

# Study of Solution Properties of Poly( $\alpha$ -methyl styrene) in Various Solvents by Dilute-Solution Viscometry

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## SYNOPSIS

The values of Mark-Houwink-Sakurada constants were determined for poly( $\alpha$ -methyl styrene) (P $\alpha$ Ms) of high and low molecular weights in a variety of solvents by a new approach, which requires only polydisperse samples. The results are in accord with those reported in the literature. In addition, the present work reports the values of the Flory interaction parameter for P $\alpha$ Ms in 13 solvents of distinct solvent power at various temperatures. Three refined methods pertaining to both polar and nonpolar solvents were applied to estimate the solubility parameter ( $\delta_2$ ) of P $\alpha$ Ms resulting in  $\delta_2 = 18.75 \pm 0.15$  (J/mL)<sup>1/2</sup> at 30°C. Finally, the scatter data of the Huggins coefficient over a range of expansion factors varying from 0.7 to 2.6 seem to conform better to a newly proposed empirical equation than to the contemporary model after Imai. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Dilute-solution viscometry (DSV) is a simple and yet reliable method to probe the solution properties of polymers. This particular technique has played an important role in connection with the recent investigations of the hydrodynamic and thermodynamic of poly( $\alpha$ -methyl styrene) (P $\alpha$ Ms) by a number of workers.<sup>1-6</sup> However, these studies cover only a limited number of solvents. In this work, a wider spectrum of solvents is employed.

It is well known that the DSV is based on the Mark-Houwink-Sakurada (MHS) equation that depicts the dependence of the intrinsic viscosity ( $[\eta]$ ) on the viscosity-average molecular weight of a polymer ( $M_v$ ), i.e.,

$$[\eta] = KM_v^a \quad (1)$$

where  $K$  and  $a$  are the empirical constants. Conventionally, the MHS constants are derived from the double logarithmic plot of  $[\eta]$  against the molecular weight ( $M$ ) of the polymer fraction. The present analysis resorts to a simpler procedure elaborated below for the same purpose.

It has been established recently that<sup>7</sup>

$$\ln[2(1-a)K] = \ln K_\theta - (a - \frac{1}{2}) \ln M_0 \quad (2)$$

where  $K_\theta$  is the unperturbed parameter, and  $M_0$ , the characteristic molecular weight connecting the empirical and theoretical values of  $[\eta]$ . In addition, we have for a whole polymer<sup>8</sup>

$$M_v = M_w + S(a - 1) \quad (3)$$

where  $M_w$  is the weight-average molecular weight, and  $S$ , a parameter pertaining to the polydispersity of the polymer. Combining eqs. (1)–(3) allows one to estimate the exponent  $a$  from the experimental  $[\eta]$  value, once the constants  $K_\theta$  and  $M_0$  have been calibrated by the relevant literature data, and the molecular characteristic parameters  $M_w$  and  $S$  predetermined for the polymer sample. The constant  $K$  is then accessible by eq. (2).

In this work, the polymer-solvent interaction parameter ( $\chi$ ) is computed by<sup>7</sup>

$$\chi = \frac{1}{2} - \frac{1.59V_1(2a-1)K_\theta}{C_1v_2^2(1-a)M_0^{1/2}} \quad (4)$$

where the coefficient  $C_1 = 1.55$ ,  $V_1$  is the molar volume of the solvent, and  $v_2$  is the partial specific vol-

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ume of the polymer. This equation has been successfully applied to polystyrene in various solvents.<sup>9</sup> Subsequently, the solubility parameter of P $\alpha$ Ms ( $\delta_2$ ) may be estimated by a method after Ito and Guillet.<sup>10</sup> It utilizes the equation written as

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\gamma}{V_1}\right) \quad (5)$$

where  $\delta_1$  is the solubility parameter of the solvent;  $R$ , the gas constant; and  $\gamma$ , the entropy correction to  $\chi$  at temperature  $T$ . If the second term on the right-hand side of eq. (5) is constant, a plot of the left-hand side of eq. (5) against  $\delta_1$  would yield a straight line with the gradient rendering  $\delta_2$ .

The present study also aims at acquiring the MHS constants for the P $\alpha$ Ms of high molecular weight from the viscosity data of low molecular weight samples in various solvents. For this end, a simple approach is introduced to deal with the arising situation.

## EXPERIMENTAL

Three P $\alpha$ Ms samples, designated by H, M, and L hereafter, were purchased from Aldrich. Their  $M_w$ 's in the order of  $\sim 1 \times 10^4$  will be shown later. Reagent-grade solvents were obtained from different suppliers: namely, nitrobenzene (Hopkin & William Ltd.); toluene and *p*-xylene (BDH); cyclohexane and tetrahydrofuran (J. T. Baker); 1-chlorobutane, 2-hexanone, and 1,2,3,4-tetrahydronaphthalene (tetralin) (Fluka);  $\alpha$ -chloronaphthalene (TCI, Tokyo); chlorobenzene (Merck), and dimethylformamide, *n*-butyl acetate, and *p*-dioxane (Ajax). All chemicals were used as received.

Relatively viscosity ( $\eta_r$ ) varying from 1.2 to 1.8 were monitored by appropriate Ubbelohde viscometers that produced solvent flow times of  $> 120$  s. Temperature control achieved by a Townson & Mercer water bath was recorded as  $\pm 0.02^\circ\text{C}$ . The kinetic energy and shear corrections were negligible. The Huggins equation was applied to estimate the  $[\eta]$  and the Huggins coefficient ( $k_1$ ) using least-squares regression analysis. The reproducibilities of  $[\eta]$  and  $k_1$  were estimated to be  $\pm 3.0\%$  and  $\pm 12\%$ , respectively.

## RESULTS AND DISCUSSION

### Viscometric and Thermodynamic Parameters

The values of MHS constants for P $\alpha$ Ms of  $M_w \geq 5 \times 10^4$  in a total of six solvents at various tempera-

tures are collected from the literature<sup>1,3,6,11-13a</sup> and displayed in Table I, which also includes the data of  $V_1$  (Ref. 14)  $\delta_1$  and  $\delta_1'$ . Here, the parameter  $\delta_1'$  refers to the solubility parameter of solvent without the contribution due to the hydrogen bonding ( $\delta_h$ ), viz.,  $\delta_1' = (\delta_1^2 - \delta_h^2)^{1/2}$ . The data of  $\delta_1$  and  $\delta_1'$  are obtained from the literature.<sup>10,15-18</sup>

It is interesting to note that the first two pairs of data for the MHS constants in Table I are derived from the viscosity data of moderately concentrated P $\alpha$ Ms solutions reported recently.<sup>11,19,20</sup> These data are treated by<sup>21,22</sup>

$$\eta_{sp}/c = [\eta]' + k_1'[\eta]'\eta_{sp}^n \quad (6)$$

where  $\eta_{sp}$  is the specific viscosity of the polymer solution of concentration  $c$ ; and  $n$ ,  $[\eta]'$ , and  $k_1'$  are the empirical constants. Equation (6) has been applied to treat the polymer solutions with  $\eta_r < \sim 2600$  successfully.<sup>22</sup> The results obtained from eq. (6) for the systems of interest are shown in Table II, which provides adequate information to compute the above-mentioned MHS constants. Indeed, the two sets of MHS constants listed for P $\alpha$ Ms in toluene at  $30^\circ\text{C}$  in Table I are comparable, indicating the validity of eq. (6).

On the basis of the relevant data in Table I, eq. (2) yields  $K_\theta = (7.14 \pm 0.16) \times 10^{-4}$  dL/g and  $M_0 = (1.86 \pm 0.30) \times 10^5$  using least-squares regression analysis. The former value will be used consistently for the unperturbed parameter of P $\alpha$ Ms throughout this work. The experimental values of  $K_\theta$  varying from 6.7 to  $7.8 \times 10^{-4}$  dL/g were reported in the literature.<sup>13a</sup> Now, we proceed to compute parameter  $\chi$  using eq. (4). In this connection, the values of  $v_2$  are available in Ref. 13b and assumed to be independent of the solvents. The results are presented in Table I.

Table III exhibits the data of  $[\eta]$  and  $k_1$  obtained in this work. As noted, the values of  $[\eta]$  for these samples are rather low in comparison with those that can be predicted from the corresponding MHS constants in Table I. This means that we are virtually dealing with the P $\alpha$ Ms chains of low molecular weight that warrant a new estimate of  $M_0$ .

Although the hydrodynamic and thermodynamic properties of P $\alpha$ Ms have received considerable attention recently, only a few workers have, indeed, extended these studies to its low molecular weight species. Among them, Cottam et al.<sup>23</sup> established that

$$[\eta] = K_\theta M_v^{1/2} (\text{dL/g}) \quad (7)$$

for P $\alpha$ Ms fractions in cyclohexane at the  $\theta$  temperature over the entire range of  $2 \times 10^3 < M_w < 1$

**Table I Dilute-solution Properties of P $\alpha$ MS Fractions of High Molecular Weight<sup>a</sup> in Various Solvents**

No.	Solvent, <sup>b</sup> <i>T</i> (°C)	<i>V</i> <sub>1</sub> (Ref. 14) (mL/mol)	$\delta'_1$ ( $\delta_1$ ) <sup>c</sup> (J/mL) <sup>1/2</sup>	<i>a</i>	<i>K</i> × 10 <sup>4</sup> (dL/g)	$\chi$	Ref.
1	$\alpha$ -CN, 30.0	137.1	20.5 (20.6)	0.750	0.63	0.440	<sup>d</sup>
2	TOL, 30.0	107.4	18.4 (18.5)	0.720	0.92	0.463	<sup>d</sup>
3	TOL, 30.0	107.4	18.4 (18.5)	0.744	0.71	0.455	11
4	TOL, 30.0	106.8	18.5 (18.6)	0.713	0.97	0.465	2
5	TOL, 25.0	106.8	18.5 (18.6)	0.710	1.10	0.466	12
6	BZ, 30.0	90.0	18.5 (18.6)	0.720	1.03	0.469	6
7	<i>t</i> -DE, 10.0	157.4	17.5 (17.5)	0.497	7.08	0.500	11
8	<i>t</i> -DE, 30.0	160.3	17.1 (17.1)	0.640	1.45	0.473	11
9	CLBT, 5.0	102.6	—	0.570	3.36	0.492	1
10	CLBT, 25.0	105.1	16.8 (17.2)	0.590	2.70	0.490	1
11	CLBT, 50.0	108.4	—	0.594	2.65	0.489	1
12	CYHX, 46.0	111.6	16.2 (16.2)	0.539	4.87	0.496	3
13	CYHX, 39.0	110.6	16.4 (16.4)	0.508	6.66	0.499	3
14	CYHX, 38.6	110.6	16.4 (16.4)	0.500	7.60	0.500	13a
15	CYHX, 36.0	110.2	16.5 (16.5)	0.498	7.47	0.500	3
16	CYHX, 35.0	110.1	16.5 (16.5)	0.500	7.30	0.500	11
17	CYHX, 32.0	109.7	16.6 (16.6)	0.466	10.50	0.503	3
18	CYHX, 28.0	109.1	16.7 (16.7)	0.434	14.70	0.506	3
19	CYHX, 24.0	108.6	16.8 (16.8)	0.407	18.90	0.508	3
20	CYHX, 20.0	108.1	16.9 (16.9)	0.386	22.70	0.509	3

<sup>a</sup>  $M_w^1 \geq 5 \times 10^4$ .<sup>b</sup> Abbreviations for solvents:  $\alpha$ -CN =  $\alpha$ -chloronaphthalene; TOL = toluene; BZ = benzene; *t*-DE = *trans*-decalin; CLBT = 1-chlorobutane; CYHX = cyclohexane.<sup>c</sup> Refs. 10, 15–18.<sup>d</sup> The MHS constants are based on the data presented in Table II. In this connection,  $[\eta]$  is computed by  $[\eta] = [\eta]'/0.97$ , an empirical relationship found to be valid for many polymer–solvent systems.<sup>8</sup>

× 10<sup>6</sup>. In addition, the pertinent literature data furnished by three research groups for the P $\alpha$ MS fractions in toluene at 25°C<sup>2,12,23</sup> lead to

$$[\eta] = 3.50 \times 10^{-4} M_w^{0.60} \text{ (dL/g)} \quad (8)$$

over the range  $3 \times 10^3 < M_w < 5 \times 10^4$ . Clearly, these two equations are relevant to the present analysis.

Using the values of  $[\eta]$  cited in Table III for cyclohexane at 36.5°C (a  $\theta$  state) and toluene at 25°C,

**Table II Results obtained from the Viscosity Data of Moderately Concentrated P $\alpha$ MS Solutions Using Eq. (6)**

System	$M_w \times 10^{-4}$	<i>n</i>	$[\eta]' \times 10$ (dL/g)	$k'_1 \times 10$	$\langle \eta_r \rangle^a$	Ref.
$\alpha$ -CN, 30–50°C <sup>b</sup>	6.02	0.81	2.43	4.8	640	19
	14.60	0.77	4.86	3.1	210	11
	112.00	0.76	21.70	3.0	2730	11
	165.00	0.75	30.30	3.1	470	20
TOL, 30°C	14.60	0.78	4.65	3.0	420	20
	33.20	0.75	9.04	2.9	640	20
	112.00	0.75	20.40	3.4	430	20

<sup>a</sup>  $\eta_r$  = relative viscosity. In any case, the linear correlation coefficients (*r*) obtained by plotting  $\eta_{sp}/C$  against  $\eta_{sp}^0$  are close to unity, i.e.,  $r \geq 0.9994$ .<sup>b</sup> In good solvent, the temperature effect on  $[\eta]$  is vanishingly small.<sup>1</sup>

Table III Dilute-solution Properties of P $\alpha$ MS Samples H, M, and L in Various Solvents

No.	Solvent, <sup>a</sup> T (°C) (Sample)	V <sub>1</sub> (Ref. 14) (mL/mol)	$\delta'_1$ ( $\delta_1$ ) <sup>b</sup> (J/mL) <sup>1/2</sup>	$[\eta] \times 10$ (dL/g)	$k_1 \times 10$	$a'$	$\chi$	$a^c$
1	$\alpha$ -CN, 45.5 (H)	138.1	20.1 (20.2)	—	—	0.617 $\pm$ 0.004	0.428	0.775
	(M)			1.19	6.4			
	(L)			1.05	6.5			
2	TOL, 30.0 (H)	107.4	18.4 (18.5)	—	—	0.601 $\pm$ 0.006	0.452	0.752
	(M)			1.17	4.5			
	(L)			0.98	5.6			
3	TOL, 25.0 (H)	106.8	18.5 (18.6)	—	—	0.600 $\pm$ 0.000	0.452	0.750
	(M)			1.14	5.3			
	(L)			0.99	5.8			
4	CLBT, 50.0 (H)	108.4	16.3 (16.4)	—	—	0.522 $\pm$ 0.001	0.492	0.578
	(M)			0.90	6.4			
	(L)			0.80	5.9			
5	CYNX, 36.5 (H)	110.3	16.6 (16.6)	—	—	0.500 $\pm$ 0.001	0.500	—
	(M)			0.85	10.8			
	(L)			0.76	10.3			
	CYHX, 28.0 (H)	109.1	16.7 (16.7)	—	—	0.487	0.505	0.444
	(M)			0.57	13.5			
	(L)			—	—			
CYHX, 46.0 (H)	111.7	16.5 (16.5)	—	—	0.505	0.498	0.519	
(L)			0.82	12.6				
6	XYL, 30.0 (H)	124.4	17.8 (17.8)	—	—	0.578 $\pm$ 0.003	0.459	0.713
	(M)			1.07	5.2			
	(L)			0.93	5.8			
7	NTBZ, 30.0 (H)	103.1	21.5 (21.9)	—	—	0.548 $\pm$ 0.006	0.481	0.649
	(M)			0.99	6.0			
	(L)			0.85	7.0			
8	CLBZ, 30.0 (H)	102.7	19.5 (19.7)	—	—	0.600	0.455	0.750
	(L)			1.14	6.0			
9	TETL, 50.0 (H)	139.7	18.6 (18.9)	—	—	0.618	0.427	0.776
	(L)			1.21	4.3			
10	THF, 30.0 (H)	82.0	17.5 (19.2)	—	—	0.605 $\pm$ 0.005	0.462	0.758
	(M)			1.14	6.3			
	(L)			1.01	6.2			
11	DOX, 30.0 (H)	86.1	19.0 (20.3)	—	—	0.598	0.463	0.747
	(L)			1.13	6.1			
12	HEXN, 30.0 (H)	124.7	15.9 (17.1)	—	—	0.415	0.532	(−0.20) <sup>d</sup>
	(L)			0.69	13.7			
13	BUTA, 30.0 (H)	133.1	16.2 (17.1)	—	—	0.439	0.526	(0.11) <sup>d</sup>
	(L)			0.73	12.2			
14	DMF, 30.0 (H)	77.8	21.9 (24.6)	—	—	0.389 $\pm$ 0.014	0.525	(−0.83) <sup>d</sup>
	(M)			0.64	13.9			
	(L)			0.59	12.8			
				0.47	14.2			

<sup>a</sup> Abbreviations for solvents: XYL = *p*-xylene; NTBZ = nitrobenzene; CLBZ = chlorobenzene; TETL = tetralin; THF = tetrahydrofuran; DOX = *p*-dioxane; HEXN = 2-hexanone; BUTA = *n*-butyl acetate; DMF = dimethylformamide; the rest are given in Table I.

<sup>b</sup> Refs. 10, 15–18.

<sup>c</sup> Exponent  $a$  predicted by eq. (9).

<sup>d</sup> These are tentative values that may not be accessible experimentally because of the super sub- $\theta$  conditions.

eqs. (7) and (8) readily compute the values of  $M_v$ , which result in the molecular characteristics of the samples displayed in Table IV via eq. (3), whereas eq. (2) results in  $M_0$ , which is hereafter designated by  $M'_0$  for the low molecular weight regime, equal to  $1.16 \times 10^4$ . However,  $K_p$  remains unchanged. It follows that the exponent  $a$ , designated by  $a'$  hereafter for  $M_w < 5 \times 10^4$ , may be estimated by the method elaborated in the Introduction section for the other systems. Accordingly, parameter  $\chi$  is estimated by eq. (4) based on the estimates of  $a'$  and  $M'_0$ . Table III collects the results of these calculations. Indeed, the three P $\alpha$ Ms samples produce consistent values of  $a'$ , particularly for good solvents. In any case, the experimental uncertainties in  $a'$  are estimated to be less than 0.015. For P $\alpha$ Ms in 1-chlorobutane, Table III reveals  $a' = 0.522$  at 50°C. However, on the basis of the data presented by Mays et al.,<sup>1</sup> the MHS constants are found to be  $a' = 0.50$  and  $K = 7.3 \times 10^{-4}$  dL/g for the same polymer-solvent pair, but at 25°C, over  $6.9 \times 10^3 < M_w < 5.4 \times 10^4$ . This means that the  $[\eta]$  of a short-chain polymer in the moderate solvent does depend marginally on the temperature. Perhaps, one of the striking features of Table III is the sub- $\theta$  behavior of P $\alpha$ Ms in polar solvents, particularly, dimethylformamide (DMF), which results in  $a' \ll 0.5$ . In addition, solution numbers 12, 13, and 14 produce  $\chi$  values significantly smaller than its critical value at the critical point ( $\chi_c$ ) estimated to be  $0.60 \pm 0.03$  for these cases.<sup>24</sup> Hence, there were no signs of phase separation in these studies. This is in line with the finding of Hadjichristidis et al.<sup>3</sup> who studied the polymer in cyclohexane under a condition substantially below the  $\theta$  state.

Assuming that the thermodynamic interactions expressed in terms of  $\chi$  are unsusceptible to the chain length, eq. (4) leads to

$$a = (1 + \beta)/(2 + \beta). \quad (9)$$

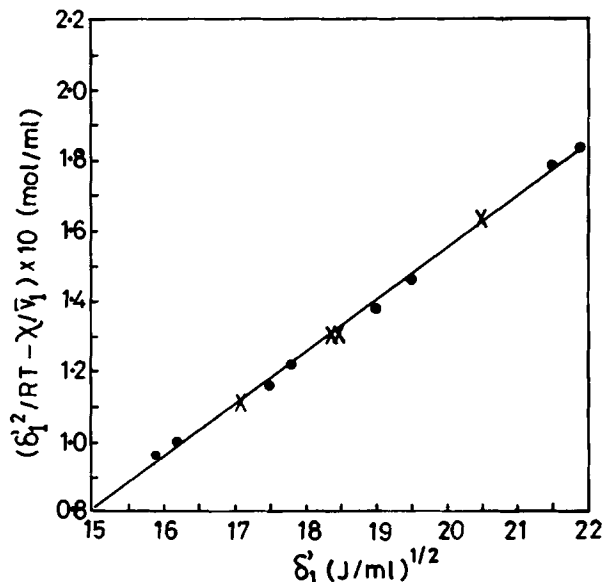
where

$$\beta = (2a' - 1)M_0^{1/2}/(1 - a')M_0'^{1/2} \quad (9a)$$

Table III lists the predictions of exponent  $a$  from eq. (9). The standard deviation between the exper-

**Table IV Molecular Characteristics of the P $\alpha$ MS Samples**

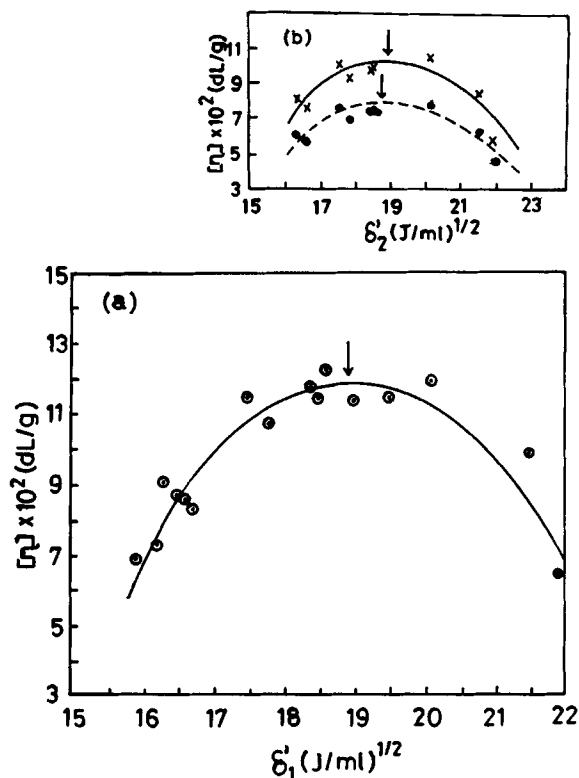
Sample	$M_w \times 10^{-4}$	$S \times 10^{-4}$
H	2.02	1.20
M	1.58	0.90
L	1.19	1.10



**Figure 1** Plot of  $(\delta_1^2/RT - \chi/V_1)$  against  $\delta_1$  for P $\alpha$ MS. Symbols: (x) literature; (●) this work.

imental and predicted exponent  $a$ 's is estimated to be 0.02, which is of the same order of magnitude as the experimental error of the former. Certainly, the corresponding  $K$  (not shown) may be readily computed by eq. (2). This approach is particularly useful for extending the existing lists of MHS constants to many new polymer-solvent systems. However, the three exceptionally low values of exponent  $a$  resulting from the sub- $\theta$  solvents, namely, 2-hexanone, *n*-butyl acetate, and DMF are rather questionable. Under these conditions, the enhanced intramolecular interactions might have caused the polymer chains to collapse, leading to aggregation and eventually precipitation,<sup>3,25</sup> particularly for polymers of high molecular weight.

Figure 1 shows a plot conforming to eq. (5) with  $\delta_1$  in place of  $\delta_1$ . It results in  $\delta_2 = 18.65 \pm 0.30$  (J/mL)<sup>1/2</sup> for P $\alpha$ Ms at 30°C. Because of the strong correlation between  $\delta_1^2$  and  $\delta_1$  appearing as variables on both sides of eq. (5), a nonlinear least-squares algorithm, which minimizes the total difference between the experimental and computed  $\chi$ 's,<sup>9</sup> is revoked to check the foregoing result. The calculation renders  $\delta_2 = 18.70$  (J/mL)<sup>1/2</sup> and  $\gamma = 0.345$ . However, the standard error of the estimate of  $\chi$  registers 0.12. This means that eq. (5) may facilitate the  $\delta_2$  determination, but by no means is it valid for the estimation of  $\chi$ . Usually, the  $\delta_2$  is considered equal to the solubility parameter of the solvent capable of producing the highest  $[\eta]$ . In Figure 2(a) and (b), variations of  $[\eta]$  with  $\delta_1$  are displayed for the samples H, M, and L cited in Table III. The maxima of the



**Figure 2** Plot of  $[\eta]$  and against  $\delta_1^2$  for the P $\alpha$ MS samples: (a) H (○); (b) M (×), L (●).

curves result in  $\delta_2 = 18.90 \pm 0.10$  (J/mL) $^{1/2}$ . Incidentally, this particular technique has also been adopted by Cowie who obtained  $\delta_2 = 18.8$  (J/mL) $^{1/2}$  for P $\alpha$ MS. $^{26}$  Indeed, all these experimental values of  $\delta_2$  for P $\alpha$ MS are in good agreement. However, if one had used the  $\delta_1$  data for the linear plot of eq. (5), one would get a significantly higher  $\delta_2 = 20.12$  (J/mL) $^{1/2}$ . Hence, it is vital to remove the hydrogen-bonding component from the  $\delta_1$  in order to avoid spurious results on  $\delta_2$  as demonstrated herein. In short, the foregoing approaches for  $\delta_2$  determination are valid only in the absence of strong intermolecular forces, as advocated by others. $^{14}$

### Huggins Coefficient

Numerous attempts have been made to correlate the coefficient  $k_1$  to the other measurable quantities of flexible polymers. Notably,  $k_1$  is related to the number-average molecular weight by a simple power model proposed by Utracki and Simha. $^{27}$  Recently, Gundert and Wolf expressed  $k_1$  as a linear function of the expansion factor  $\alpha_n^3$  ( $= [\eta]/[\eta]_\theta$ ), where  $[\eta]_\theta$  is the  $[\eta]$  under the  $\theta$  conditions. $^{28}$  Perhaps, one of

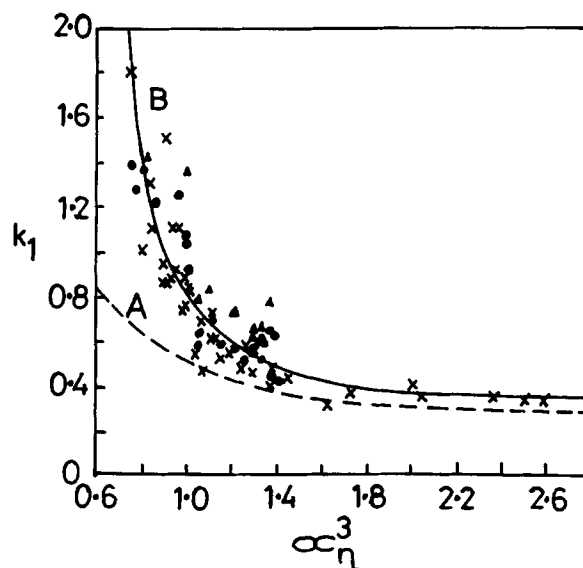
the most widely cited models is the Imai $^{29}$  equation given by

$$k_1 = k_0 \alpha_n^{-4} + C(1 - \alpha_n^{-2}) \quad (10)$$

where  $k_0$  and  $C$  are empirical constants independent of  $T$ ,  $M$ , and the solvent. The dashed curve in Figure 3 is constructed from eq. (10) with  $k_0$  and  $C$  being equal to the typical values of 0.5 and 0.3, respectively. Although the curve describes satisfactorily the  $k_1 - \alpha_n^3$  behavior of many systems including the polystyrene (PS), polyisobutylene (PIB), and poly(methyl methacrylate) (PMMS) solutions, $^{30}$  it distinctly underestimates the  $k_1$  values for P $\alpha$ MS over almost the entire range of  $0.7 < \alpha_n^3 < 2.6$ , as shown in Figure 3. Hence, a two-parameter equation is proposed empirically herein to resolve this problem, i.e.,

$$k_1 = k_\infty + A[\text{Coth}(\alpha_n^3 - B) - 1] \quad (11)$$

where  $A$  and  $B$  are the empirical constants, and  $k_\infty$ , the limiting value of  $k_1$  at  $\alpha_n^3$  approaching infinity. An intriguing feature of eq. (11) is that the predicted  $k_1$  is sensitive to parameters  $A$  and  $B$  over the practical range of  $\alpha_n^3$ . For instance, both curves A and B in Figure 3 can be constructed from eq. (11) by



**Figure 3** The dependence of  $k_1$  on the expansion factor  $\alpha_n^3$  for P $\alpha$ MS in various solvents. Dashed curve A is computed from eq. (10) with  $k_0 = 0.5$  and  $C = 0.3$ , whereas solid curve B, which serves to represent the data points, is constructed from eq. (11) with  $A = 0.280$ ,  $B = 0.6$ , and  $k_\infty = 0.335$ . Symbols: (×) literature; (●) samples H and M; (▲) sample L. The literature data were obtained from the recent work of Mays et al. $^{1-3}$

setting  $A = 0.872$ ,  $B = -0.1$ , and  $k_\infty = 0.282$  and  $A = 0.280$ ,  $B = 0.6$ , and  $k_\infty = 0.335$ , respectively.

In fact, curve B is particularly drawn to fit the data points. The resulting standard error of the estimate of  $k_1$  is 0.17, which is rather large but not unexpected considering the experimental uncertainties in both  $k_1$  and  $\alpha_\eta^3$ . Despite its deficiency, curve B definitely outperforms curve A and shows the general trend of the decrease of  $k$  with increasing  $\alpha_\eta^3$  for the P $\alpha$ Ms solutions. As noted, sample L seems to produce data points consistently lying above the solid curve in Figure 3. This may be attributed to the effects of local chain stiffness and ternary interactions, which are the important factors for understanding the unusual solution properties of short-chain polymers.<sup>31</sup> Recently, the discernibly higher values of  $k_1$  in the low molecular weight regime have also been observed for other polymer-solvent systems, involving PIB,<sup>32,33</sup> PS,<sup>34</sup> and PMMA.<sup>35</sup>

## CONCLUSIONS

The MHS constants estimated from the experimental data of the dilute-solution viscometric measurements using only the P $\alpha$ Ms samples of low molecular weight are found to be reliable, provided that the solvents are thermodynamically favorable to sustain a noncollapse state of polymer coils. The  $\delta_2$  of P $\alpha$ Ms, determined using a wide spectrum of solvents including the polar solvents, is comparable to that of PS.<sup>9</sup> However, if the  $k_1$  values of the solutions of P $\alpha$ Ms and other polymers including PS at a fixed  $\alpha_\eta^3$  are compared, the former is appreciably higher. Indeed, this peculiar  $k_1 - \alpha_\eta^3$  relationship for P $\alpha$ Ms-solvent systems defies the predictions of contemporary theories of polymer solutions.

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