversion of $I(S)$ to $I(M)$ will yield the correct value of $\langle M\rangle_w$ as that obtained by experiment. For a first approximation, Tung's distribution function[19] can be used to express the $I(S)$ curve, that is $I(S)=1-e^{-aS^b}$ where $a$ and $b$ are distribution parameters. Substituting (4) into this equation, we obtain $I(M)$, from which we have

$$\langle M\rangle_w = \Gamma\left(1+\frac{2}{b}\right)\Big/ a^{\frac{2}{b}}\overset{*}{K}_s^2. \tag{5}$$

From the values of $a$ and $b$ evaluated from the experimental curve $I(S)$, and of $\langle M\rangle_w$ from light scattering, a first approximation to the value of $\overset{*}{K}_s$ can be calculated from equation (5). $\overset{*}{K}_s$ thus obtained is $3.02 \times 10^{-15}$. With this value of $\overset{*}{K}_s$, the conversion of $I(S)$ into $I(M)$ gives:

$$\langle M\rangle_n = 1.84 \times 10^6,$$
$$\langle M\rangle_w = 2.63 \times 10^6,$$
$$\langle M\rangle_z = 3.36 \times 10^6.$$

The value of $\langle M\rangle_w$ thus calculated from $I(M)$ is already in agreement with that obtained from light scattering experiment. If $I(S)$ did not completely fit Tung's distribution function, the calculated value of $\langle M\rangle_w$ would disagree with the experimental value. Then slightly different $\overset{*}{K}_s$ values should be tried until the calculated $\langle M\rangle_w$ agrees with the experimental value. We have tried the values of $\overset{*}{K}_s=3.1 \times 10^{-15}$ and $2.9 \times 10^{-15}$ and obtained $\langle M\rangle_{w\ \mathrm{calcd}}=2.49 \times 10^6$ and $2.84 \times 10^6$ respectively. Apparently $\langle M\rangle_{w\ \mathrm{calcd}}$ is rather sensitive to the assigned value of $\overset{*}{K}_s$.

After obtaining the value of $\overset{*}{K}_s$, we can also obtain the monodisperse $[\eta]$—$M$ relationship in $\theta$-solvent. Since

$$[\eta]_\theta = \overset{*}{K}_\theta M^{1/2}, \tag{6}$$

the experimentally measured value of $[\eta]_\theta$ is a weight average, so

$$\langle[\eta]_\theta\rangle_w = \overset{*}{K}_\theta\langle M^{1/2}\rangle_w. \tag{7}$$

From equation (4)

$$\langle s\rangle_w = \overset{*}{K}_s \langle M^{1/2}\rangle_w, \tag{8}$$

hence

$$\langle[\eta]_\theta\rangle_w / \langle s\rangle_w = \overset{*}{K}_\theta / \overset{*}{K}_s. \tag{9}$$

From data listed in Table 2, $[\eta]_\theta - \langle S\rangle_w$ plot for three fractions gives a straight line passing through the origin (Fig. 9), the slope of which gives

$$\overset{*}{K}_\theta / \overset{*}{K}_s = 1.52 \times 10^{13}, \quad \text{so} \quad \overset{*}{K}_\theta = 4.59 \times 10^{-2}.$$

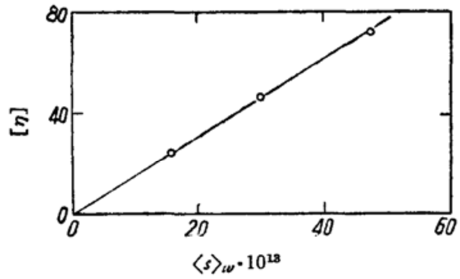


Fig. 9. $[\eta]_\theta$-$\langle S\rangle_w$ relation for Fractions A, C, and D.

The value of $\overset{*}{K}_\theta$ is a little higher than $K_\theta = 4.45 \times 10^{-2}$ for the polydisperse relation $\langle[\eta]_\theta\rangle_w = K_\theta \langle M^{1/2}\rangle_w$. This is quite reasonable, as

$$K_\theta / \overset{*}{K}_\theta = \langle M^{1/2}\rangle_w / \langle M\rangle_w^{1/2} < 1.$$

The value of $\Phi$ in $[\eta]$—$\overline{h^2}$—$M$ relationship is then corrected for polydispersity of the sample according to Newman *et al.*[6]

$$\langle[\eta]\rangle_w = \Phi \frac{\langle(\overline{h^2})^{3/2}\rangle_n}{\langle M\rangle_n} = \Phi \frac{\langle\overline{h^2}\rangle_z^{3/2}}{\langle M\rangle_w} \cdot \frac{1}{q}, \tag{10}$$

$$\frac{1}{q} = \frac{\langle M\rangle_w}{\langle M\rangle_n} \cdot \frac{\langle(\overline{h^2})^{3/2}\rangle_n}{\langle\overline{h^2}\rangle_z^{3/2}}. \tag{11}$$

In $\theta$-solvent, $\overline{h_0^2} \propto M$, therefore

$$\frac{1}{q} = \frac{\langle M\rangle_w}{\langle M\rangle_n} \cdot \frac{\langle M^{3/2}\rangle_n}{\langle M\rangle_z^{3/2}},$$

where

$$\langle M^{3/2}\rangle_n = \int_0^\infty M^{3/2} \frac{W(M)}{M} dM \Big/ \int_0^\infty \frac{W(M)}{M} dM = \langle M^{1/2}\rangle_w \cdot \langle M\rangle_n.$$

From equation (8), we have

$$\frac{1}{q} = \frac{\langle M\rangle_w \cdot \langle s\rangle_w}{\langle M\rangle_z^{3/2} \cdot \overset{*}{K}_s} = 0.673. \tag{12}$$

From the experimental value of $[\eta]_\theta=72.0$, $\langle M\rangle_w=2.63\times10^6$, $\langle\overline{h^2}\rangle_z^{1/2}=1210$ Å, we obtain $\Phi=1.6_1\times10^{23}$. This value is somewhat lower than the value given by Flory[1]. Assuming the correction factor $1/q$ to be the same for all other compositions of the mixed solvent, i.e., in the calculation of correction factor for polydispersity, the deviation from the Gaussian statistics of the polymer chain when the solvent becomes better is not taken into consideration, we obtained $\Phi$ values as listed in Table 1 which show no significant variation of $\Phi$ with $A_2$ of the solution. No trend of increasing $\Phi$ with decreasing $A_2$ is observed as $A_2\to0$[3]. This gives no support to the conclusions arrived by Птицын and Эйзнер[20] who interpreted the solvent dependence of $\Phi$ by non-Gaussian statistics.

From experimental values of $\langle\overline{h_0^2}\rangle_z$ of the sample in $\theta$-solvent and from $\langle M\rangle_z$ obtained by molecular weight distribution measurements, the value of $(\overline{h_0^2}/M)^{1/2}$ for polymethylmethacrylate chain is calculated to be $66\times10^{-10}$ which is 2.1 times larger than the free rotation value $31\times10^{-10}$ [1].

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