Solution Properties of Poly(methyl Methacrylate) by Viscometric Measurements in Organic Solvents. I

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ABSTRACT

Poly(methyl methacrylate) prepared by benzoyl peroxide was fractionated. The variation of the intrinsic viscosity and Huggins and Kramer constants with temperature and solvent was studied. From the viscosity data the thermodynamic interaction parameters Θ and ψ were evaluated and are discussed. The Fox-Flory and constant K was determined by using Kurata-Stockmayer, Fox-Flory, Stockmayer-Fixman, and Berry equations.

INTRODUCTION

The solution properties of poly(methyl acrylate) in various solvents by light scattering, osmometry, and viscosity techniques have been investigated by many workers [1-15]. Viscometric studies of high polymer solutions at and above the Flory temperature, Θ, have been widely used in determining the Fox-Flory constant, K. Some of the methods of determination of K from measurements in good solvents were reviewed by Cowie [1]. Many empirical and semiempirical methods [16-31] for the estimation of K from viscometric measurements in good solvents have recently been proposed.

    In the present investigation the viscosity behavior of poly(methyl methacrylate) in four solvents was studied within the temperature range of 25 to 60°C, and the thermodynamic parameters K and ψ were evaluated and are discussed using the Fox-Flory [32], Stockmayer-Fixman [33], Kurata-Stockmayer [34, 35], and Berry equations [36].

<div align="center">THEORETICAL</div>

    In the theory developed by Flory and Fox [32] and Kurata et al. [34, 35], the intrinsic viscosity $[\eta]$ is related to the Fox-Flory constant K, the molecular weight M, and the hydrodynamic expansion factor α_n by

$$[\eta] = \phi \left(\frac{\overline{r}_0^{\,2}}{M} \right)^{3/2} M^{1/2} \alpha_n^{\,3} = KM^{1/2} \alpha_n^{\,3} \tag{1}$$

where ϕ is a universal parameter and $\overline{r}_0^{\,2}$ denotes the unperturbed mean-square end-to-end distance.

    The thermodynamic parameters χ and Z are defined [15, 33] by

$$\chi = \frac{Z \Delta W_{12} x_1}{kT} \tag{2}$$

where ΔW_{12} is the change in energy for the formation of an unlike contact pair, x_1 is the number of segments in the solvent molecule, and Z is the lattice coordination number:

$$Z = \left(\frac{3}{2\pi} \right)^{3/2} B \left(\frac{\overline{r}_0^{\,2}}{M} \right)^{-3/2} M^{1/2} \tag{3a}$$

where

$$B = (2\overline{\nu}^2 / N_A V_1)(\tfrac{1}{2} - \chi) = B_0 (1 - \Theta/T) \tag{3b}$$

$\overline{\nu}$ is the (partial) specific volume of the polymer, V_1 is the molar volume of the solvent, and N_A is Avogadro's number. The linear expansion factor α ($\alpha^2 = \overline{s}^2$, $\overline{s}_0^{\,2} = \overline{r}^2 / \overline{r}_0^{\,2}$, $\overline{s}^2$ denoting the mean square molecular radius) for linear polymers has been related to χ (or Z) through many theoretical and semiempirical equations, notably by Fox and Flory [32] (Eq. 4), Kurata and Stockmayer [34, 35] (Eq. 7a), and Berry [36] (Eq. 8).

$$\alpha^5 - \alpha^3 = 2C_M(^1/_2 - \chi)M^{1/2} \tag{4}$$

where

$$C_M = (27/2^{5/2}\pi^{3/2})(\bar{\nu}^2/V_1 N_A)(M/\bar{r}^2)^{3/2} \tag{5}$$

$$\alpha^3 = 1 + 2z \tag{6}$$

$$\alpha^3 - \alpha = \frac{4}{3}z_g(\alpha) \tag{7a}$$

where

$$g(\alpha) = 8\alpha^3(3\alpha^2 + 1)^{-3/2} \tag{7b}$$

$$\alpha^3 = 2 + 0.325Z \ldots 2 < z < 11 \tag{8}$$

The exact relation between α and z is still an open question, and a large number of other recent publications [37-45] are devoted to the excluded volume effect and its relation to solution properties. The equations developed have been widely used with partial success. Similarly, the exact relation between α and α_n has not been fully established [40, 46]. The relations $\alpha = \alpha_n$ due to Flory [32], $\alpha_n^3 = \alpha^{2.5}$ due to Kurata and Yamakawa [47], and $\alpha_n^3 = \alpha^{1.95} \pm 0.15$ near Θ due to Norisuye et al. [46] have been suggested. In any case, at Θ, for any polymer-solvent system, $\alpha = \alpha_n = 1$ holds and hence evaluation of K and Θ is the most accurate method.

On the other hand, for evaluation of K from $[\eta]$ at $T > \Theta$ (in good solvent), a number of equations relating $[\eta]$ and M through K (after eliminating α, α_n, z, etc.) have been suggested. Fox and Flory [32] (F-F) obtained

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + K^{5/3}C_T(M/[\eta]) \tag{9}$$

Kurata and Stockmayer [34, 35] (K-S) arrived at

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 0.363\phi B[g(\alpha_n)M^{2/3}/[\eta]^{1/3}] \tag{10}$$

Stockmayer and Fixman [33] (S-F) and others derived

$$[\eta]/M^{1/2} = K + 0.51\phi BM^{1/2} \tag{11}$$

Berry [36] proposed

$$[\eta]/M^{1/2})^{1/2} = K^{1/2} + 0.42K^{3/2}B(\overline{r}_0^{\ 2}/M)^{-3/2}(M/[\eta]) \qquad (12)$$

Besides these, several other proposed equations [48, 49] have had partial success. According to all these equations, the value of K is obtained from the intercepts on the ordinates of the plots of the quantity on the left-hand side versus a function of M and $[\eta]$ on the right-hand side.

EXPERIMENTAL

Polymerization and Fractionation

Poly(methyl methacrylate) (PMMA) was prepared by the polymerization of double distilled monomer at 60°C using benzoyl peroxide as the initiator. The polymer was fractionated by the standard procedure using benzene as the solvent and n-hexane as the nonsolvent. The molecular weight of the fractions were determined viscometrically by using the equation

$$[\eta] = 5.2 \times 10^{-5}\ \overline{M}_w^{\ 0.76} \qquad \text{in benzene}$$

Solvents

The solvents benzene, toluene, ethyl acetate, and ethyl methyl ketone were of BDH AnalaR grade. The solvents were purified by the standard procedure and freshly distilled before use.

For viscometric studies, an Ubbelohde type suspended level dilution viscometer was used. The viscometer was calibrated with double distilled water. Kinetic energy and density corrections were applied. $[\eta]$ was evaluated as an average value of the intercepts of the plots of ln η_r/c versus c and η_{sp}/c versus c both graphically and by the least square method.

RESULTS AND DISCUSSION

The intrinsic viscosities $[\eta]$, Huggin's constant (k'), and Kramer's constant (k'') for representative fractions at various temperatures in various solvents for PMMA systems are given in Table 1. The variation of $[\eta]$ with temperature for PMMA (Fig. 1) in different solvents was studied. From the intrinsic viscosity data of PMMA systems, the parameters Θ, ψ, and k were obtained from the Fox-Flory plots of

TABLE 1. [η], k', and k'' of Some Poly(methyl Methacrylate) Fractions in Various Solvents

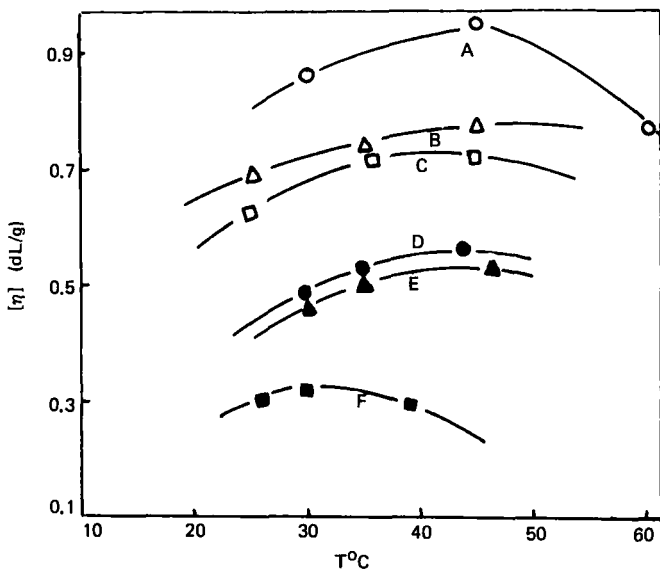| Fraction no. and method	Solvent		Temperature (°C)		
			26	30	39
I: 1.3275 × 10^5	Toluene	[η]	0.303	0.317	0.322
		k'	1.993	1.867	0.577
		k''	-0.30	-0.28	-0.31
			30	45	60
II: 5.2505 × 10^5	Benzene	[η]	0.567	0.79	0.845
		k'	0.3144	0.655	0.542
		k''	-0.34	-0.42	-0.33
			25	35	45
I: 6.389 × 10^5	Ethyl methyl ketone	[η]	0.609	0.71	0.697
		k'	0.321	0.336	0.276
		k''	-0.33	-0.38	-0.34
			30	35	
III: 1.898 × 10^5	Ethyl acetate	[η]	0.43	0.50	
		k'	0.72	0.65	
		k''	-0.44	-0.38	

FIG. 1. $[\eta]$ versus T plots of different poly(methyl methacrylate) fractions in various solvents: (o) Fraction I ($\overline{M}_w$ = 5.4305 × 10⁵) in benzene; (△) Fraction II ($\overline{M}_w$ = 5.161 × 10⁵) in butanone; (□) Fraction III ($\overline{M}_w$ = 4.952 × 10⁵) in butanone; (•) Fraction II ($\overline{M}_w$ = 2.035 × 10⁵) in ethyl acetate; (▲) Fraction III ($\overline{M}_w$ = 1.898 × 10⁵) in ethyl acetate; (■) Fraction II ($\overline{M}_w$ = 0.99944 × 10⁵) in toluene.

$(\alpha^5 - \alpha^3)/M^{1/2}$ versus $1/T$ (Fig. 2), assuming K = 4.8 × 10⁻⁴ and temperature independence for the polymer.

The values of Θ and ψ (Table 2) were also calculated by Stockmayer-Fixman's method plotting S versus $1/T$ (Fig. 3), where S is the slope of the plots of $[\eta]/M^{1/2}$ versus $M^{1/2}$ (Fig. 4) at different solvents.

The experimental values of $[\eta]$ for the PMMA fractions in the different solvents studied at a given temperature are in the order ethyl methyl ketone > benzene > ethyl acetate > toluene. This is roughly in the order of decreasing solvent power as judged from solubility parameter (δ) data [50]. It has been noted [51, 52] that in the polar solvents or solvents which are self-associated, the unperturbed dimensions decrease with increasing polarity or increasing association. The order of the values of $[\eta]$ for a given polymer fraction in a given set of solvents may therefore be understood in terms of the combined effects of segment solvent interactions, polarity and association of solvent, etc.
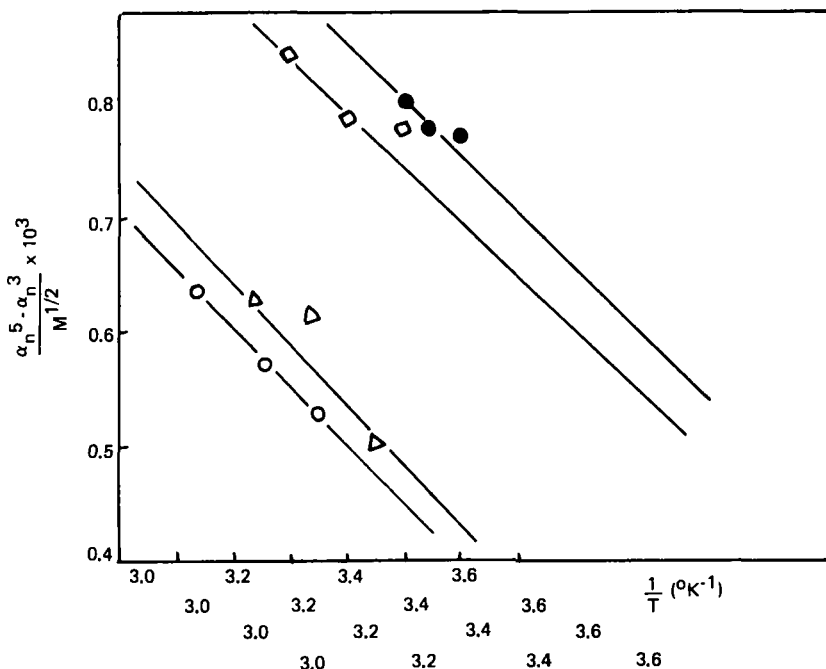
FIG. 2. Plots of $\alpha_n^5 - \alpha_n^3$ versus $1/T$ for different poly(methyl methacrylate) fractions in various $M^{1/2}$ solvents: ($\circ$) Fraction II ($\overline{M}_w$ = 5.161 $\times$ 10^5) in butanone; ($\triangle$) Fraction III ($\overline{M}_w$ = 4.952 $\times$ 10^5) in buta-none; ($\square$) Fraction II ($\overline{M}_w$ = 2.035 $\times$ 10^5) in ethyl acetate; ($\bullet$) Fraction III ($\overline{M}_w$ = 1.898 $\times$ 10^5) in ethyl acetate.

Defining a solvent with Θ values very much below the working tem-perature ($\approx$ 300 K) as a good solvent, and a solvent showing Θ values equal to or higher than the working temperature as a poor solvent, in general, when K (or $\overline{r}_0^2$) is practically independent of temperature, the [η] values of a given fraction in a given solvent are expected to in-crease sharply with T in the vicinity of Θ (i.e., for poor solvents) and increase only slightly with T at temperatures much higher than Θ ac-cording to [51, 52]

TABLE 2. Θ and ψ Values for Poly(methyl Methacrylate) Systems

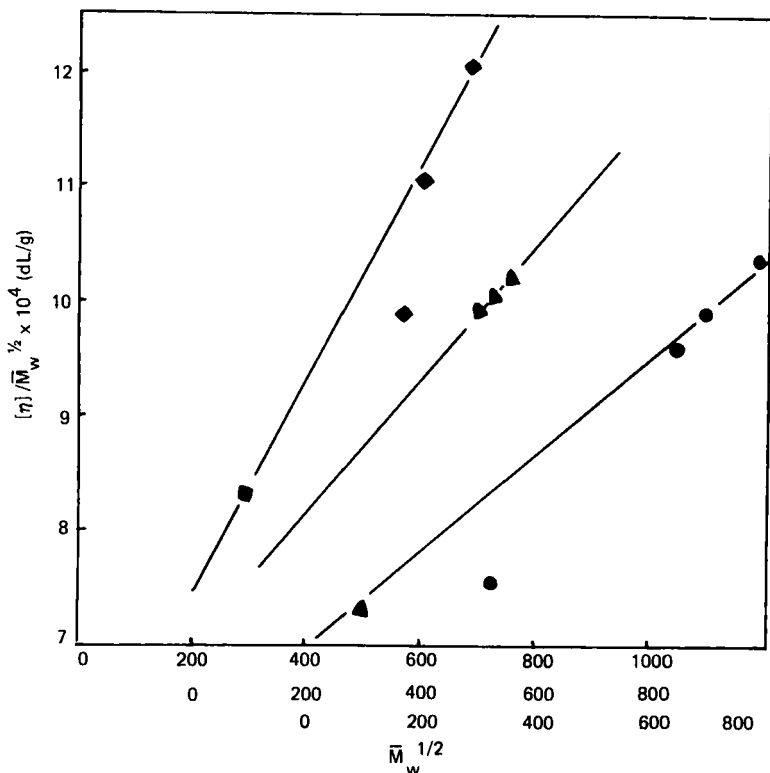| Solvent	Fraction no. and ($\overline{M}_w \times 10^{-5}$)	Θ (°K)		ψ	
		F and F	S and F	F and F	S and F
Benzene	I (5.2505)	287.3	227.35	0.0714	0.031
Toluene	II (0.93919)	256.4	255.1	0.136	0.125
	IV (0.27935)	233.1	236.4	0.1655	0.1535
Butanone	II (5.161)	250	277.7	0.175	0.1944
	III (4.952)	251.8	280.9	0.1890	0.2078
Ethyl acetate	II (1.853)	246.9	296.7	0.433	0.3333
	III (1.802)	245.1	300.3	0.3955	0.369
	IV (1.787)	240.96	298.5	0.2771	0.32

FIG. 3. Plots of $\eta/\overline{M}_w^{1/2}$ versus $\overline{M}_w^{1/2}$ (Stockmayer-Fixman plots for poly(methyl methacrylate)-butanone system): ($\bullet$) 25°C; ($\blacktriangle$) 35°C; ($\blacksquare$) 45°C.

$$\frac{d \ln \overline{r}_0^{\,2}}{dT} = 2\left(\frac{5\alpha^2}{3} - 1\right)\left[(5 - \gamma)\alpha^2 - (3 - \gamma)\right]^{-1} \frac{d \ln [\eta]}{dT} \qquad (13)$$

$$- \frac{2\gamma}{3}(\alpha^2 - 1)\left[(5 - \gamma)\alpha^2 - (3 - \gamma)\right]^{-1}\left[(2\beta_2 - \beta_1) - (\frac{1}{2} - \chi)^{-1}\frac{d\chi}{dT}\right]$$

β_1 and β_2 are bulk expansion coefficients of the solvent and liquid polymer and γ is given by $\alpha_n^3 - \alpha^\gamma$. The value of η increases slightly with increasing temperature in the case of all the solvents studied, and a flat maximum was obtained (A, B, C, D, E, F) in the $[\eta]$ versus T curves (Fig. 1). Kawai [53] observed a maximum in the $[\eta]$ versus
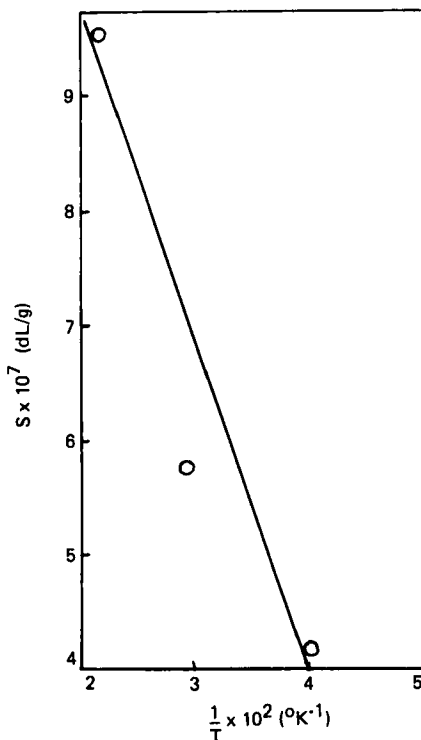
FIG. 4. Plot of S versus 1/T for poly(methyl methacrylate)-butanone system.

T curves of PMMA in the fairly good solvent acetone and explained this result by the opposite behavior of the temperature coefficients of α_n and K. Moore [54] reported that such a maximum could not be confirmed by his measurements. The Huggin's constant k' decreases with increasing temperature in the case of toluene, but in the case of good solvents such as benzene, methyl ethyl ketone, and ethyl acetate, the Huggin's constant k' decreases sharply with decreasing temperature.

The Θ and K values for all systems studied were positive, showing that the heat of mixing was endothermic. As found for other systems, the values of ψ were also positive but lower than the ideal value of 0.5 predicted by the theory and varied from solvent to solvent. However, the value of Θ approaches 0.5 (0.43) in the case of ethyl acetate. The values of Θ, ψ, and χ for PMMA systems are in good agreement with those reported by Fox [6] who also determined these values by applying the F-F equation. In the case of benzene and ethyl acetate, the Θ

values calculated by applying the F-F and S-F methods varied considerably whereas in the case of toluene and methyl ethyl ketone, the values are approximately the same. The values of ψ calculated by the F-F and S-F methods are comparable. Since the correctness of the parent equations (4 to 8) is still uncertain, these values of ψ and K cannot be taken as absolute [50]. The values of ψ show a variation with molecular weight, increasing slightly with decreasing M, which is probably due to a change in the value of the constant C_M as anticipated by the Flory-Fisk equation. Comparison of the ψ values obtained by various methods shows that the values calculated by viscometry are of the same order as those obtained by osmometry but lower than those from the precipitation method. Higher values of ψ obtained by precipitation probably reflect the variation of the latter with concentration.

The Fox-Flory constant K may be obtained from viscosity data by two methods: 1) in good solvents by using suitable extrapolation procedures based on equations relating to α, α_n, and z; and 2) by certain empirical and semiempirical methods.

K from $[\eta]$ in Good Solvents

This method is convenient since viscometry could be employed for good solvents with facility. Since the exact relations among α, α_n, and z are not yet established, the values of K and Θ obtained are at best approximate, but serve at least as a good estimate of K, the accuracy being greater the closer T is to Θ. Keeping the approximations involved in mind, we have chosen the widely used plots of K-S (Fig. 5), F-F (Fig. 6), S-F (Fig. 7), and Berry (Fig. 8) for getting an estimate of K. From the nature of the extrapolations involved, not much meaning may be attached to the apparent variation of K with T. When the value of K was evaluated from $[\eta]$ at $T > \Theta$, the extrapolation methods gave values of K comparable to those obtained at T close to Θ. The values of K (Table 3) were computed at higher temperatures in comparison to the Θ temperature. That is why the values of K in the case of all solvents calculated using all the methods are higher than the literature values [50]. Such deviations have also been observed by others [55] and were attributed to the fact that the parent equations relating to α and z hold good only at low values of z. The higher K values found by the S-F, K-S, and Berry methods are attributed to the tendency of the plots to bend downward [at higher M or Z] and to give a higher intercept on the ordinate and hence a higher K on extrapolation.

The effect of temperature is rather interesting. With an increase of temperature, $\bar{r}_0^2$, and hence K, is expected to decrease [15] due to a greater freedom to rotation around the skeletal bonds. On the other hand, an increase of $\bar{r}_0^2$ (and K) with temperature may be explained
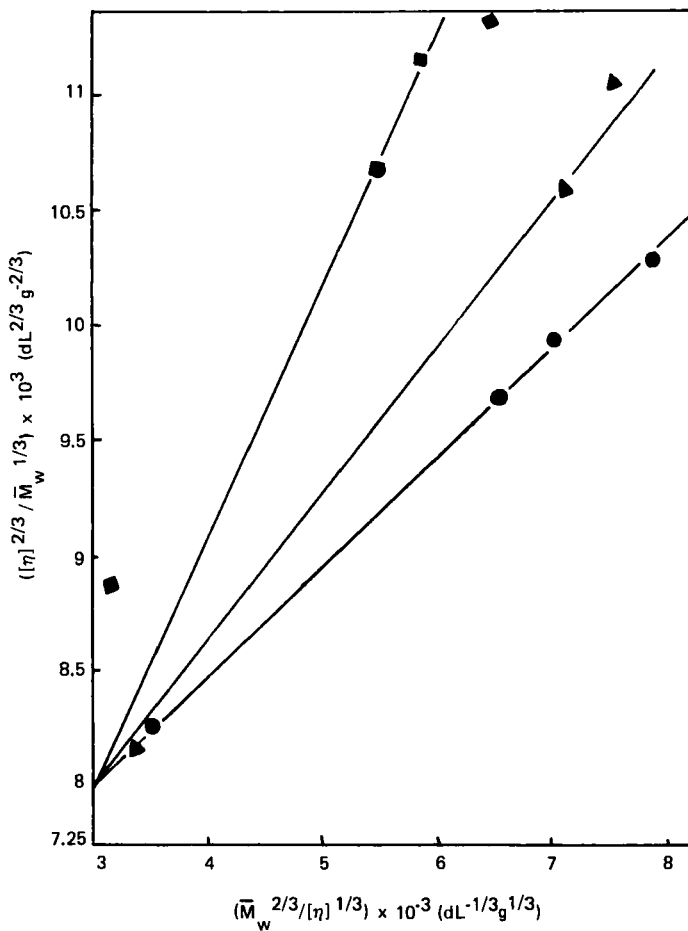
FIG. 5. Plots of $\eta^{2/3}/\overline{M}_w^{1/3}$ versus $\overline{M}_w^{2/3}/\eta^{1/3}$ (Kurata-Stock-mayer plots for poly(methyl methacrylate-butanone system): ($\bullet$) 25°C; ($\blacktriangle$) 35°C; ($\blacksquare$) 45°C.
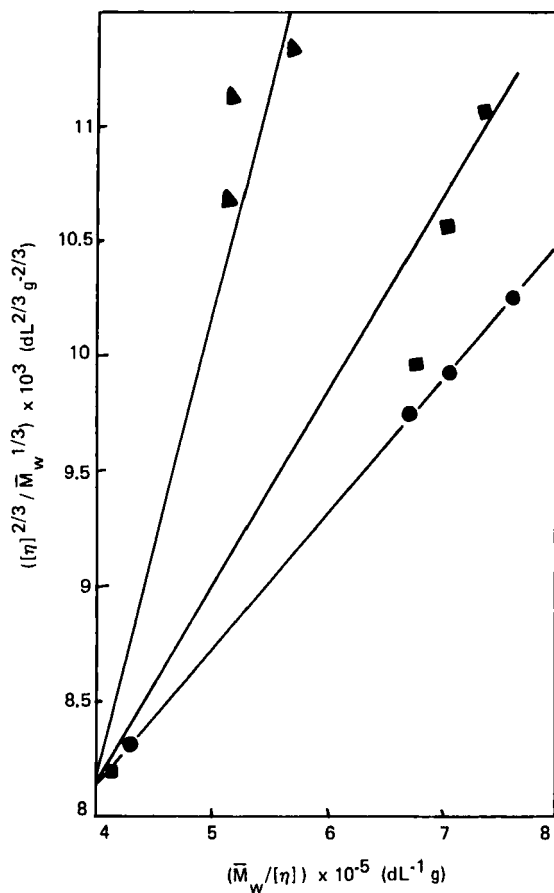
FIG. 6. Plots of $\eta^{2/3}/\overline{M}_w^{1/3}$ versus $\overline{M}_w/[\eta]$ (Fox-Flory plots for poly(methyl methacrylate)-butanone system): ($\bullet$) 25°C; ($\blacktriangle$) 35°C; ($\blacksquare$) 45°C.
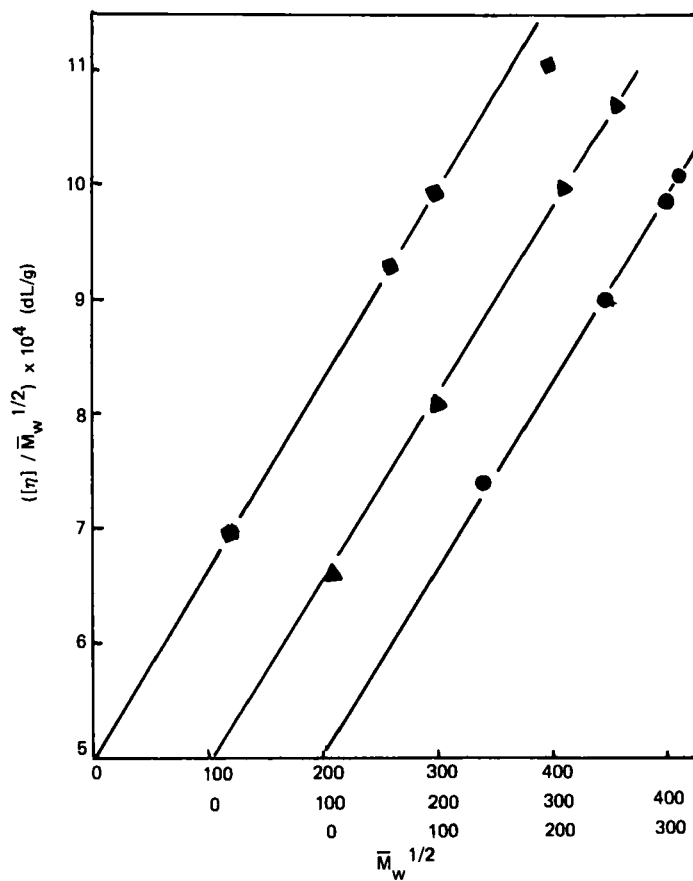
FIG. 7. Plots of $\eta/\overline{M}_w^{1/2}$ versus $\overline{M}_w^{1/2}$ (Stockmayer-Fixman plots for poly(methyl methacrylate-toluene system): (●) 26°C; (▲) 30°C; (■) 39°C.
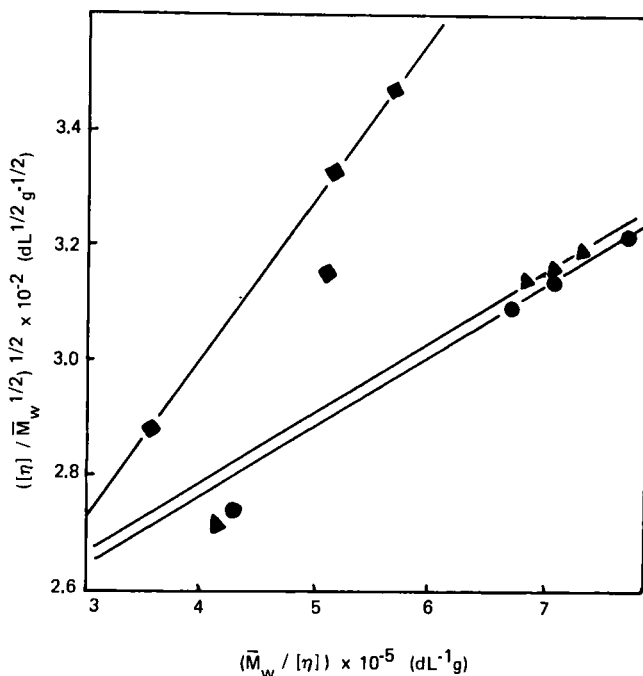
FIG. 8.   Plots of $\eta/\overline{M}_w^{1/2}$ versus $\overline{M}_w/\eta$ (Berry plots for poly-(methyl methacrylate)-butanone system): ($\bullet$) 25°C; ($\blacktriangle$) 35°C; ($\blacksquare$) 45°C.

[56] on the basis of the increased freedom of rotation of the side chains. Our present knowledge of the effects does not warrant the separation [57] of the solvents and temperature effects on K as determined by viscosity measurements, even at T = Θ. The temperature coefficient of K from stress-strain measurements on the bulk polymer is often found [51] to be not only different in magnitude but even opposite in sign to that deduced by viscometry. To a first approximation [58, 59], the variation of K with Θ, for a set of chemically similar solvents may be taken to reflect the temperature coefficient of K.

TABLE 3. K Values of Poly(methyl Methacrylate) by Measurement of $[\eta]$ at $T \geq \Theta$

No.	Solvent	T (°C)	$K \times 10^4$			
			From S-F plots	From K-S plots	From F-F plots	From Berry plots
1	Benzene	30, 45	6.6	10.33	10.31	10.37
		60	6.4	10.27	10.30	10.33
2	Ethyl methyl ketone	25, 35	7.0	7.16	7.35	7.1
		45	5.5	7.16	7.35	7.4
3	Ethyl acetate	30, 35	11.32	11.45	8.45	10.68
4	Toluene	26, 30, 39	5	4.13	4.07	4

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