Second Virial Coefficients and Radii of Gyration for Poly(α-methylstyrene) in Cyclohexane below the Θ Temperature

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ABSTRACT: Classical and low-angle laser light-scattering experiments were performed to measure the second virial coefficient, A_2, and radius of gyration, R_g, of linear poly(α-methylstyrene) (PαMS) in the poor solvent cyclohexane. The molecular weights, M_w, of the polymers used cover the range of 60 000−3 500 000, and all samples have narrow molecular weight distributions. The experimental temperatures are controlled down to about 16 °C below the Θ temperature (36.2 °C). At this temperature, the scaling exponent of R_g with M_w is 0.414; this appears to be the lowest exponent ever reported for linear chains of synthetic polymers in solution. A strong molecular weight dependence of the measured A_2 values for this PαMS/cyclohexane system is observed. These results are compared with the predictions of available theories and with other experimental results.

Introduction

Sparked by a theoretical paper by Stockmayer,[1] there has been considerable interest over the past 25 years, on the part of both theorists and experimentalists, in the "coil−globule" transition of polymer chains in poor solvents.[2] Besides contributing to our general understanding of polymer physics, such studies also constitute a fundamental step toward understanding the nature of and basis for protein folding.[3]

Most of the experimental work on synthetic polymers in poor solvents has involved polystyrene (PS). However, in recent years several studies of the poly(α-methylstyrene) (PαMS)/cyclohexane system have appeared.[4−7] Like PS, PαMS samples which encompass a broad range of molecular weights and exhibit very narrow molecular weight distributions can be obtained. An additional advantage of the PαMS/cyclohexane system, as first noted by Selser,[4] is that this system allows studies to be conducted on high molecular weight samples further below the Θ temperature than is possible with PS/cyclohexane. For example, it was found via light scattering that a PαMS sample of M_w = 976 000 showed no tendency for phase separation in cyclohexane at 26 °C (ca. 10 °C below the Θ temperature) over the concentration range from 6.6×10^{-4} to 2.21×10^{-3} g/mL.[4] It was noted by Selser that this "noncollapse" behavior of PαMS was similar to that previously observed for poly(*p*-chlorostyrene) in *n*-propylbenzene.[8,9] Thus, substantially different sub-Θ behavior has been observed for different polymer−solvent systems.

In this paper, we report the results of some static light-scattering experiments conducted on the PαMS samples in cyclohexane at temperatures down to about 16 °C below the Θ temperature (36.2 °C). From the R_g results of the present measurements, we extend the study of sub-Θ behavior of PαMS to much greater values of $\tau M^{1/2}$, where τ is the reduced temperature ($\tau = (T - \Theta)/\Theta$) and M is the molecular weight of polymer, than that reported previously.[6,7] The results obtained are compared with other experimental findings and with theoretical predictions.

Experimental Section

Poly(α-methylstyrene) standards, prepared by anionic polymerization, were obtained from Polymer Laboratories and Pressure Chemical Co. The highest molecular weight polymer, JL-4, was made in our laboratory by anionic polymerization in tetrahydrofuran (THF) at −78 °C using high-vacuum techniques[10] with *sec*-butyllithium as initiator. The tacticity of anionically produced PαMS has been reported by Cotts and Selser[6] as 53% syndiotactic, 41% heterotactic, and 5% isotactic triads.

Because these PαMS standards have been repeatedly characterized in our laboratory by a combination of low-angle laser light scattering (LALLS), membrane osmometry, and size-exclusion chromatography (SEC), the molecular weights and polydispersities of these PαMSs are well known. Detailed characterization procedures have been previously reported.[11]

The solvent used in the present work was HPLC grade cyclohexane (Aldrich; 99.9+% by gas chromatography). Literature values[12] for the physical constants of the solvent were employed, with the refractive index and density values of 1.4262 and 0.7786 g/mL at 20 °C and of 1.4235 and 0.7739 g/mL at 25 °C, respectively. The values of refractive index and density at other temperatures were obtained through extrapolation or interpolation. Light-scattering measurements on the PαMS/cyclohexane system were conducted using a Chromatix KMX-6 unit (modified to allow control of temperature to ±0.1 °C) with a 2 mW vertically polarized He−Ne laser source operating at 633 nm or with a Brookhaven 200SM goniometer with an Ar^+ laser operating at 488 nm over an angular range of 30−150°. For most light-scattering measurements, a custom-designed, temperature-controlled closed loop filtration system was employed for sample clarification. Details of this clarification system have been reported previously.[13] Concentration ranges in which light-scattering measurements could be conducted without encountering phase separation were established in the earlier photon correlation spectroscopy work with the PαMS/cyclohexane system.[7] The refractive index increment d*n*/d*c* was measured as a function of temperature and wavelength using an Otsuka Electronics DRM-1020 double-beam differential refractometer.

A BI-ZP4.0 Zimm Plot software program, purchased from Brookhaven Instrument Corp., was utilized to analyze light-scattering results. Toluene was used as the calibration standard with its Rayleigh ratio (R_0) taken as 39.6×10^{-6} cm^{-1} at 488 nm and 25 °C.[14] Rayleigh ratios of toluene at temperatures other than 25 °C were obtained through the following equation:[15]

$$R_0{}^t/R_0{}^{25} = (I_t/I_{25})(n_t/n_{25}) \qquad (1)$$

where I is the scattering intensity, n is the refractive index, and t and 25 denote the temperature (°C). Thus, by measuring

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Table 1. Molecular Characteristics of PαMS Samples

samples	$M_w \times 10^{-4}$ [a]	$M_n \times 10^{-4}$ [b]	M_w/M_n [c]	M_z/M_w [c]
PL-55	5.90	5.38	1.13	1.11
PC-4	11.8	11.5	1.03	1.03
PL-155	17.7	16.6	1.05	1.05
PC-6	30.5	28.9	1.07	1.06
PL-285	31.3	31.0	1.04	1.03
PC-10	51.5	48.6	1.06	1.06
PC-17	66.5	59.4	1.09	1.06
PL-770	90.3		1.05	1.04
PC-16	114		1.11	1.08
PL-1250	140		1.09	1.08
JM-6	310		1.10	1.09
JL-4	341		1.15	1.17

[a] Via LALLS. [b] Via membrane osmometry. [c] Via SEC.

Table 2. d*n*/d*c* of PαMS in Cyclohexane at Different Temperatures and Wavelengths

temperature (°C)	wavelength (nm)	
	633	488
24	0.1830	0.1853
30	0.1835	0.1881
36.2	0.1852	0.1911

Table 3. Radius of Gyration (nm) of PαMS Samples below Θ Temperature

	temperature (°C)					
$M_w \times 10^{-4}$	36.2	28	24	22	20	16
66.5	22.7		20.0			
90.3	26.4	23.5	21.7		19.1	
114	29.6	26.1	23.8		21.0	
140	32.6	28.8	27.1		23.5	21.9
310	48.8		38.6	34.9	31.9	
341	51.3		40.7	36.4	33.3	

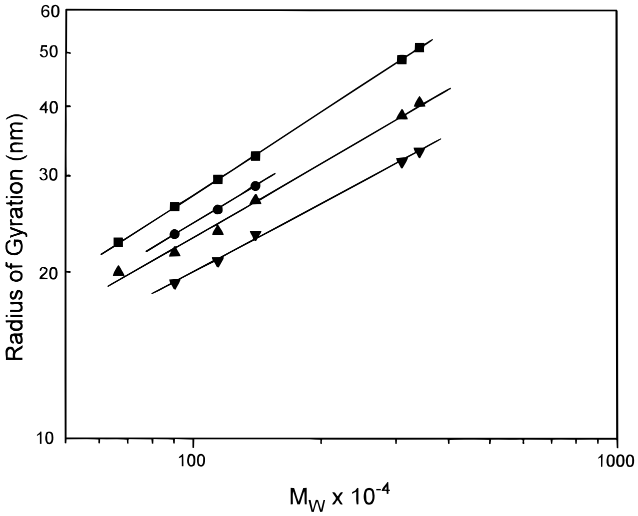

Figure 1. Plot of radii of gyration versus molecular weight for PαMS in cyclohexane at temperatures below the Θ temperature: (■) 36.2 °C, (●) 28 °C, (▲) 24 °C, and (▼) 20 °C.

Table 4. Hydrodynamic Factors Φ[a] and ρ of PαMS Samples

	36.2 °C		28 °C		24 °C	20 °C	
$M_w \times 10^{-4}$	Φ	ρ	Φ	ρ	Φ	Φ	ρ
30.5	2.40	1.31					
66.5	2.32	1.31					
90.3	2.33	1.31	2.60	1.41	3.01	3.79	1.22
114	2.35	1.31	2.70	1.36	3.22	4.19	1.27
140	2.39	1.30	2.72	1.40	2.87	3.93	1.25
310	2.35	1.31			3.04	4.67	1.21
341	2.35	1.30			2.96	4.86	1.23

[a] Φ in units of 10^{23} mol^{-1}.

the scattering light intensities at respective temperatures, we were able to obtain the Rayleigh ratios of toluene at 30 and 36.2 °C as 40.6×10^{-6} and 41.1×10^{-6} cm^{-1}, respectively. Rayleigh ratios of toluene at other temperatures were obtained through extrapolation.

Results and Discussion

Molecular weights and polydispersity values are presented in Table 1. It can be seen from these data that samples covering a broad range of molecular weights and exhibiting narrow and symmetrical molecular weight distributions were used.

The d*n*/d*c* values obtained for PαMS in cyclohexane at 488 and 633 nm are listed in Table 2. The d*n*/d*c* values at other temperatures are obtained through extrapolation at the respective wavelength.

Radii of gyration, R_g(nm), values are tabulated in Table 3 and shown in Figure 1. These data lead to the following power law relationships:

$$36.2\ °\mathrm{C},\ R_g = 2.82 \times 10^{-2} M_w^{0.499} \tag{2}$$

$$28\ °\mathrm{C},\ R_g = 4.08 \times 10^{-2} M_w^{0.463} \tag{3}$$

$$24\ °\mathrm{C},\ R_g = 4.65 \times 10^{-2} M_w^{0.450} \tag{4}$$

$$20\ °\mathrm{C},\ R_g = 6.54 \times 10^{-2} M_w^{0.414} \tag{5}$$

It is believed that the exponent in eq 5 is the lowest yet reported for a linear synthetic polymer in solution; however, this exponent is much larger than the value of $^1/_3$ which is predicted for globular particles by theory[16] and observed experimentally for globular proteins.[17] Further evidence that a globular state is not approached for the PαMS/cyclohexane system is seen on examining Table 4, which contains the hydrodynamic factors Φ $(=[\eta]M/(6\langle S^2\rangle)^{3/2})$ and ρ $(=\langle S^2\rangle^{1/2}R_H)$ derived by combining the R_g values of Table 3 with previously reported[7] results for intrinsic viscosity, $[\eta]$, and hydrodynamic radius, R_H. The Φ and ρ values of 2.4×10^{23} mol^{-1} and 1.31, respectively, measured at 36.2 °C are typical of values reported for other flexible chains at the Θ temperature. For globular particles, it is predicted[18] that $\rho = 0.775$ and $\Phi = 9.23 \times 10^{23}$ mol^{-1}. Although we observed tendencies toward these values as the temperature is lowered below Θ, even at 20 °C we clearly have not reached the globular state based on this analysis. However, Figure 2 reveals that the constant $K_\eta = ([\eta]M/\Pi N_A R_g^2 R_H)$, where N_A is Avogadro's number, increases systematically (linearly with $\tau M^{1/2}$) from its value for flexible coils to a value near 5, which is anticipated for spherical objects, as temperature is decreased. This trend may reflect the expected collapse of the chain toward the spherical conformation.[19]

The contraction behavior of PαMS based entirely on the R_g results is presented in Figure 3. In this experiment, we were able to extend the $|\tau|M^{1/2}$ values to over 100, which is larger than that previously reported using hydrodynamic measurements.[7] The leveling off is seen at $\alpha_g^3|\tau|M^{1/2}$ values of about 28 ± 3 g$^{-1/2}$ mol$^{1/2}$, corresponding to a $|\tau|M^{1/2}$ value of about 60 g$^{-1/2}$ mol$^{1/2}$ or greater. It is interesting to note that a maximum value appears to be reached around a $|\tau|M^{1/2}$ value of 70, and then $\alpha_g^3|\tau|M^{1/2}$ gradually decreases. Such behavior was not detected in our previous hydrodynamic measurements.[7] It cannot be entirely ruled out that this maximum may be due to the experimental errors, which are larger in such experiments. More experimental

Table 5. M_w and A_2[a] Measured at Three Different Temperatures

	20 °C		24 °C		30 °C	
sample	$M_w \times 10^{-4}$	$-A_2 \times 10^5$	$M_w \times 10^{-4}$	$-A_2 \times 10^5$	$M_w \times 10^{-4}$	$-A_2 \times 10^5$
PL-55	6.00	6.11	6.10	1.65		
PL-155	18.0	9.18	17.6	3.89	17.9	1.41
PL-285	31.3	14.6	31.4	6.01	33.2	2.65
PC-10			47.5	8.10	48.9	3.39
PC-17			67.0	10.1	67.4	4.32
PL-770			88.2	12.0	88.2	5.74
PC-16			102	14.3	108	7.31

[a] In units of mol mL/g^2.

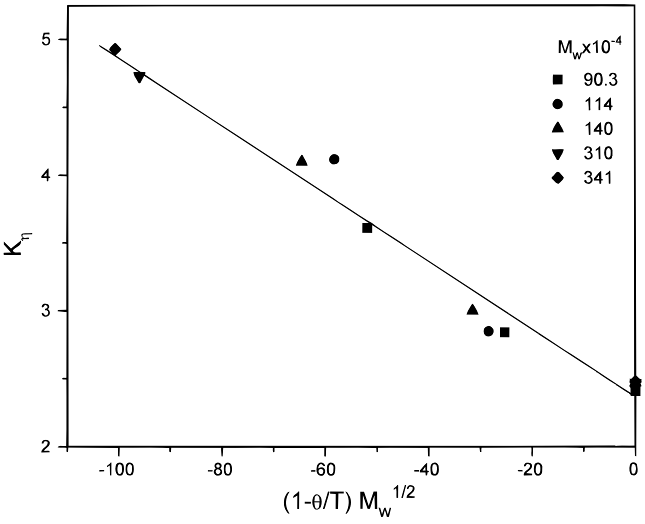

Figure 2. Plot of K_η versus $\tau M_w^{1/2}$.

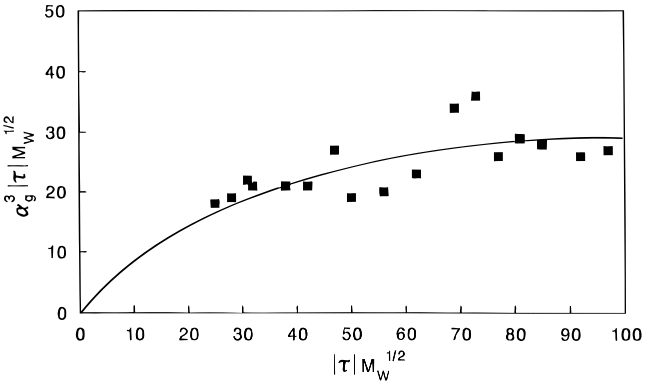

Figure 3. Master curve of expansion factors of radius of gyration of PαMS in cyclohexane.

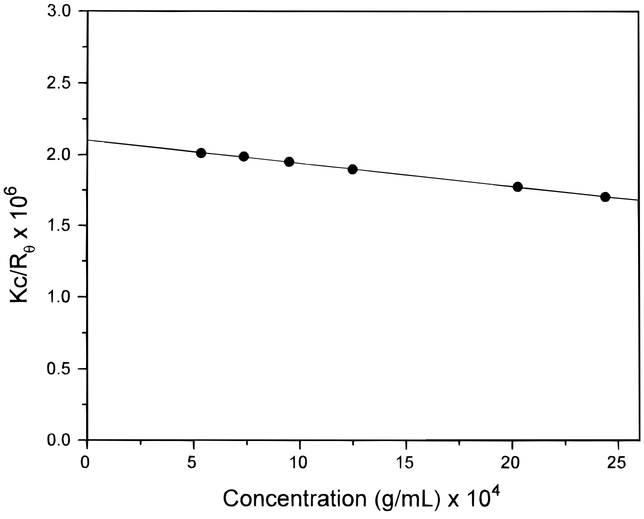

Figure 4. Plot of KMX-6 LALLS data for PαMS 475K.

work is required to resolve this issue, but it should be noted that Grosberg and Kuznetsov[20,21] recently have predicted such behavior through their single-chain collapse theory.

Values of second virial coefficients measured at three temperatures below Θ are presented in Table 5. These data were generated using the Chromatix light-scattering unit because its design allowed scattering intensities to be reliably measured at lower concentrations than were possible with the Brookhaven unit. Results for A_2 (mol mL/g^2) obtained in our laboratory for a few samples using either Brookhaven or Sofica units are also in agreement with the data given in Table 5. Strictly linear concentration dependencies were observed in the LALLS experiments implying an absence of aggregation (see Figure 4 as an example). Furthermore, the molecular weights measured under sub-Θ conditions (Table 5) are in agreement with values measured previously for the same samples in good solvents.[22,23] Very strong molecular weight dependencies are observed at each temperature below Θ for the PαMS/cyclohexane system as follows:

$$30\ °\text{C},\ -A_2 = 5.5 \times 10^{-10} M_w^{\ 0.84} \qquad (6)$$

$$24\ °\text{C},\ -A_2 = 6.0 \times 10^{-9} M_w^{\ 0.72} \qquad (7)$$

$$20\ °\text{C},\ -A_2 = 2.4 \times 10^{-7} M_w^{\ 0.50} \qquad (8)$$

We believe the exponent in eq 8 may be somewhat in error because of the limited range of molecular weights which could be investigated at this temperature due to solubility problems with higher molecular weight samples. These data are in contrast to the finding by Tong et al. and Perzynski et al. for PS in cyclohexane below Θ,[24] where A_2 was found to be independent of M_w. We have confirmed the finding that A_2 is approximately independent of molecular weight for the high molecular weight PS/cyclohexane system below the Θ temperature recently in our laboratory.[25] In addition, Yamakawa and co-workers have published similar observations.[26] Thus PαMS and PS clearly exhibit different sub-Θ A_2 behavior in cyclohexane. It is interesting to note in this regard that Wolf and Adam observed strong molecular weight dependence of A_2 on M_w for PS in *tert*-butyl acetate both below the upper critical solution temperature (UCST) and above the lower critical solution temperature (LCST).[27] In addition, they observed the overall magnitude of A_2 to increase with M_w above the LCST but to decrease with M_w below the UCST. We observe the former molecular weight dependence in this work, but for a system involving the UCST. Suitable theories accounting for the complex behavior of A_2 below Θ are not available for comparison. Recently, Ya-

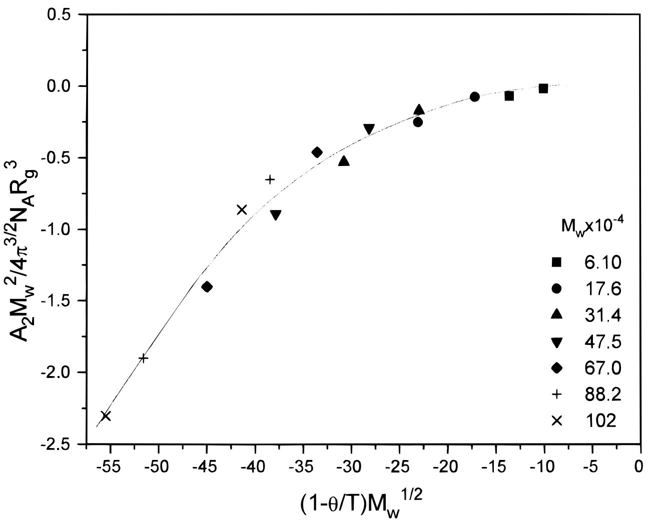

Figure 5. Plot based on the two-parameter theory involving both A_2 and R_g for various PαMS samples as a function of $\tau M_w^{1/2}$.

makawa has proposed a model that takes into account chain end effects to explain the very weak molecular weight dependence of A_2 for PS/cyclohexane under sub-Θ conditions.[28] However, the strong molecular weight dependence of the present PαMS/cyclohexane system still awaits theoretical explanation. Obviously the chemical structure difference between PS and PαMS segments plays a major role in the difference of the A_2–M_w relationship between the two systems. Unfortunately current molecular theories neglect the detailed chemical structures of polymer chains. Thus, a revision of theories needs to be done to incorporate the local characteristics of polymer chains into the global property treatment.

In Figure 5 we present a plot based upon the two-parameter theory for the various PαMS samples as a function of reduced temperature. This plot clearly shows that A_2M/R_g^3 is a single-valued function of $(1 - \Theta/T)M^{1/2}$, as expected from the two-parameter theory.[29] The scatter is surprisingly small given the cumulative errors in plots of this type, especially for experiments done under sub-Θ conditions.

In conclusion, we observed considerable contraction of PαMS coils below the Θ temperature. However, the globular state is not approached based on consideration of the scaling exponents of R_g with M_w and on comparison of measured hydrodynamic parameters, ρ and Φ, with values predicted by theory. An asymptotic region is observed in the plot of $\alpha_g^3|\tau|M^{1/2}$ versus $|\tau|M^{1/2}$ with a possible maximum value. These results are consistent with the interpretation of Grosberg and Kuznetsov[20,21] that true equilibrium single-chain collapse has not yet been observed for typical flexible polymer chains. Furthermore, a strong dependence of A_2 on both temperature and M_w is observed for the PαMS/cyclohexane system.

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