Sub-Θ Hydrodynamic Behavior of Poly(α-methylstyrene) in Cyclohexane

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ABSTRACT: The hydrodynamic properties of poly(α-methylstyrene) (PαMS) in cyclohexane from 16 °C below the Θ temperature to 10 °C above Θ have been investigated by dilute-solution viscometry and photon correlation spectroscopy. Seven near-monodisperse samples covering the range $5.9 \times 10^4 \leq \bar{M}_w \leq 3.41 \times 10^6$ were used. These data have been analyzed with regard to chain contraction below Θ (the so-called "coil–globule" transition). No evidence for the existence of a globular state was found. It is found that the temperature dependencies of chain contraction parameters, based on the intrinsic viscosity $[\eta]$ and the hydrodynamic radius R_H, can be expressed in terms of master curves of $\alpha^3|\tau|M^{1/2}$ versus $|\tau|M^{1/2}$, where α is the chain expansion or contraction factor (from $[\eta]$ or R_H), τ is the reduced temperature ($\tau \equiv (T-\Theta)/\Theta$), and M is molecular weight. An asymptotic region (plateau), generally associated with the collapsed state, is reached with the R_H data and approached with the $[\eta]$ data. Attainment of the plateau occurs at higher values of $\alpha_\eta^3|\tau|M^{1/2}$ than for $\alpha_H^3|\tau|M^{1/2}$, where α_η and α_H are, respectively, $[\eta]$- and R_H-based contraction factors. For polystyrene the reverse order has been observed. These results suggest a strong dependence of polymer contraction on chemical structure.

Introduction

Although the properties of macromolecules in both good ($A_2 \gg 0$, where A_2 is the osmotic second virial coefficient) and Θ ($A_2 = 0$) solvents have received vast attention, chain behavior in poor solvents ($A_2 < 0$) has received little attention for many years. Recent theoretical developments[1-7] dealing with the "coil-to-globule" transition have, however, led to a number of experimental studies[8-24] of this problem. The vast majority of these studies[8-23] have dealt with polystyrene (PS), which has the advantage of being readily available in near-monodisperse form over an extremely broad range of molecular weights.

In this work, we report the results of hydrodynamic measurements on dilute solutions of poly(α-methylstyrene) (PαMS) in cyclohexane below the Θ temperature. Like PS, PαMS chains of very high molecular weight and low polydispersity can be prepared. In addition, PαMS is known[25] to exhibit a negligible dependence of unperturbed dimensions on temperature, whereas PS exhibits larger unperturbed chain dimensions as the temperature is decreased.[26] In addition, it has been noted[25,27] that PαMS remains in solution at moderate concentrations ($c \simeq 10^{-3}$ g mL^{-1}) for high molecular weights well below the Θ temperature. For example, Selser[27] found via light scattering that a PαMS sample of $\bar{M}_w$ = 976 000 showed no signs of aggregation in cyclohexane at 26 °C (ca. 10 °C below Θ) over the concentration range of 6.6×10^{-4} to 2.21×10^{-3} g mL^{-1}. It was pointed out by Selser[27] that the "noncollapse" of PαMS was similar to that observed for poly(*p*-chlorostyrene) in *n*-propylbenzene.[28,29] Thus, different polymer–solvent systems appear to exhibit substantially different sub-Θ behavior.

Recently, results of a photon correlation spectroscopy (PCS) and low-angle, time-averaged light-scattering study of the PαMS–cyclohexane system, including measurements below Θ, have appeared.[30] In the present paper, we report the results of both PCS and intrinsic viscosity experiments conducted below Θ for this same system. The present measurements extend the study of the sub-Θ behavior of PαMS to much greater values of $|\tau|M^{1/2}$, where τ is the reduced temperature ($\tau \equiv (T-\Theta)/\Theta$) and M is the molecular weight, than that reported previously.[30] These results permit a comparison of the sub-Θ contraction of PαMS with that of PS.

Table I
Molecular Characteristics of PαMS Samples

sample	$\bar{M}_w \times 10^{-4}$ [a]	$\bar{M}_n \times 10^{-4}$ [b]	$\bar{M}_w/\bar{M}_n$ [c]	$\bar{M}_z/\bar{M}_w$ [c]
PL-55	5.90	5.38	1.13	1.11
PC-4	11.8	11.5	1.03	1.03
PC-6	30.5	28.9	1.07	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
JL-4	341		1.15	1.17

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

Experimental Section

PαMS standards, prepared by anionic polymerization, were obtained from Polymer Laboratories and Pressure Chemical Co. The highest molecular weight polymer, JL-4, was prepared at the University of Alabama at Birmingham by polymerization in tetrahydrofuran (THF) at −78 °C using high-vacuum techniques[31] with *sec*-butyllithium as initiator. The tacticity of anionically produced PαMS has recently been reported by Cotts and Selser[30] as 53% syndiotactic, 41% heterotactic, and 5% isotactic triads.

Molecular weights and polydispersities were determined by a combination of low-angle laser light scattering (LALLS), membrane osmometry, and size-exclusion chromatography (SEC). Experimental details have been previously reported.[25]

The solvent used in the present work was HPLC grade cyclohexane (Aldrich, 99.9+% by gas chromatography). Literature values[32] for the physical properties of this solvent were employed. Intrinsic viscosities $[\eta]$ and Huggins coefficients k_H were determined via extrapolation of data obtained for several concentrations to infinite dilution using the Huggins equation. In most cases, flow times were manually measured to ±0.1 s. The temperature in these experiments was controlled to within ±0.02 °C of the desired temperature using a water bath. Solutions and

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Table II
Intrinsic Viscosities[a] and Huggins Coefficients for PαMS in Cyclohexane

		T = 46 °C		T = 39 °C		T = 36 °C		T = 32 °C		T = 28 °C		T = 24 °C		T = 20 °C	
sample	$\bar{M}_w \times 10^{-4}$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
PL-55	5.90			0.177	0.78	0.176	0.81	0.174	0.88	0.168	1.1	0.164	1.1	0.158	1.5
PC-4	11.8	0.265	0.70	0.253	0.77	0.250	0.76	0.243	0.74	0.235	0.88	0.222	0.94	0.206	1.3
PC-6	30.5	0.440	0.73	0.409	0.78	0.404	0.75	0.379	0.91	0.360	0.95	0.328	1.3	0.298	1.8
PC-17	66.5	0.682	0.63	0.607	0.79	0.591	0.83	0.549	0.88	0.494	1.1	0.439	1.3	0.40	
PL-770	90.3	0.792	0.62			0.695	0.74	0.624	0.86	0.549	1.0	0.50		0.43	
PC-16	114	0.896	0.61			0.761	0.76	0.688	0.86	0.620	1.0	0.56		0.50	

sample	$\bar{M}_w \times 10^{-4}$	T/°C	$[\eta]$
JL-4	341	25	0.85

[a] Units: dL g^{-1}.

solvents were filtered directly into Ubbelohde viscometers through 1.0-μm (nominal pore size) Gelman Acrodisc CR filters; concentrations were chosen to give relative viscosities between about 1.1 and about 1.4.

For the highest molecular weight samples at the lowest temperatures, the Schott-Gerate AVS/G automated viscometer was employed. Concentrations used with this unit were at least 1 order of magnitude lower than those used in the manual measurements and were as low as 1.2×10^{-5} g mL^{-1} for sample JL-4 ($\bar{M}_w = 3.41 \times 10^6$) at 25 °C. Measurements were possible at these reduced concentrations because of the greater precision of measurements (±0.01 s) with the Schott unit. This improved reproducibility is due to the automatic timing and superior thermal control (better than ±0.01 °C) of this unit. Extrapolations to infinite dilution were not necessary because of the extremely low concentrations that were used.

PCS experiments were conducted using a custom-built goniometer,[33,34] a Jodon Model HN-50 helium–neon laser, and a Brookhaven Instruments Co. BI-2030 AT correlator. Measurements were confined to scattering angles of 20° and 25°. Solution clarification was accomplished using a closed-loop filtration system.[34] Gelman Acrodisc CR filters of 0.2- and 0.45-μm nominal pore sizes were used. The closed-loop system is especially applicable to measurements in poor solvents. Initially, a measured volume of solvent is continuously filtered until a constant intensity is observed at the detector output. Modest additions of a known volume of stock polymer solution allow the concentration dependence of D_{app}, the apparent z-average diffusion coefficient, to be measured from lowest to highest concentrations. The onset of any aggregation would be detected by a marked increase in photon count rate accompanied by a sharp decrease in D_{app}. Temperature control was ±0.1 °C.

Intensity correlation functions were converted to electrical correlation functions, which were then analyzed by the method of cumulants[35] to second order. Values of the normalized second moment Q were, with the exception of sample JL-4, always less than 0.1 and thus substantiate the lack of aggregation. Somewhat larger second-moment values of ca. 0.3 were observed for sample JL-4 at 25 °C. This result is probably attributable to the extremely low concentration (4.8×10^{-6} g mL^{-1}) used for this sample. Such a low concentration resulted in a poorer signal-to-noise ratio, but appreciably higher concentrations resulted in aggregation and phase separation. It should also be mentioned that the value of Q will increase with increasing polydispersity (Table I). Pusey[36] has shown that

$$Q + 1 = \bar{M}_w/\bar{M}_v \quad (1)$$

where $\bar{M}_v$ is the viscosity-average molecular weight. While an increase in Q is observed, this increase exceeds that based on eq 1. In what follows, the PCS results for the JL-4 sample comprise only one data point. Consequently, the Q value, although somewhat large for this sample, does not impact the conclusions of this work.

Results and Discussion

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

Table III
MHS Parameters for PαMS in Cyclohexane

T/°C	$K \times 10^4$ [a]/(dL g$^{-3/2}$ mol$^{1/2}$)	a[a]
46	4.87	0.539
39	6.66	0.508
36	7.47	0.498
32	10.5	0.466
28	14.7	0.434
24	18.9	0.407
20	22.7	0.386

[a] K and a values were obtained by linear regression analyses.

Table IV
Flow Times for PαMS PC-16 ($\bar{M}_2 = 1.14 \times 10^6$) in Cyclohexane at 28 °C (Concentration = 3.56×10^{-3} g/mL)[a]

time at 28 °C/h	flow times/s
0	161.46, 161.48
19	161.47, 161.53
42	161.62, 161.61
66	161.67, 161.69

[a] The solution was sealed into the viscometer using wired-on septa. Septa were removed for flow-time measurements at the indicated time intervals and were then replaced.

$[\eta]$ and k_H values are collected in Table II; some of these results have been previously reported.[37] The $[\eta]$ data lead to the Mark–Houwink–Sakurada (MHS) parameters listed in Table III. In all cases the MHS plots were strictly linear with correlation coefficients ≥0.999. This finding, along with the absence of any visible turbidity, suggests the absence of any appreciable aggregation. Also, repeated measurements of flow times for some of the solutions (see Table IV) showed no change over periods ranging from 1 to 3 days. Thus, no signs of aggregation were detected in the viscosity experiments.

A progressive decrease in the MHS exponent occurs as the temperature is lowered. The exponent of 0.386 obtained at 20 °C is believed to be the lowest reported for linear chains. The Huggins coefficient is also sensitive to chain contraction, with average values ranging from 0.66 ± 0.05 at 46 °C to 1.5 ± 0.3 at 20 °C. No dependence of k_H on molecular weight was observed. A theoretical value of 0.99 has been suggested[38] for hard spheres.

The z-average translational diffusion coefficients D_z and k_d values were calculated from the concentration dependence of D_{app} by the expression

$$D_{app} = D_z(1 + k_d C) \quad (2)$$

and are listed in Table V. The concentration dependencies of D_{app} were strictly linear (Figure 1), again suggesting the absence of aggregation. For sample JL-4 at 25 °C, the time dependence of the PCS parameters was

Table V
Diffusion Coefficients and Diffusion Virial Coefficients for PαMS in Cyclohexane at $T < \Theta$

		$T = 28$ °C		$T = 20$ °C	
sample	$\bar{M}_w \times 10^{-4}$	$D_z \times 10^7$/ (cm^2 s^{-1})	$-k_d$/ (mL g^{-1})	$D_z \times 10^7$/ (cm^2 s^{-1})	$-k_d$/ (mL g^{-1})
PL-55	5.90	4.95	15	4.55	28
PC-4	11.8	3.86	21	3.38	37
PC-6	30.5	2.45	64	2.13	64
PC-17	66.5	1.72	73	1.55	115
PL-770	90.3	1.55	63	1.41	252
PC-16	114	1.35	95	1.33	845

sample	$\bar{M}_w \times 10^{-4}$	$T = 25$ °C $D_z \times 10^8$ [a]/(cm^2 s^{-1})
JL-4	341	9.46

[a] No concentration dependence was measured for this sample. D_{app} measured at the extremely low concentration of 4.8×10^{-6} g mL^{-1} was assumed to be approximately equivalent to D_z.

Table VI
Time Dependence of PCS Parameters for PαMS JL-4 in Cyclohexane at 25 °C (Concentration = 4.8×10^{-6} g/mL) over 3 Days

day	Γ	Q
1	226.6 ± 6.9[a]	0.30 ± 0.03[a]
2	228.8 ± 4.6[b]	0.32 ± 0.02[b]
3	227.6 ± 12.8[c]	0.33 ± 0.02

[a] Average of 10 measurements. [b] Average of 5 measurements. [c] Average of 9 measurements.

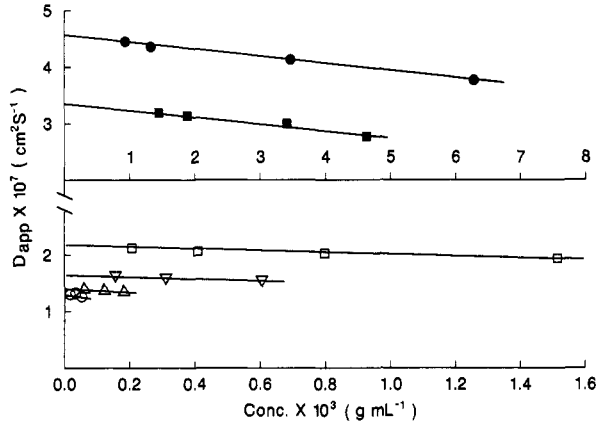

Figure 1. Concentration dependence of apparent diffusion coefficients for PαMS in cyclohexane at 20 °C. Symbols: ●, PL-55; ■, PC-4; □, PC-6; ▽, PC-17; △, PL-770; ○, PC-16.

studied over 3 days (Table VI) to be certain that measured values corresponded to a stable state. Excellent agreement was observed between both decay rate Γ values and second-moment values. These data again substantiate the lack of appreciable aggregation. Attempts to conduct PCS measurements for sample JL-4 at 24 °C ($c = 4.8 \times 10^{-6}$ g mL^{-1}) resulted in detectable aggregation after 7 h and visible turbidity after 24 h.

Plots of log D_z versus log $\bar{M}_w$ at 28 and 20 °C yielded the following expressions:

$$D_z^{28\,°C} = 6.49 \times 10^{-5} \bar{M}_w^{-0.44_2} \quad (3)$$

$$D_z^{20\,°C} = 4.78 \times 10^{-5} \bar{M}_w^{-0.42_5} \quad (4)$$

The D_z and k_d data at 28 °C are in accord with the findings of Cotts and Selser[30] at 25 °C for the same polymer–solvent system. The k_d values, like the k_H values, are quite sensitive to the thermodynamic state, showing an increase in magnitude in poorer solvents. Unlike k_H, k_d values are also strongly dependent on molecular weight; negative values of k_d were always obtained under these sub-Θ conditions.

From the D_z values, hydrodynamic radii R_H can be calculated from

$$R_H = kT/6\pi\eta_0 D_z \quad (5)$$

where k is Boltzmann's constant, T is the absolute temperature, and η_0 is the solvent viscosity.[32] Similarly, equivalent sphere viscometric radii R_v can be calculated as[39]

$$R_v = ([\eta]M)^{1/3}(10/3\pi N_A)^{-1/3} \quad (6)$$

where M is the molecular weight and N_A is Avogadro's number. Values of R_H and R_v at 28 and 20 °C are given in Table VII and double logarithmic plots of these equivalent sphere radii versus molecular weight are shown in Figures 2 and 3.

All values of R_v/R_H are larger than unity, the value which corresponds to a hard sphere. R_v/R_H increases with increasing molecular weight and shows no significant temperature dependence on comparing values obtained at 8 and 16 °C below Θ. Theory[43-45] predicts an increase in R_v/R_H on going from good to Θ solvents. We are not, however, aware of theoretical predictions for R_v/R_H below Θ, nor are we aware of any predicted molecular weight dependence. Clearly, the R_v/R_H values indicate that, even in highly contracted states, spherical globular particles are not obtained, at least for the PαMS–cyclohexane system.

The data of Figures 2 and 3 lead to the following power law dependencies:

$$R_H^{28\,°C} = 4.01 \times 10^{-2} \bar{M}_w^{0.44_1} \text{ (nm)} \quad (7)$$

$$R_H^{20\,°C} = 4.60 \times 10^{-2} \bar{M}_w^{0.42_6} \text{ (nm)} \quad (8)$$

$$R_v^{28\,°C} = 2.83 \times 10^{-2} \bar{M}_w^{0.47_9} \text{ (nm)} \quad (9)$$

$$R_v^{20\,°C} = 3.36 \times 10^{-2} \bar{M}_w^{0.46_0} \text{ (nm)} \quad (10)$$

Since the radius should scale with $M^{1/3}$ for polymer globules,[6] the exponent in eqs 7–10 are another strong indication that a globular state is not achieved.

Comparison of the contraction of PαMS in cyclohexane with findings for other systems requires the calculation of chain expansion or contraction factors α_η and α_H where

$$\alpha_\eta = ([\eta]/[\eta]_\Theta)^{1/3} \quad (11)$$

$$\alpha_H = R_H/R_{H,\Theta} \quad (12)$$

and the subscript Θ denotes measurements at the Flory Θ temperature. For a typical system exhibiting an upper critical solution temperature, at temperatures above Θ α will have values greater than unity, indicative of chain expansion. At temperatures below Θ, chain contraction occurs, and α values are less than 1. $[\eta]$ scales with molecular weight as

$$[\eta]_\Theta = 7.35 \times 10^{-4} \bar{M}_w^{1/2} \text{ (dL g}^{-1}\text{)} \quad (13)$$

for PαMS in cyclohexane at the Θ temperature (36.2 °C).[37] This result is in excellent agreement with data previously reported by Noda and co-workers for the same system.[40]

Table VII
Hydrodynamic and Viscometric Radii of PαMS in Cyclohexane

		T = 28 °C			T = 20 °C		
sample	$\bar{M}_w \times 10^{-4}$	R_H/nm	R_v/nm	R_v/R_H	R_H/nm	R_v/nm	R_v/R_H
PL-55	5.90	5.24	5.39	1.03	4.84	5.28	1.09
PC-4	11.8	6.72	7.60	1.13	6.52	7.27	1.12
PC-6	30.5	10.6	12.0	1.13	10.3	11.3	1.10
PC-17	66.5	15.1	17.3	1.15	14.2	16.1	1.13
PL-770	90.3	16.7	19.9	1.19	15.6	18.4	1.18
PC-16	114	19.2	22.4	1.17	16.6	20.8	1.25

		T = 25 °C		
sample	$\bar{M}_w \times 10^{-4}$	R_H/nm	R_v/nm	R_v/R_H
JL-4	341	25.7	35.8	1.39

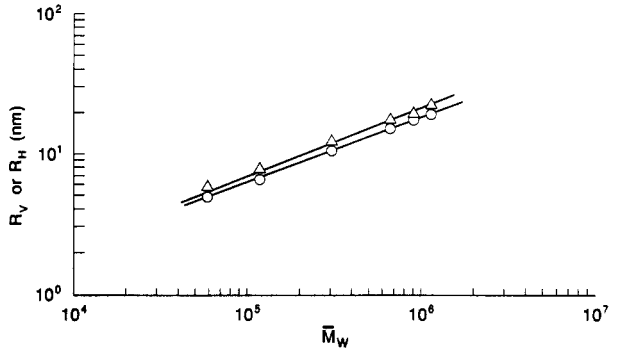

Figure 2. Dependence of R_v (Δ) and R_H (O) on molecular weight for PαMS in cyclohexane at 28 °C.

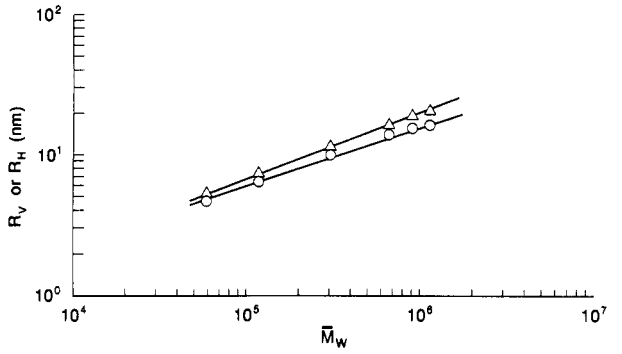

Figure 3. Dependence of R_v (Δ) and R_H (O) on molecular weight for PαMS in cyclohexane at 20 °C.

R_H varies with molecular weight as

$$R_H = 2.12 \times 10^{-2} \bar{M}_w^{1/2} \quad \text{(nm)} \qquad (14)$$

based on the combined Θ condition data of Cowie and Bywater at 37 °C[41] and Noda and co-workers at 34.5 °C.[42] Equation 14 is also in agreement with recent data reported by Cotts and Selser[30] for the same system. Thus, chain expansion and contraction ratios may be calculated using the data of Tables II and VII and eqs 13 and 14.

A comparison of the contraction behavior based on hydrodynamic properties for PαMS and polystyrene is given in Figure 4. For PS the recent α_η data of Chu and Wang[23a] are utilized, while the α_H data are from Vidakovic and Rondelez.[18] These latter data are in excellent agreement with the more recent α_H determinations by Chu and Wang.[23b] Our α_H data for PαMS are supplemented by the data of Cotts and Selser.[30]

In plots of $\alpha^3|\tau|M^{1/2}$ versus $|\tau|M^{1/2}$ attainment of a plateau region where the former parameter is independent of the latter has been taken as evidence for reaching the "collapsed state".[17,19-24] For polystyrene this leveling off is seen at $\alpha_\eta^3|\tau|M^{1/2}$ values of about 24 $g^{1/2}$ $mol^{1/2}$, corresponding to $|\tau|M^{1/2}$ of about 40 $mol^{1/2}$ $g^{-1/2}$ or greater. Values of $\alpha_H^3|\tau|M^{1/2} \simeq 37$ $g^{1/2}$ $mol^{-1/2}$ are obtained at $|\tau|M^{1/2}$ of about 50 $g^{1/2}$ $mol^{-1/2}$ or greater. For the PαMS–cyclohexane system, the asymptotic value $\alpha_H^3|\tau|M^{1/2} \simeq 22$ $g^{1/2}$ $mol^{-1/2}$ is achieved at $|\tau|M^{1/2} \geq 35$ $g^{1/2}$ $mol^{-1/2}$. No clear asymptote is seen for $\alpha_\eta^3|\tau|M^{1/2}$ over the range of $|\tau|M^{1/2}$ values investigated in this work. However, on the basis of available data, a leveling off at $\alpha_\eta^3|\tau|M^{1/2} \simeq 40$ $g^{1/2}$ $mol^{-1/2}$ seems likely for $|\tau|M^{1/2}$ values ≥ 70 $g^{1/2}$ $mol^{-1/2}$.

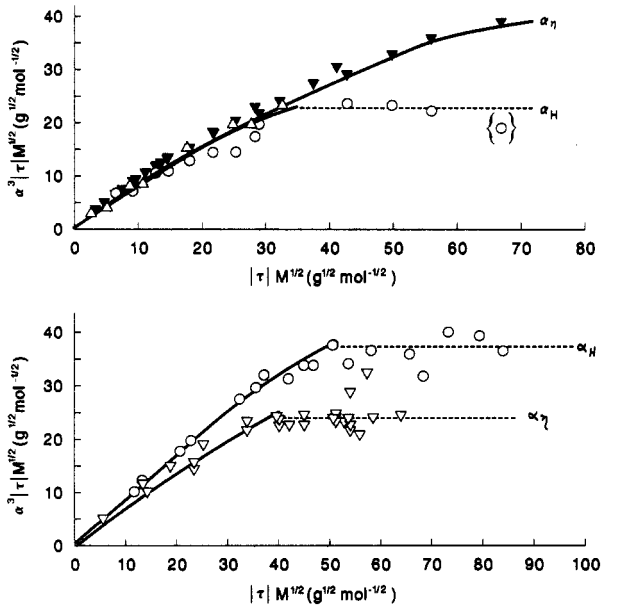

Figure 4. Plot of scaled expansion factor $\alpha^3|\tau|M^{1/2}$ versus scaled reduced temperature $|\tau|M^{1/2}$ for PαMS (top) and PS (bottom) in cyclohexane. For PαMS the symbols are as follows: O, α_H data (this work); Δ, α_H data (ref 30); ▼, α_η data (this work). For PS the symbols are as follows: O, α_H data (ref 18); Δ, α_η data (ref 23). The α_H data point for sample JL-4 at 25 °C is bracketed because of the larger measured Q value for this sample.

The most interesting aspect of Figure 4 is the reversal of the asymptotes for PαMS as compared to those for polystyrene. With PαMS the asymptotic value (assuming it could be attained) for $\alpha_\eta^3|\tau|M^{1/2}$ is much larger than that for $\alpha_H^3|\tau|M^{1/2}$. For polystyrene this order is reversed. This effect is considerably greater than any conceivable errors in the measurement of $[\eta]$ or D_z. For example, the $[\eta]$ values in this work would have to be reduced by about 50% for the PαMS contraction to track that of PS in Figure 4. Thus, there is little doubt regarding the different contraction behavior of the two types of polymer chains. This disparity of results for these two very similar systems was initially surprising. However, a dependence of polymer contraction on chemical structure is to be expected. Reasons include differences in chain stiffness,[5] short-range correlations, and ternary (three-body) interactions, which

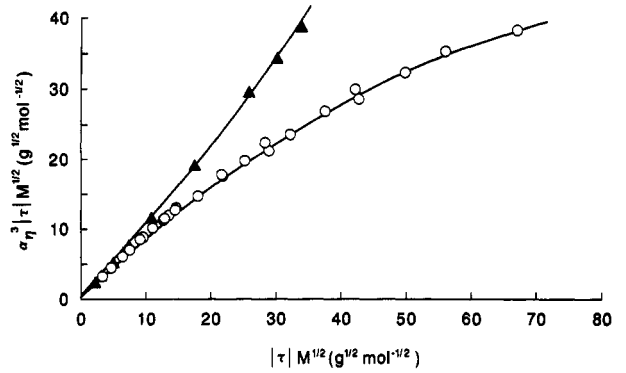

Figure 5. Plot of scaled expansion factor $\alpha_\eta^3|\tau|M^{1/2}$ versus scaled reduced temperature $|\tau|M^{1/2}$ for PαMS in cyclohexane above (▲) and below (○) θ. Notice that there is only a very limited regime where expansion and contraction are symmetrical. The splitting is interpreted as a consequence of the importance of ternary interactions below (but not above) θ.

are expected to become very important below θ, where hydrodynamic properties appear to be rather sensitive to ternary interactions.[46] Very large differences in the asymptotic "collapse" behavior have also been noted by Chu et al.[20] for polystyrene under different θ conditions. Unusual sub-θ behavior has also been noted for other polymer–solvent systems.[29]

Finally, we note that $[\eta]$ data obtained above θ and those results below θ indicate a very limited regime where the expansion and contraction of the coil is symmetrical (Figure 5). Symmetry is seen only in the region $-10 \leq |\tau|M^{1/2} \leq 10$. This splitting and the reasonable linearity of $\alpha_\eta^3|\tau|M^{1/2}$ above θ, where only two-body interactions are expected to contribute significantly to coil expansion, indicate the importance of three-body interactions at temperatures less than θ.

In conclusion, the sub-θ contraction of PαMS in cyclohexane has been studied using intrinsic viscosity and PCS experiments. The dependencies of coil radii on molecular weight and the relatively small contractions observed demonstrate conclusively that a collapsed globular state is not reached. Nevertheless, an asymptotic region is observed in the plot of $\alpha_H^3|\tau|M^{1/2}$ versus $|\tau|M^{1/2}$ and approached in the plot of $\alpha_\eta^3|\tau|M^{1/2}$ versus $|\tau|M^{1/2}$, similar to that reported by other workers[17,19-24] for different polymer–solvent systems. Significant differences are noted in this asymptotic behavior for different polymers systems.

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Registry No. PαMS, 25014-31-7; cyclohexane, 110-82-7.