Measurement of the unperturbed dimensions of stereoregular poly(methyl methacrylate)

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The results of measurements of unperturbed dimensions for a series of stereoregular poly(methyl methacrylates) are reported. The measurements were made by a recently developed method involving a gel permeation chromatograph coupled with an on-line low angle laser light scattering photometer. Measurements were performed in a thermodynamically good solvent, tetrahydrofuran at 25°C. The unperturbed dimensions were obtained by means of viscosity plots. Comparison of the results obtained by this method with those currently available in the literature, as well as with values predicted by statistical calculations, show good agreement. It was determined that a measurable difference occurs in the Mark–Houwink relationship between isotactic and syndiotactic poly(methyl methacrylate); isotactic poly(methyl methacrylate) is 30% more extended than syndiotactic poly(methyl methacrylate) in its unperturbed state; and isotactic poly(methyl methacrylate) exhibits a smaller degree of polymer solvent interaction than the syndiotactic form.

Keywords Measurement; unperturbed dimensions; poly(methyl methacrylate); solvent interaction; gel permeation chromatography

INTRODUCTION

Numerous authors[1,2] have published measurements of unperturbed dimensions of polymers. However, relatively few have been able to evaluate the unperturbed dimensions of polymers of established stereoregular content[3]. Here we report the results of measurements of the unperturbed dimensions for a wide range of stereoregular forms of poly(methyl methacrylate).

There are two basic ways in which measurements of the unperturbed dimensions are obtained: (1) determination of unperturbed dimensions directly, by measurements in theta solvents, and (2) determination of the perturbed dimensions in a good solvent and extrapolation of these values to the unperturbed state using one of the several existing theories. Both methods have been widely used[1] and the agreement between the two methods shown to be good[1–3]. We chose to use the latter method which requires measurement of the intrinsic viscosities in a thermodynamically good solvent for a series of narrow distribution samples of known molecular weight. To obtain the appropriate intrinsic viscosity, $[\eta]$, and molecular weight, M, we have used a recently proposed method[4]. This involves using a gel permeation chromatograph, g.p.c., coupled with an on-line low angle laser light scattering photometer, LALLS. The method uses the molecular weight distribution of the polymer to generate the necessary values for M_i amd $[\eta]_i$. Basically, the light scattering apparatus is used to determine the weight average molecular weight, M_i, at incremental points across the polymer distribution, and then the 'Universal Calibration' for g.p.c. is used to calculate the corresponding intrinsic viscosities. Inevitably eluted at each i^{th} point is a combination of M and configuration that gives the identical chain dimensions.

EXPERIMENTAL

Sample preparation and characterization

Preparation and characterization of the samples used in this work has previously been described[5]. *Table 1* describes briefly the conditions used, and the results of characterization. Two of the samples are available commercially. Sample 1 is a syndiotactic polymer from Polysciences Corp., Warrington, PA. Sample 2 is a conventional 'atactic' polymer obtained from Cellomer Associates. The remaining samples were prepared in this laboratory using the conditions described in *Table 1*.

^{13}C nuclear magnetic resonance spectroscopy was used for tacticity determination. The α-methyl group was used for characterization, which exhibits resonances at 22.06, 19.01 and 16.55 ppm corresponding to isotactic, heterotactic and syndiotactic triads.

Apparatus

The basic experimental apparatus consisted of a gel permeation chromatograph coupled with an on-line low angle laser light scattering photometer, (g.p.c./LALLS). The g.p.c. was a Waters model 201 equipped with 4-μStyragel columns of nominal pore size 10^3, 10^4, 10^5, and 10^6 Å. The LALLS was a Chromatix KMX-6, Palo Alto, CA. A 0.5μ fluoropore filter, Millipore Corporation, Bedford, MA, was placed between the columns and the LALLS, giving a clean signal relatively free from dust particles. Tetrahydrofuran, THF, Fisher Certified grade, was used as the g.p.c. elution solvent at a flow rate of 1.0 ml min^{-1}. Injection volumes were kept between 0.30 and 0.40 ml; polymer concentrations ranged from 1.0×10^{-3} to 2.0×10^{-3} g ml^{-1}.

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Table 1 Synthesis and characterization of poly(methyl methacrylate)s

Sample	Initiator	Solvent	Temperature (°C)	N.m.r. triads			N.m.r. diads		dn/dc
				i	*h*	*s*	*I*	*S*	(ml g^{-1})
1	*	*	*	5	20	75	15	85	0.0844
2	**	**	**	5	37	58	23	77	0.0845
4a	Thermal	None	210	15	42	43	36	54	0.0862
5b	9-Fluorenyl Lithium	Toluene	−40	76	16	8	83	17	0.0885
7	$LiAlH_4$	Diethyl ether	30	90	4	6	92	8	0.0876
8b	PhMgBr	Toluene	0	100	0	0	100	0	0.0884

* Syndiotactic PMMA (Polysciences)
** Conventional PMMA (Cellomer Assoc.)

Table 2 Intrinsic viscosity–molecular weight relationship for stereoregular PMMA

Sample 8b		Sample 7		Sample 5b		Sample 4a		Sample 2		Sample 1	
100% Iso		92% Iso		83% Iso		35% Iso		23% Iso		15% Iso	
[η] dl/g	$M \times 10^{-5}$	[η] dl/g	$M \times 10^{-5}$	[η] dl/g	$M \times 10^{-5}$	[η] dl/g	$M \times 10^{-5}$	[η] dl/g	$M \times 10^{-5}$	[η] dl/g	$M \times 10^{-5}$
0.472	1.66	0.450	1.50	0.204	0.48	0.219	0.69	0.190	0.54	0.180	0.57
0.492	1.76	0.504	1.74	0.228	0.54	0.235	0.73	0.192	0.60	0.201	0.65
0.512	2.05	0.535	2.01	0.238	0.59	0.251	0.80	0.215	0.67	0.222	0.76
0.551	2.22	0.590	2.25	0.244	0.66	0.255	0.86	0.232	0.74	0.235	0.87
0.654	2.55	0.620	2.61	0.274	0.74	0.265	0.93	0.251	0.82	0.257	1.03
0.664	2.85	0.650	2.98	0.300	0.82	0.281	1.03	0.261	0.92	0.274	1.12
0.680	3.16	0.661	3.05	0.301	0.93	0.315	1.10	0.299	1.02	0.330	1.34
0.793	3.61	0.775	3.62	0.338	1.05	0.321	1.23	0.305	1.12	0.371	1.71
0.821	3.95	0.957	4.51	0.389	1.15	0.332	1.35	0.355	1.25	0.402	0.98
0.896	4.21	0.999	5.03	0.423	1.31	0.351	1.48	0.337	1.37	0.457	2.36
0.921	4.87	1.10	6.10	0.435	1.47	0.407	1.65	0.415	1.52	0.531	2.61
0.991	5.23	1.30	6.98	0.459	1.65	0.427	1.76	0.419	1.66	0.589	3.02
1.05	5.55	1.27	7.54	0.521	1.86	0.440	1.91	0.435	1.86	0.605	3.51
1.09	6.10	1.30	8.10	0.530	2.04	0.464	2.05	0.451	2.03	0.750	4.51
				0.562	2.31	0.499	2.20	0.490	2.13	0.805	5.00
				0.612	2.60	0.552	2.52	0.534	2.53	0.920	5.64
				0.675	2.88	0.569	2.73	0.569	2.75	0.890	6.13
$K = 1.665 \times 10^{-4}$		$K = 1.690 \times 10^{-4}$		$K = 1.719 \times 10^{-4}$		$K = 9.84 \times 10^{-5}$		$K = 9.577 \times 10^{-5}$		$K = 8.892 \times 10^{-5}$	
$a = 0.660$		$a = 0.659$		$a = 0.658$		$a = 0.692$		$a = 0.695$		$a = 0.694$	

$[\eta] = KM^{\alpha}$

Differential refractometry

Measurement of the refractive index increment, d*n*/d*c*, for the six PMMA samples listed in *Table 1* has previously been described[5]. Importantly, we have noted a measurable change in d*n*/d*c* with tactic content with the values given in *Table 1*. The difference in d*n*/d*c* is up to 5% over the range of stereoregular forms. Moreover, this difference is believed to be significant since the square of this term is used in the optical constant required for the calculation of molecular weight.

A Chromatix KMX-16 differential refractometer was used which employs a He–Ne laser generating a wavelength of 633 nm. All measurements were made at 25°C in THF, Fisher Certified grade. The refractometer was calibrated at 25°C with aqueous solutions of NaCl.

Determination of the second virial coefficient

The second virial coefficient, A_2, was obtained by static analyses of the sample from the slope of a plot of Kc/R_θ *versus* c, where K is the optical constant, c is the concentration and R_θ is the Rayleigh ratio. No dependence of A_2 on the molecular weight was incorporated into our calculations, a procedure which has been shown to result in negligible errors[6]. For PMMA it was determined that A_2 was measurably smaller for the isotactic samples, 5b, 7, and 8b, than for the syndiotactic samples, 1, 2 and 4a. An average value of 5.01×10^{-4} mol cm^3/g^2 was used for samples 5b, 7 and 8b, whereas 6.15×10^{-4} mol cm^3/g^2 was used for samples 1, 2, and 4a. In view of the relatively small magnitude of the term containing A_2 in the g.p.c./LALLS equation, uncertainty in M from this approximation is insignificant.

Measurement of the molecular weights and intrinsic viscosities

Data were acquired at 0.25 ml g.p.c. elution intervals and the corresponding values of M_i and $[\eta]_i$ were calculated according to the method previously described[4]. The values collected (see *Table 2*) represent data obtained from the portion of the distribution where adequate detector response was obtained from both the differential refractometer and the LALLS. The scattered intensity, as measured by the LALLS, is a product of the concentration and the molecular weight, whereas the differential refractometer is sensitive only to concentration. As a result, the LALLS is extremely

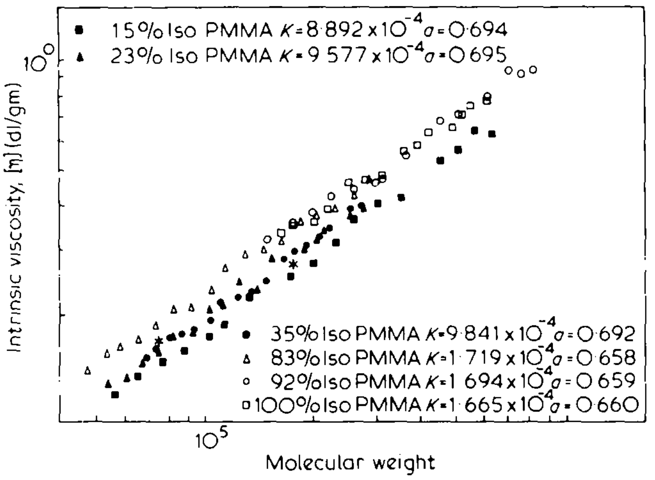

Figure 1 Comparison of the intrinsic viscosity–molecular weight relation for six different stereoregular forms of poly(methyl methacrylate).* Data obtained by conventional viscometry

sensitive to the high end of the distribution and correspondingly less sensitive to the low end. This results in an offset between the two detectors which increases with distribution and makes calculation of the molecular weights of the sample at both ends imprecise for broad distributions. Consequently, data acquisition is limited to a region where adequate response from the two detectors can be obtained. This usually resulted in 14–17 usable data points for each sample. Outside this range, data scatter is excessive.

Table 2 lists the $[\eta]_i$ and M_i data obtained for the six stereo forms of PMMA. In the lower portion of *Table 2* the Mark–Houwink constants K and a are listed. The data suggest that there is little measureable difference among the three isotactic samples, 5b, 7, and 8b, or among the three more syndiotactic samples, 1, 2, and 4a. Considerable difference is observed, however, between the sets of three isotactic and the three more syndiotactic samples. The isotactic samples exhibit Mark–Houwink exponents generally about 0.66, whereas an average of 0.69 is obtained for the more syndiotactic set.

Figure 1 shows all the data in *Table 2* plotted graphically as $[\eta]$ *versus* M. The open symbols are the isotactic samples, 5b, 7, and 8b, and the filled symbols are the more syndiotactic samples, 1, 2, and 4a. The difference between the isotactic and syndiotactic sets is obvious. All the data for the isotactic sets lie above those for the more syndiotactic polymers, although at high molecular weight, $\sim 10^6$, the least squares lines through the data tend to converge.

Figure 1 also shows two points indicated by an asterisk, *. These two data are for conventional $[\eta]$ and M measurements for two commercially-available narrow distribution PMMA standards; Polysciences, Inc., Warrington, PA. Good agreement is shown between the results obtained by the conventional methods and those obtained by the g.p.c./LALLS method.

Calculation of unperturbed dimensions

Measurement of K_θ. Numerous relations have been proposed for the calculation of unperturbed dimensions from measurements of intrinsic viscosity and molecular weight in a thermodynamically good solvent. Basically, all methods involve taking into account the expansion of a polymer in a thermodynamically good solvent. The parameter of interest is K_θ where

$$K_\theta=(\langle\bar{r}\rangle_0^2/M)^{3/2}$$

and $\langle\bar{r}_0^2\rangle$ is the unperturbed mean square end-to-end distance. In each of equations (1)–(6), the unperturbed parameter, K_θ, is obtained from the intercept of the appropriate plot involving intrinsic viscosity and molecular weight values obtained from measurements in thermodynamically good solvents. In addition, from the slope of each we obtain thermodynamic parameters characterizing the polymer–solvent interactions.

Here the intrinsic viscosity and molecular weight data obtained for the six stereo forms of PMMA are evaluated using on each six different extrapolation procedures. The six methods we chose were Fox and Flory[7], equation (1); Stockmayer and Fixman[1], equation (2); Berry[4], equation (3); Dondos and Benoit[9], equation (4); Cowie[2], equation (5); and Inagaki *et al.*[6], equation (6):

$$[\eta]^{2/3}/M^{1/3}=K_\theta^{2/3}+K_\theta^{5/3}C_f(M/[\eta]) \tag{1}$$

$$[\eta]/M^{1/2}=K_\theta+0.051\varphi BM^{1/2} \tag{2}$$

$$([\eta]/M^{1/2})^{1/2}=K_\theta^{1/2}+0.42K_\theta^{3/2}B(\bar{r}_0^2/M)^{-3/2}(M/[\eta]) \tag{3}$$

where $C_f=(\alpha^5-\alpha^3)/M^{1/2}$, and α is the expansion factor; φ is the 'Universal' constant of Flory; $B=\beta/M_s^2$, M_s is the molar weight of a chain segment and β is the 'binary cluster integral'.

$$[\eta]/M^{1/2}=K_\theta+0.51\varphi BM^{1/2}(1-DM^{1/2}) \tag{4}$$

where $D=12\times10^{-4}(a-0.5)^9$

$$[\eta]/M^{1/2}=(\varphi(\varepsilon)/\varphi_0)K_\theta+0.9166(\varphi(\varepsilon)/\varphi_0)K_\theta k^{7/10}M^{7/10} \tag{5}$$

where $$\varepsilon=(2a-1)/3 \tag{5a}$$

where a is the Mark–Houwink exponent, and

$$\varphi(\varepsilon)=\varphi_0(1-2.63\varepsilon+2.86\varepsilon^2) \tag{5b}$$

$$[\eta]^{4/5}/M^{2/5}=0.786K_\theta^{4/5}+0.950K_\theta^{4/5}k^{2/3}M^{1/3} \tag{6}$$

where $$k=0.33B[M/\langle\bar{r}^2\rangle_0]^{3/2} \tag{6a}$$

Figures 2–7 show examples for each of equations (1)–(6) graphically for two different tactic forms of PMMA, one highly isotactic, sample 8b, and the other syndiotactic, sample 2. The data for the remaining four samples have been omitted for clarity. In each figure a straight line is obtained with the unperturbed parameter K_θ as the intercept. Least squares analysis was used to obtain K_θ values, which are listed in *Table 2* for each of the six samples. In each case the percent standard deviation for the K_θ values was determined to be 10%. Error results primarily from extrapolation rather than from data scatter.

The agreement between the K_θ values predicted by the six different methods, equations (1)–(6), is quite good. For example, for the 100% isotactic sample, *Figures 2–6*, the K_θ values ranged from 7.8 to 9.2 × 10 dl g^{-1} with an,

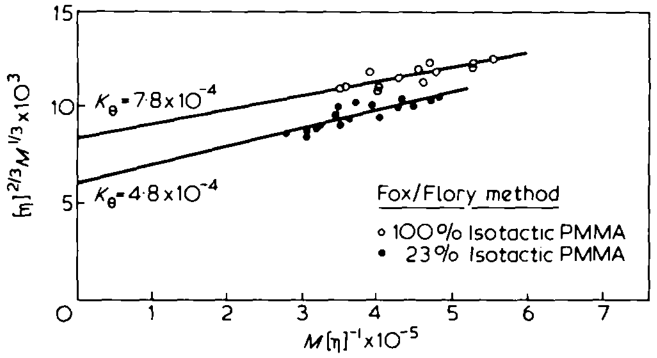

Figure 2 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate), using the method of Fox and Flory

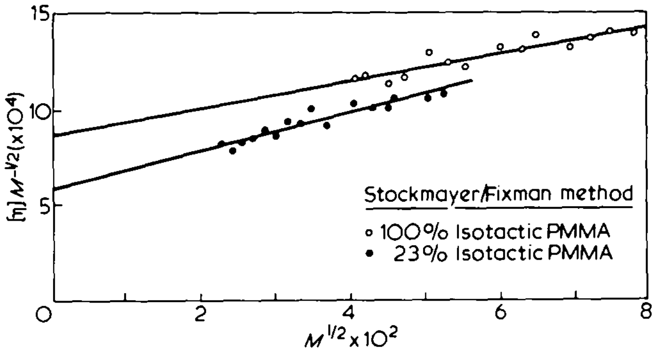

Figure 3 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate) using the method of Stockmayer and Fixman

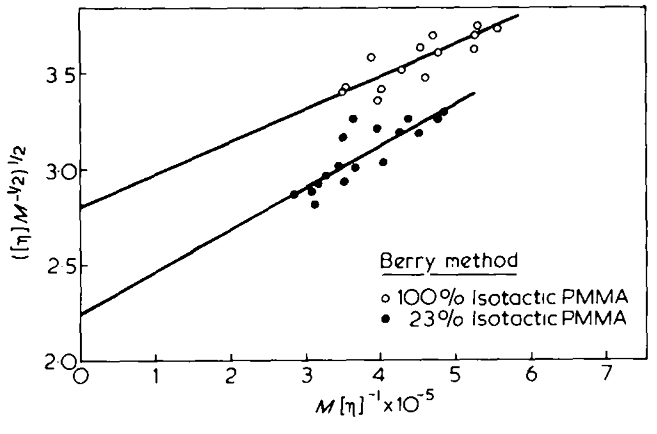

Figure 4 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate) using the method of Berry

average of $8.4\times10^{-4}\pm0.5\times10^{-4}$. Whereas for the 23% isotactic sample, also shown in *Figures 2–7*, K_θ ranged from 4.8 to 6.0×10^{-5} dl g^{-1} with an average of 5.4×10^{-4} $\pm0.4\times10^{-4}$. It is also apparent from *Table 2* that there is little measurable difference among the three isotactic samples, 5b, 7, and 8b, or among the three syndiotactic samples, 1, 2, and 4a. There is, however, considerable difference between the sets of isotactic and syndiotactic polymers. Comparison of the values in *Table 2* with those in the literature from both direct and indirect measurements (see *Table 3*) shows good agreement. Values range from 7.0 to 8.7 for the 'isotactic' polymers which compares well with our values of 6.7 to 9.2. For 'syndiotactic' samples, literature values range from 4.4 to 6.8, which also compares well with our values of 4.3 to 6.0. The agreement between the six different extrapolation procedures, equations (1) to (6), is good, within the precision of the methods, ±10%. We thus chose to use the arithmetic average of the K_θ values, reported in column 8 of *Table 2*, for subsequent calculation of the characteristic ratio.

Calculation of the characteristic ratio

The characteristic ratio, C_∞, is a parameter which compares the unperturbed mean square end-to-end

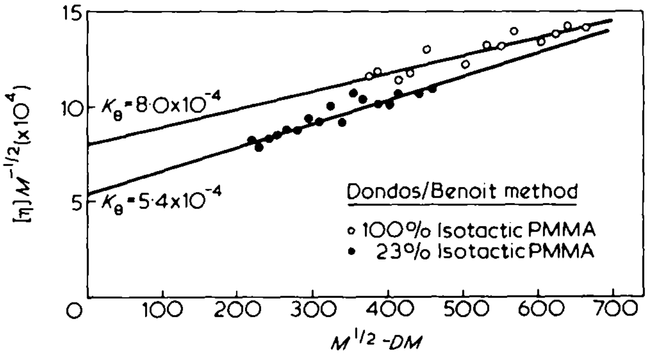

Figure 5 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate) using the method of Dondos and Benoit

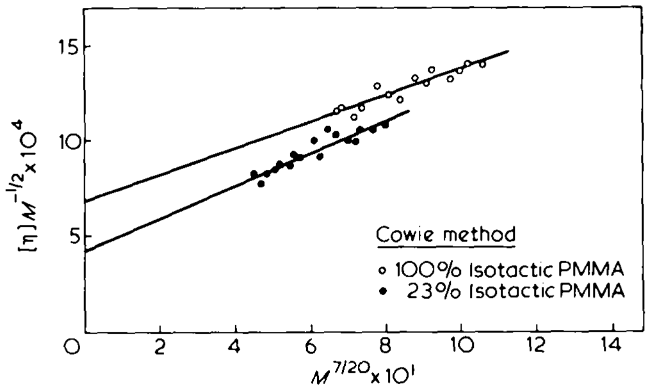

Figure 6 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate) using the method of Cowie

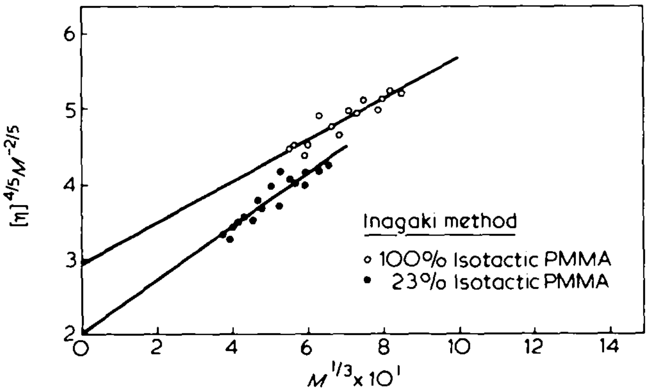

Figure 7 Estimation of the unperturbed dimensions for two different stereoregular forms of poly(methyl methacrylate) using the method of Inagaki

Table 3 K_θ values for stereoregular PMMA

	$K_\theta \times 10^4$ (dl g^{-1})							
Sample	Dondos/ Benoit	Stockmayer/ Fixman	Berry	Inagaki	Fox/Flory	Cowie	Average	C_∞
(8b) 100% isotactic	8.0	8.6	8.0	8.8	7.8	9.2	8.4	10.2
(7) 92% isotactic	8.2	8.8	8.2	9.0	8.0	9.1	8.5	10.3
(5b) 83% isotactic	7.2	7.5	6.8	7.7	6.7	8.0	7.3	9.3
(4a) 35% isotactic	5.4	5.7	4.8	5.5	4.6	5.9	5.3	7.5
(2) 23% isotactic	5.4	5.8	5.0	5.5	4.8	6.0	5.4	7.5
(1) 15% isotactic	5.2	5.7	4.5	5.4	4.3	5.8	5.1	7.3

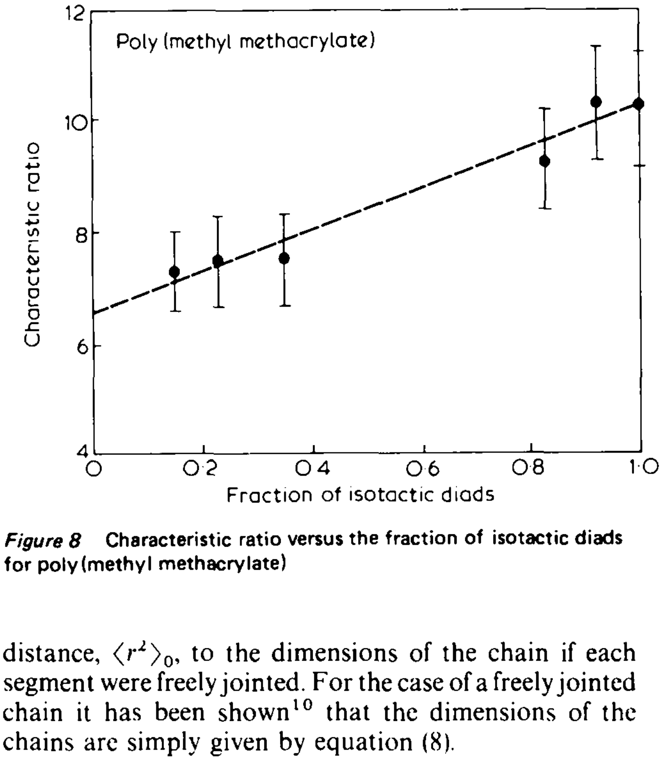

Figure 8 Characteristic ratio versus the fraction of isotactic diads for poly(methyl methacrylate)

distance, $\langle r^2\rangle_0$, to the dimensions of the chain if each segment were freely jointed. For the case of a freely jointed chain it has been shown[10] that the dimensions of the chains are simply given by equation (8).

$$\langle r^2\rangle_0 = nl^2 \qquad (8)$$

where n represents the number of skeletal bonds and l^2 is the average squared length of each bond. The characteristic ratio is defined by:

$$C_n = \langle r^2\rangle_0/nl^2 \qquad (9)$$

where C_n is the characteristic ratio for a chain of length n. For a freely jointed chain C_n is unity for all values of n. For all other cases C_n will differ from unity by an amount which will depend on the extension of the chain.

The characteristic ratio is related to the parameter K_θ and consequently may be obtained from equation (10)[10]

$$C_\infty = (K_\theta/\varphi)^{2/3} M_b/l^2 \qquad (10)$$

where M_b is the mean molecular weight per skeletal bond, l is the bond length, and φ is Flory's universal constant. The value obtained for C_∞ will depend on the value chosen for φ. Several values ranging from 1.8 to 2.87 $\times 10^{21}$ have been proposed. We have chosen to use 2.5 $\times 10^{21}$, as recommended by Yamakawa[11]. *Table 2*, column 9 lists the characteristic ratios calculated from the average K_θ values reported in column 8. For the three isotactic samples, 5b, 7, and 8b, we obtain an average value of 9.9 whereas for the three syndiotactic samples, 1, 2, and 4a, we obtain an average of 7.5. The isotactic polymers are thus shown to exhibit dimensions $\simeq 30\%$ larger than the syndiotactic forms. These values are in good agreement with those of other researchers as collected in Reference 3.

Figure 8 shows graphically the effect of stereoregularity on the unperturbed dimensions. Here we have plotted the characteristic ratio, C_∞, *versus* the fraction of isotactic diads in the chain, f_i. The broken line drawn through the data is presumptuous, yet the trend is obvious. The more isotactic polymers exhibit approximately 30% larger unperturbed dimensions. The bars in *Figure 8* represent standard deviations of 10% that result primarily from the extrapolation to obtain K_θ from which C_∞ is calculated.

Statistical calculations of unperturbed dimensions

Methods have been developed whereby statistical calculations can predict the dimensions of a polymer chain using a rotational isomeric scheme and assumptions about the geometry of the pendant groups. These calculations have been extended to predict the effect of tacticity on the unperturbed dimensions by Monte Carlo methods. These methods have been employed to generate chains generally consisting of 200 units with random sequencing of *meso* and racemic diads. The results of these calculations for PMMA[12] are shown in *Figure 9*, along with published data. The three curves, labelled A, B, and C, *Figure 9*, are attempts by the authors[12] to fit the available data. They[12] concluded that agreement with experimental values of C_∞ is obtained by taking $E\alpha \approx 1.1$ kcal mol^{-1} and $E\beta \approx 0.6$ kcal mol^{-1}, α and β being the statistical weights for the *meso*, $g\tau$ and racemic, $\tau\tau$ states, respectively, relative to the *meso* $\tau\tau$ state. Comparison of our data in *Figure 8* with the statistical curves shown in *Figure 9* reveals good agreement. That is, the data obtained by the g.p.c./LALLS method agrees with curve B for which $E\alpha = 1.2$ kcal mol^{-1} and $E\beta = -0.6$ kcal mol^{-1}.

Polymer solvent interaction parameter

The slopes of equations (1) through (6) reflect the degree of polymer-solvent interaction. In each case the highly isotactic samples, 5b, 7, and 8b, were found to exhibit lower slopes than the syndiotactic samples, 1, 2, and 4a, indicating less polymer-solvent interaction[8].

We are interested in the parameter B which characterizes the degree of polymer solvent interaction, and is given by equation (11):

$$B = \beta / M_s^2 \qquad (11)$$

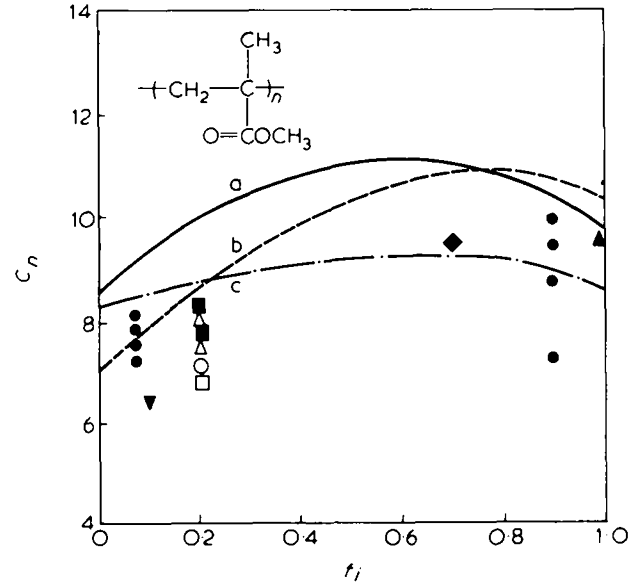

Figure 9 Characteristic ratios for Monte Carlo chains of 200 units each as a function of f_i, the fraction of meso diads in the chain. Curves are shown for (a) $E_\alpha = 1.0$, $E_\beta = -0.6$, and $\theta = 58°$; (b) $E_\alpha = 1.2$, $E_\beta = -0.6$, and $\theta' = 58°$; (c) $E_\alpha = 1.2$, $E_\beta = -0.2$, and $\theta' = 56°$, energies being in kcal mol^{-1}. The experimental results of various authors are represented by points as follows: Katime *et al.* (▲), Katime and Roig (▲), Sakurada *et al.* (●), Fox (■), Krause and Cohn-Ginsburg (◆), Chinai and Valles (△), Vasudevan and Santappa (□), from Sundarajan and Flory

where M_s is the molecular weight of the segment and β is the 'binary cluster integral'. Before we can calculate B from the Fox-Flory method, equation (1), it must be rewritten in a form from which B can be obtained.

Yamakawa[8] has proposed,

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.858 K_\theta^{2/3} \varphi_0 BM/[\eta] \qquad (1a)$$

Table 4 lists the values of B as obtained by the six different methods, equations (1) to (6), for each of the six stereo forms of PMMA. In addition to the six methods used, equations (1) to (6), two additional methods, equations (12) and (13) were used to calculate the parameter, B. These

$$[\eta]/M^{1/2} = K_\theta + 0.346\, BM^{1/2} \qquad (12)$$

$$[\eta]/M^{1/2} = 1.05 K_\theta + 0.287 \varphi_0 BM^{1/2} \qquad (13)$$

equations are modifications of the Stockmayer–Fixman equation, equation (2), and were proposed by Yamakawa (11) in an attempt to compensate for the underestimated values of B obtained from the Stockmayer-Fixman equation.

Table 4 shows that the parameter B varies considerably with the method used to obtain B. With the exception of the Cowie method, equation (5), most of the methods are, however, in qualitative agreement for a particular tactic form of PMMA. For the isotactic samples, 5b, 7, and 8b, values of B are consistently lower than for the syndiotactic samples, 1, 2, and 4a. This indicates reduced polymer-solvent interaction, consistent with the smaller values obtained for the Mark–Houwink exponent, a, for the isotactic samples (see *Table 2*).

Values of B vary from one method to another, see *Table 4*, because they depend on the functional form used for α. That is, whether we use closed forms for α of the type α^5, equation (9) or α^3, equation (10). According to Yamakawa[8], a more rigorous experimental test of the theories of α is needed before we can establish a basic equation for viscosity plots to be used for the estimation of B. No published data on B is available for comparison.

Table 4 Polymer–solvent interaction parameter, B, for stereoregular PMMA

	$B \times 10^{28}$ (cm^3)							
Sample	Dondos/ Benoit	Stockmayer/ Fixman	Berry	Inagaki	Fox/Flory	Cowie	Eq. 5.12	Eq. 5.13
(8b) 100% isotactic	7.19	5.56	5.56	7.46	3.99	17.9	8.19	9.88
(7) 92% isotactic	7.21	5.44	5.42	7.34	3.90	18.1	8.01	9.66
(5b) 83% isotactic	8.74	7.48	7.78	9.99	5.53	23.9	11.03	13.29
(4a) 35% isotactic	9.50	7.82	9.86	11.9	7.45	31.9	11.53	13.90
(2) 23% isotactic	9.59	7.89	9.37	11.9	6.98	31.8	11.63	14.02
(1) 15% isotactic	8.28	6.33	8.84	9.88	6.74	26.4	9.34	11.26

CONCLUSIONS

From this work it can be concluded that, (a) a measurable difference exists in the Mark-Houwink relationships for isotactic and syndiotactic PMMA. For a given molecular weight, the isotactic polymer exhibits a larger intrinsic viscosity, although at high molecular weights, $\sim 10^6$, this difference diminishes. The difference indicates that isotactic PMMA is more highly extended even in a thermodynamically good solvent, THF; and (b) isotactic PMMA exhibits less polymer-solvent interaction than the syndiotactic polymer.

REFERENCES

1 Stockmayer, W. H. and Fixman, M. J. *J. Polym. Sci.* 1963, **C1**, 137
2 Cowie, J. M. G. *Polymer* 1966, **7**, 487
3 Jenkins, R. and Porter, R. S. *Adv. Polym. Sci.* 1980, **36**, 000
4 Jenkins, R. and Porter, R. S. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 001
5 Jenkins, R. and Porter, R. S., in preparation
6 Owens, A. C. and Kaye, W. *J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 1151
7 Flory, P. J. and Fox, T. G. *J. Am. Chem. Soc.* 1951, **73**, 1904
8 Berry, G. C. *J. Chem. Phys.* 1967, **46**, 1338
9 Dondos, A. and Benoit, H. *Polymer* 1978, **19**, 523
10 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1971
11 Yamakawa, H. 'Modern Theory of Polymer Solutions', Harper and Row, New York, 1971
12 Sundararajan, P. R. and Flory, P. J. *J. Am. Chem. Soc.* 1974, **96**, 5025
13 Kusanagi, H., Tadokoro, H. and Chatani, Y. *Macromolecules* 1976, **9**, 531