Notes

Correlation between Unperturbed Dimension and Stereoregularity of Poly(methyl methacrylate)

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Received October 26, 1989;
Revised Manuscript Received February 11, 1991

Conformational energy calculations by Vacatello and Flory[1] and by Sundararajan[2] showed that not only content but also distribution of the stereoregular diads may influence the unperturbed dimension of a stereoregular polymer. Jenkins and Porter[3,4] have studied the unperturbed dimensions of some polymers with established stereochemical contents, but not much work has been done on polymers with known stereoregular diad distributions. In this paper, the unperturbed dimensions of poly(methyl methacrylate) (PMMA) with a Bernoulli distribution of meso and racemic diads are studied by using gel permeation chromatography coupled with an automatic capillary viscometer (GPC/[η]).

Experimental Section

Isotactic PMMA (s-9 and s-10) were polymerized at −78 °C with lithium aluminum hydride as a catalyst.[5] The other samples were prepared by methylating the corresponding poly(methacrylic acid) (PMAA) with diazomethane, and the PMAA's were polymerized in different solvents and at different temperatures.[6] The stereoregular triad content of PMMA was determined by NMR.[7] To reduce the effect due to axial dispersion of GPC, broad distribution samples (mixtures of three or four samples synthesized, respectively) were used.

Measurement of GPC/[η] was conducted on a GPC coupled with an automatic capillary viscometer. The GPC was a NJ-792 equipped with four columns of silica gel spheres with nominal pore sizes, 10^3, 10^4, 10^5, and 10^6 Å. Tetrahydrofuran was used as the GPC elution solvent at a flow rate of 1.0 mL/min. The injection volume was 1 mL, and the polymer concentration was 0.5% (g/mL). The measurement precision of the automatic capillary viscometer was 0.001 s. Viscosity was measured at 30 ± 0.005 °C.

Treatment of Data

(1) Distribution of the Diads of PMMA. If meso (m) and racemic (r) diads follow a Bernoulli distribution, there exists the following relationship among the stereoregular triads.[8]

$$(rr)^{1/2} = (rr) + (rm)/2 \tag{1}$$

The data listed in Table I are consistent with eq 1, as can be seen from Figure 1. This shows that the stereoregular diads in these samples have a Bernoulli distribution.

(2) Calculation of Viscosity. The intrinsic viscosity, $[\eta]_i$, was calculated from the usual Huggins equation in the form

$$[\eta]_i = \frac{(1 + 4K_H\eta_{spi})^{1/2} - 1}{2K_HC_i} \tag{2}$$

where C_i is the concentration corresponding to the ith elution interval and K_H is the Huggins coefficient. The values of K_H for different PMMA's were determined at 30 °C.

(3) Correction for Axial Dispersion. The $[\eta]_i$ obtained by GPC/[η] is the true intrinsic viscosity corresponding to elution interval i, but the value of $M_i[\eta]_i$ is not equal to the hydrodynamic volume of the universal calibration line, ϕ_e, because of the effect of axial dispersion. To remove this, we used a β-average hydrodynamic volume, $\langle\phi_\beta\rangle$, which is defined as

$$[\eta]_i = \sum w_i[\eta]_i = K^{1/(\alpha+1)}\sum W_i{\phi_{e,i}}^{\beta}$$
$$= K^{1/(1+\alpha)}\langle\phi_\beta\rangle^\beta \qquad [\beta = \alpha/(1+\alpha)] \tag{3}$$

where α and K are the exponent and coefficient of the Mark-Houwink viscosity equation $[\eta] = KM^\alpha$. According to Tung,[9] $\langle\phi_\beta\rangle$ can be represented as

$$\langle\phi_\beta\rangle = [Y(\beta)/Y(0)]^{1/\beta}$$

$$Y(\beta) = \frac{1}{\sigma_0(2\pi)^{1/2}}\int_{-\infty}^{\infty}\phi^\beta C(V)\exp\left[\frac{-(V-V_e)^2}{2{\sigma_0}^2}\right]dV \tag{4}$$

where $C(V)$ is the molecular weight distribution of the polymer as a function of the elution volume V. In our case, it was found that $C(V)$ could be approximated by a Gaussian distribution, e.g.

$$C(V) = \frac{1}{\sigma_T(2\pi)^{1/2}}\exp\left[\frac{-(V-V_0)^2}{2{\sigma_T}^2}\right] \tag{5}$$

From eqs 4 and 5, one obtains

$$Y(\beta) = {\phi_0}^\beta\exp\left[\frac{-(V_e-V_0)^2}{2{\sigma_0}^2}\right]\exp\left\{\left[A\beta + \frac{(V_e-V_0)}{2{\sigma_0}^2}\right]^2\frac{\tau}{2}\right\} \tag{6}$$

$$\langle\phi_\beta\rangle = \phi_0\exp\left[\frac{\tau A}{2}\left(A + \frac{(V_e-V_0)}{{\sigma_0}^2}\right)\right] \tag{7}$$

where A is the coefficient in the universal calibration equation, $A(V_e - V_0) = \ln(\phi_\beta/\phi_0)$; V_0 and ϕ_0 are the elution volume and hydrodynamic volume corresponding to the peak of the distribution of polymer; and σ_0 and σ_T are the axial dispersion and sample dispersion parameter, respectively. In this case, $A = -0.8114$ and $\sigma_0 = 1.372$.

The capillary viscometer measures the average viscosity of the fraction between the elution volumes, V_i and V_{i+1}. Therefore, the true hydrodynamic volume of each fraction

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Table I
Summary of the Data for PMMA's

samples	$K \times 10^2$, mL/g	α	$K_\theta \times 10^2$, mL/g	$M_w \times 10^5$	M_w/M_n	C_∞	(mm)	(rr)	(rm)
s-1	0.885	0.695	5.2 ● 0.5	1.9	8.5	7.4		0.93	0.07
s-2	0.973	0.688	5.5 ± 0.6	2.3	9.6	7.7	0.01	0.88	0.11
s-3	1.030	0.686	5.6 ± 0.5	5.4	10.8	7.8	0.01	0.85	0.14
s-4	1.130	0.684	5.9 ± 0.5	1.2	7.2	8.1	0.02	0.79	0.19
s-5	1.450	0.670	6.9 ± 0.8	4.5	10.5	8.8	0.03	0.69	0.28
s-6	1.430	0.673	6.7 ± 0.8	2.5	8.7	8.9	0.04	0.64	0.32
s-7	1.90	0.659	7.8 ± 0.8	3.3	12.4	9.7	0.15	0.42	0.43
s-8	2.05	0.650	8.1 ± 0.7	2.0	9.1	9.9	0.28	0.23	0.49
s-9	2.40	0.640	8.5 ± 0.7	4.5	7.5	10.3	0.88	0.01	0.11
s-10	2.47	0.636	8.5 ● 0.7	1.8	6.5	10.3	0.92		0.08

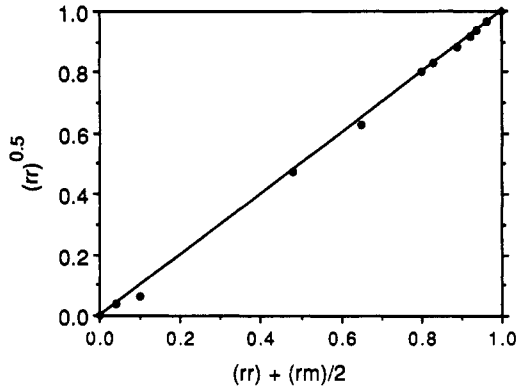

Figure 1. Comparison of experimental data with those calculated by assuming Bernoulli distribution.

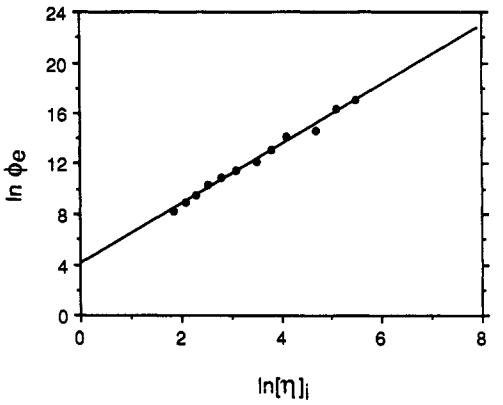

Figure 2. Plot of corrected hydrodynamic volume Φ_e vs $[\eta]_e$ for s-9.

can be written as

$$\bar{Y}(\beta,V_i) = \int_{V_i}^{V_{i+1}} Y(\beta,V_e)\,dV_e$$

$$= Y(\beta,\bar{V}_i)\int_{-0.5}^{0.5} \exp\left(-\frac{\xi^2 x^2}{2\sigma_0^2}\right) \times \exp\left[\frac{X(\tau A\beta - \xi^2 X_0)}{\sigma_0^2}\right] dX \quad (8)$$

where $\xi = \sigma_0^2/(\sigma_0^2 + \sigma_T^2)$, $\bar{V}_i = (V_i + V_{i+1})/2$, $X_0 = V_i - V_e$, and $V_{i+1} - V_i = 1$. When the polydispersity of polymer is high, e.g., $\sigma_0^2 + \sigma_T^2 \gg 1$, eq 8 can be approximated by[10]

$$\bar{Y}(\beta,V_i) = Y(\beta,\bar{V}_i)\exp(-D + 0.0211B^2) \quad (9)$$

where $D = (V_{i+1} - V_i)^2/[4(\sigma_0^2 + \sigma_T^2)]$ and $B = (\sigma_T^2 A\beta - X_0)/(\sigma_0^2 + \sigma_T^2)$. Thus, eq 3 becomes

$$\ln \phi_e = B \ln [\eta]_i + C$$

$$B = \frac{\sigma_0^2 + \sigma_T^2}{\sigma_T^2}\left(1 + \frac{1}{\alpha}\right)\left(1 - \frac{0.042}{\sigma_0^2 + \sigma_T^2}\right)^{-1}$$

$$C = -\frac{\sigma_0^2 + \sigma_T^2}{\alpha\sigma_T^2}\ln K - \frac{A^2\sigma_0^2}{2}\left(\frac{\alpha}{1+\alpha}\right) - \frac{\sigma_0^2}{\sigma_T^2}\ln \phi_0 \quad (10)$$

Equation 10 indicates that a plot of $\ln \phi_e$ vs $\ln [\eta]_i$ will be linear, as in Figure 2 and will yield B as the slope and C as the intercept. The Mark–Houwink constants can then be calculated from the slope and intercept. The K and α for all the samples are summarized in Table I.

(4) Calculation of K_θ and C_∞. According to an approximate relation of Stockmayer and Fixman[11]

$$[\eta]_i/M_i^{0.5} = K_\theta + 0.51\Phi B M_i^{0.5} \quad (11)$$

Plots of $[\eta]_i/M_i^{0.5}$ vs $M_i^{0.5}$ produced a straight line with K_θ as intercept, as shown in Figure 3 for sample s-9. The values of K_θ, obtained by using least-squares analysis, are listed in Table I. In addition, the parameter B, which characterizes the extent of polymer–solvent interaction, ranged from 6.2×10^{-28} to 8.9×10^{-28} cm^3/g^2 with an increase in the fraction of syndiotactic diads of PMMA. These values are in agreement with those published in the literature.[4]

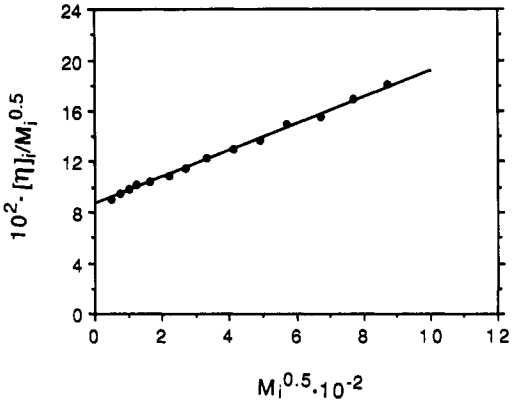

Figure 3. Estimation of $K\theta$ using Stockmayer and Fixman's method for s-9.

Characteristic ratios, C_∞, were calculatd from the equation[12]

$$C_\infty = (K_\theta/\Phi)^{2/3} M_I/2L^2 \quad (n \gg 1) \quad (12)$$

where M_I is the molecular weight per monomer and L is the bond length. In our calculation, Φ was chosen to be[13] 2.5×10^{23}. The values of C_∞ are presented in Table I. For isotactic (s-9, s-10) and syndiotactic PMMA (s-1, s-2), the values of C_∞ obtained by the present method were consistent with those collected in ref 1.

Discussion

Assuming independent internal rotation and a Bernoulli distribution of stereoregular diads, Birshtein and Ptitsyn[14]

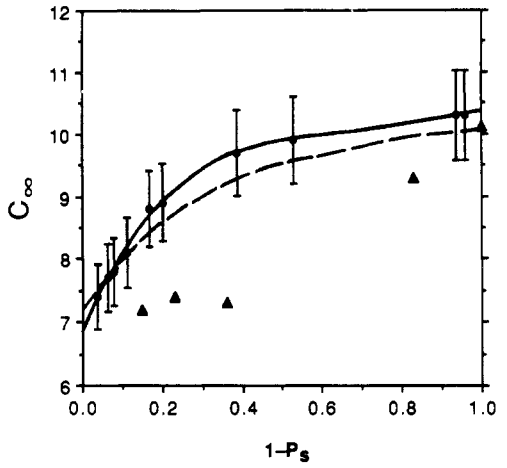

Figure 4. Comparison of experimental C_∞ with the theoretical prediction. Experimental data: (▲) taken from ref 4, (●) obtained by GPC/[η]; (—) fitted by eq 14 and (– –) predicted by Vacatello and Flory.[1]

calculated the unperturbed dimensions of a stereoregular polymer

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}\frac{(1-\eta^2-\epsilon^2)[1-(1-2P_s)(\eta^2+\epsilon^2)]}{(1-\eta)-(1-2P_s)(\eta-\eta^2-\epsilon^2)^2} \quad (13)$$

where $P_s = (rr)^{0.5}$, $\eta = \langle\cos\phi\rangle$, $\epsilon = \langle\sin\phi\rangle$, ϕ is the angle of rotation, and θ is the supplement of the bond angle. From eq 13, it is predicted that the unperturbed dimensions of syndiotactic chains are always larger than isotactic chains. This is not the case for PMMA. It is now known that the chain conformation parameters η and ϵ depend on the type of stereoregular diad. After taking this dependency into account and assigning the parameters η_i and ϵ_i to the meso diad and the parameters, η_s and ϵ_s to the racemic diad, eq 13 can be modified[10] to read

$$C_\infty = \frac{1+\cos\theta}{1-\cos\theta}\frac{(1-\eta^2-\epsilon^2)(1+\epsilon'\epsilon+\eta'\eta)}{(1-\eta)+(\eta-\eta^2-\epsilon^2)(\eta'-\eta'\eta-\epsilon'\epsilon)} \quad (14)$$

where $\eta = P_s\eta_s + (1-P_s)\eta_i$, $\epsilon = P_s\epsilon_s + (1-P_s)\epsilon_i$, $\eta' = P_s\eta_s - (1-P_s)\eta_i$, and $\epsilon' = P_s\epsilon_s - (1-P_s)\epsilon_i$. For PMMA, the best fit of the data was obtained with $\eta_i = 0.72$, $\epsilon_i = 0.11$, $\epsilon_s = 0.56$, and $\eta_s = 0.66$ in eq 14; see Figure 4.

A more realistic method has been described by Flory[12] to calculate the unperturbed dimension by using the rotational isomeric scheme and considering the geometry of the pendant group. More recently, Sundararajan[2] and Vacatello and Flory,[1] respectively, extended these calculations to predict the effect of tacticity on the unperturbed dimensions of PMMA with a Bernoulli distribution of stereoregular diads. It is interesting to compare the experimental data with the above predictions. As can be seen from Figure 4, the values of C_∞ obtained by our GPC/[η] method agreed quite well with the predictions of a six-state scheme[1] when the normalized energy parameters are, respectively, $E_\alpha = -0.46$ kcal/mol, $E_{\bar{\alpha}} = -0.77$ kcal/mol, $E_\beta = -3.42$ kcal/mol, $E_\rho = -0.06$ kcal/mol, and $E_{\bar{\rho}} = -2.14$ kcal/mol. It is gratifying that the observed curvature in Figure 4 is in agreement with the theory.

Both theoretical predictions and experimental measurements indicate that the unperturbed dimension of isotactic PMMA, in either solution or solid,[15] is about 30% larger than syndiotactic PMMA. However, the glass transition temperature of isotactic PMMA, which relates to the dynamic flexibility of the polymeric chain, is about 70 °C lower than syndiotactic PMMA. This seems to be inconsistent with the prediction by existing glass temperature theories.[16] This unusual phenomenon may be due in part to the opposite temperature dependence of C_∞ observed for the two types of stereochemistry;[1] e.g., isotactic PMMA has a larger equilibrium chain dimension but a larger negative temperature dependence, while syndiotactic PMMA has a smaller equilibrium chain dimension but a larger positive temperature dependence. The temperature dependence of C_∞ may reflect dynamic flexibility of the polymer and therefore could be more significant for T_g.

Acknowledgment. Financial support from the Selected Research Program of Academia Sinica and the National Natural Science Foundation of China is gratefully acknowledged.

References and Notes

(1) Vacatello, M.; Flory, P. J. *Macromolecules* **1986**, *19*, 405.
(2) Sundararajan, P. R. *Macromolecules* **1986**, *19*, 415.
(3) Jenkins, R.; Porter, R. S. *Adv. Polym. Sci.* **1980**, *36*, 1.
(4) Jenkins, R.; Porter, R. S. *Polymer* **1982**, *23*, 25.
(5) Tsuruta, T. *J. Macromol. Chem.* **1966**, *1*, 31.
(6) Lando, J. B.; Semen, J.; Farmer, B. *Macromolecules* **1970**, *3*, 524.
(7) Bovey, F. A. *J. Polym. Sci.* **1963**, *A1*, 843.
(8) Bovey, F. A. *Polymer Conformation and Configuration*; Academic Press: New York, 1969.
(9) Tung, L. H. *J. Appl. Polym. Sci.* **1966**, *10*, 375.
(10) Lu, X.; Jiang, B. *Acta Polym. Sin. (Chinese)* **1989**, *1*, 25.
(11) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci.* **1963**, *C1*, 137.
(12) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1971.
(13) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.
(14) Birshtein, T. M.; Ptitsyn, O. B. *J. Phys. Chem. U.S.S.R.* **1952**, *26*, 1215.
(15) O'Reilly, J. M.; Teegarden, D. M.; Wignall, G. D. *Macromolecules* **1985**, *18*, 2747.
(16) Privalko, V. P.; Lipatov, Y. S. *J. Macromol. Sci., Phys.* **1973**, *B7* (3), 431.