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Notes

Temperature Dependence of Chain Dimensions for Highly Syndiotactic Poly(methyl methacrylate)

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Introduction

Several rotational isomeric state (RIS) models of varying complexity have been put forth for poly(methyl methacrylate) (PMMA) chains.[1-4] The early two-state model of Sundararajan and Flory[1] considered only g and t conformations, since it was believed that the $\bar{g}$ states could be excluded because of strong steric overlap due to the planar geometry of the ester substituents. Experimental tests of certain predictions of this theory indicated good agreement for syndiotactic PMMA, but not for isotactic PMMA;[5] the incorporation of additional gauche states was suggested.[6] More recently, a three-state[4] and a six-state[3] RIS model have appeared. The purpose of the present paper is to generate reliable experimental data for unperturbed chain dimensions and their temperature dependence for highly syndiotactic PMMAs and to utilize these experimental findings to test recent theories.[3,4]

Experimental Section

Some PMMA samples were obtained as "standard polymers" from Polymer Laboratories and Pressure Chemical Co. These polymers were produced by controlled anionic polymerization. Others were prepared in our laboratories via solvent/nonsolvent (toluene/methanol-water) fractionation of free-radically produced PMMA. These latter polymerizations were conducted using azobisisobutyronitrile (AIBN) as initiator and benzene as solvent at 50 °C. Conversions were limited to <60% to avoid branching.

Tacticity of the polymers was examined by both ^{1}H NMR and ^{13}C NMR spectroscopies. In the former analysis the peaks corresponding to the α-methyl protons were used, while the latter analysis was based on intensities of the carbonyl regions.[7] The syndiotactic diad content was identical for the anionically and free-radically produced materials (78 (±2)% syndiotactic).

Polydispersities were examined by size exclusion chromatography (SEC). Tetrahydrofuran was utilized as the mobile phase; details of SEC analyses in our laboratories have been presented earlier.[8] Refractive index increments (dn/dc) were measured in dry, distilled 2-butanone at 25 °C with the Chromatix KMX-16 refractometer (wavelength, $\lambda = 633$ nm). Average dn/dc values of 0.110 and 0.114 were obtained for the anionically and free radically produced polymers, respectively. The KMX-6 photometer was used for light scattering determinations of weight-average molecular weight (M_w) under the same conditions. Details of such experiments in our laboratories have previously appeared.[8]

Intrinsic viscosities $[\eta]$ and Huggins coefficients (k_H) were determined by use of conventional Ubbelohde dilution viscometers having negligible kinetic energy corrections. Temperature was controlled to ±0.02 °C by using a water bath with a Fisher Scientific heater/circulator. The measurements at 10 °C involved, in addition, the use of an external Fisher Scientific refrigerator/circulator. The ketones used in these measurements (2-hexanone, 4-heptanone, and 3-octanone) were obtained from Aldrich, analyzed by gas chromatography (>99.5%), and used as received. Solutions giving relative viscosities of 1.1–1.6 were employed; results obtained over this concentration range gave strictly linear Huggins plots. $[\eta]$ values are estimated to be accurate to ±2%.

Results and Discussion

Molecular weights and polydispersities of the PMMA samples are presented in Table I. As expected, the anionically produced polymers exhibit extremely narrow molecular weight distributions. The fractionated polymers also exhibit narrow, symmetrical distributions.

$[\eta]$ and k_H values are summarized in Table II. The θ temperatures of 72 and 33.8 °C for 3-octanone and 4-heptanone, respectively, are those reported previously by Fox.[9] We suspected that 2-hexanone might also serve as a θ solvent at some lower temperature. Cloud point measurements indicated a θ temperature less than 0 °C; we chose to operate at 10 °C due to convenience in thermal control and to avoid contamination of solutions by moisture condensation at lower temperatures.

Mark–Houwink–Sakurada (MHS) parameters are presented in Table III. The exponents confirm that 3-octanone and 4-heptanone are near-θ solvents at the respective measurement temperatures. As expected, on the basis of cloud points, 2-hexanone is a moderate solvent for syndiotactic PMMA at 10 °C.

Unperturbed dimensions may be reliably determined from the viscosity data of Table II by using the Burchard–Stockmayer–Fixman (BSF) procedure.[10,11] BSF plots in the two near-θ solvents are strictly linear; deviation from linearity is noted at very high molecular weights for the data obtained in 2-hexanone. The breakdown of the two-parameter theory at large excluded volumes is well-documented.[12] Derived values of K_θ are presented in Table III. No polydispersity corrections were applied due to the narrow distributions of the PMMA samples. From the K_θ values Flory's[13,14] characteristic ratio, C_∞, defined as

$$C_\infty = \lim_{n\to\infty} \langle r^2\rangle_0/nl^2 \tag{1}$$

where $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance, n is the number of main-chain bonds, and l is the average main-chain bond length, may be calculated. The necessary $\langle r^2\rangle_0$ values are obtained from the Fox–Flory[15] equation.

$$K_\theta = \Phi_0\,(\langle r^2\rangle_0/M)^{3/2} \tag{2}$$

where Φ_0 appears to be a universal hydrodynamic constant for linear, flexible, unperturbed coils ($\Phi_0 = 2.5 \times 10^{21}$ [16,17]) and M is molecular weight. C_∞ values of 7.80, 7.30, and 7.07 were obtained at 72, 33.8, and 10 °C, respectively.

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Table I
Molecular Weights and Polydispersities of PMMA Samples

$10^{-4}M_w$	M_w/M_n	M_z/M_w	$10^{-4}M_w$	M_w/M_n	M_z/M_w
162[a]	1.13	1.12	23.3[b]	1.24	1.25
80.1[a]	1.10	1.09	18.6[b]	1.18	1.17
47.3[a]	1.06	1.07	13.8[b]	1.22	1.16
46.9[b]	1.34	1.29	8.57[b]	1.17	1.14
34.5[a]	1.07	1.08			

[a] Products of anionic polymerization. [b] Products of free-radical polymerization.

Table II
Intrinsic Viscosities[a] and Huggins Coefficients of PMMA Samples

	3-octanone, 72 °C		4-heptanone, 33.8 °C		2-hexanone, 10 °C	
$10^{-4}M_w$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
162	0.649	2.62	0.615	1.43	1.03	0.88
80.1	0.480	2.14	0.430	1.31	0.686	0.82
47.3	0.368	1.98	0.350	1.21	0.497	0.80
46.9	0.355	1.80	0.327	1.22	0.467	0.82
34.5	0.312	1.98	0.295	1.04		
23.3	0.256	1.54	0.236	1.21	0.319	0.76
18.6	0.233	1.19	0.210	1.24	0.264	0.85
13.8	0.202	1.09	0.180	1.23	0.223	0.79
8.57	0.160	1.17	0.148	1.05	0.164	0.97

[a] In deciliters per gram.

Table III
MHS Parameters[a] and Unperturbed Dimensions for Syndiotactic PMMA

solvent	temp, °C	10^4K, dL g^{-1}	a	10^4K_θ,[b] dL g^{-1} mol$^{-3/2}$	C_∞
3-octanone	72	6.85	0.480	5.52	7.80
4-heptanone	33.8	5.53	0.491	5.00	7.30
2-hexanone	10	1.32	0.628	4.76	7.07

[a] K and a are the MHS parameters obtained from linear regression fits of the data of Table II (corr coeff ≥0.999). [b] Obtained via the BSF extrapolation.[10,11]

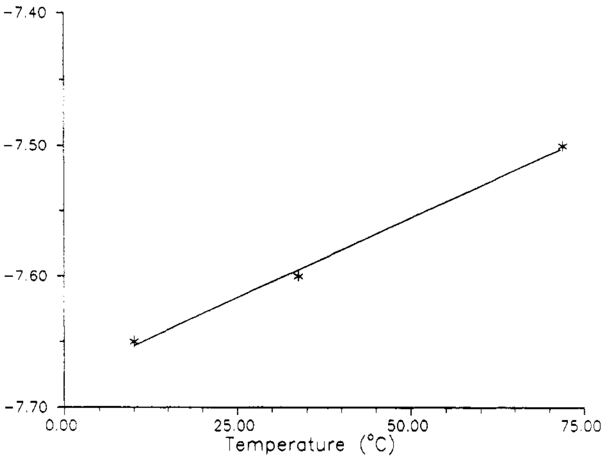

Figure 1. Plot of ln K_θ as a function of temperature for highly syndiotactic PMMA in a family of ketone θ solvents.

The temperature coefficient of chain dimensions d ln $\langle r^2\rangle_0/\mathrm{d}T$ may also be derived from the data of Table III as

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = {}^2/_3\,\mathrm{d}\ln K_\theta/\mathrm{d}T \qquad (3)$$

Excellent linearity is observed in the plot of ln K_θ versus T (Figure 1); d ln $\langle r^2\rangle_0/\mathrm{d}T$ = 1.61 (±0.2) × 10^{-3} K^{-1} is obtained.

The chain dimensions presented above may be compared with results from prior experimental studies of predominantly syndiotactic PMMA.[9,18-22] C_∞ values ranging from ca. 7 to ca. 8.4 were reported in the vicinity of room temperature, in general agreement with our value of 7.3 at 33.8 °C. Unfortunately, in most instances, precise information on stereochemistry of these "syndiotactic" PMMAs is lacking. In addition, failure to correct for deviations from the actual θ state also probably contributes to the rather large scatter in literature values of C_∞.

Prior experimental values of d ln $\langle r^2\rangle_0/\mathrm{d}T$ range from 0 to 4.0 × 10^{-3} K^{-1}.[9,19-21,23] The very large scatter in earlier experimental values of this parameter prompted the current study. Accurate evaluation of d ln $\langle r^2\rangle_0/\mathrm{d}T$ from dilute solution data requires that specific solvent effects be minimized and deviations from actual θ conditions be taken into account (24). The use of a family of chemically similar θ solvents in the present work should eliminate the influence of a specific solvent effect on d ln $\langle r^2\rangle_0/\mathrm{d}T$; the BSF correction adjusts for deviations from θ conditions. Furthermore, the accurate determination of the temperature coefficient is facilitated by measuring $[\eta]$ in the different θ solvents for the *same* polymer samples. Application of the BSF method to these data cancels out the errors in M_w determination in the evaluation of d ln $\langle r^2\rangle_0/\mathrm{d}T$, as previously discussed.[24]

The present data may be compared with predictions of recent RIS models.[3,4] The six-state model of Vacatello and Flory[3,25] overestimates C_∞ slightly, with a predicted value of 8.5 at 300 K for an 80% syndiotactic polymer, compared to C_∞ = 7.3 (±0.4) at 307 K in the present work. This model does, however, predict a temperature coefficient of 2 × 10^{-3} K^{-1} for syndiotactic PMMA, in accord with experiment.

The three-state scheme of Sundararajan[4] predicts $C_\infty \simeq 7.0$ for syndiotactic PMMA, in good accord with the present findings, when values of 1.0, −1.0, and 1.5 kcal/mol are assigned to statistical weight parameters E_α, E_β, and E_ρ, respectively. No prediction for the temperature coefficient is made by using these parameters. Such calculations, if available, would provide a more rigorous test of the three-state RIS model for PMMA.

In summary, the present experimental data allow, to a limited extent, the evaluation of the validity of RIS models for PMMA conformational statistics. In future work, we plan to measure unperturbed dimensions and their temperature variation for PMMA samples of varying tacticity. These data will allow a more complete comparison of theory and experiment to be carried out.

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(25) See Table VI of ref 3 for the pertinent energy parameters for the six-state scheme.

Registry No. PMMA, 9011-14-7; $CH_3CO(CH_2)_4H$, 591-78-6; $CH_3(CH_2)_2CO(CH_2)_3H$, 123-19-3; $CH_3CH_2CO(CH_2)_5H$, 106-68-3.