to the decrease of the intermolecular distance between the α-helical PBLGs.

In addition, in order to better understand this behavior from the macroscopic viewpoint, we measured the volume change of the PBLG liquid crystal and pure CH_2Cl_2 liquid as a function of pressure. The volume ratio V/V_0 (V_0 is the volume at atmospheric pressure, and V is the volume at any given pressure) of PBLG/CH_2Cl_2 liquid crystal and of pure CH_2Cl_2 liquid is shown as a function of pressure in Figure 3. It is shown that the volume ratio of pure CH_2Cl_2 liquid decreases monotonically with an increase in pressure, while the volume ratio of PBLG/CH_2Cl_2 liquid crystal varies abruptly at about 70 kg/cm^2. These ratios clearly change in different ways. From this, it is concluded that the side-chain conformation changes from "extended"[17] to "compact" with increasing pressure up to about 70 kg/cm^2 and that the large change of V/V_0 arises thereby, while above 70 kg/cm^2 the small observed volume change comes from the decrease of the intermolecular distance between the PBLG α-helices. This interpretation parallels that of the change in $\Delta\nu$.

Finally, we suggest that the conformational change of the PBLG side chains and the intermolecular distance are important factors in understanding the pressure effect.

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Communications to the Editor

Sub-Θ Noncollapse of Poly(α-methylstyrene)

Continuing and lively interest in the study of sub-Θ shrinkage and particularly of the "collapse transition" or the "coil–globule transition" of linear, flexible polymers in solution has resulted in a considerable literature from theoretical[1–22] as well as experimental[23–27] work since that interest was sparked more than 30 years ago.[1] To date, the most extensively investigated system of this kind has been that of polystyrene in cyclohexane for temperatures more or less in the range 1–10 °C below the Θ temperature.[29,30,32–34,37] In certain of these studies,[30,32,33,36,37] the transition itself is reported to have been observed. A noteworthy feature common to these sub-Θ studies has been the restrictive requirement that only extremely dilute solutions be employed.

During a recent photon correlation spectroscopy (PCS) study[38] of the size dependence on temperature and molecular weight of four sharp fractions of linear, atactic, high molecular weight samples of poly(α-methylstyrene) in cyclohexane (see Table I here and in ref 39 for additional sample information), it was observed that even though samples were of "normal" dilute solution concentration (Table I and Figure 1) and had been prepared at 50–55 °C, all four maximum concentration solutions remained clear upon cooling to room temperature, exhibiting no evidence of cloudiness, aggregation, or separation. Since room temperature varied between about 25 and 27 °C and the PαMS/cyclohexane Θ temperature is Θ = 34.5 ± 0.5 °C,[40] it was quickly appreciated that PαMS in cyclohexane would lend itself to the study of polymer behavior at sub-Θ temperatures. This communication presents the results of a study of PαMS/cyclohexane sub-Θ behavior.

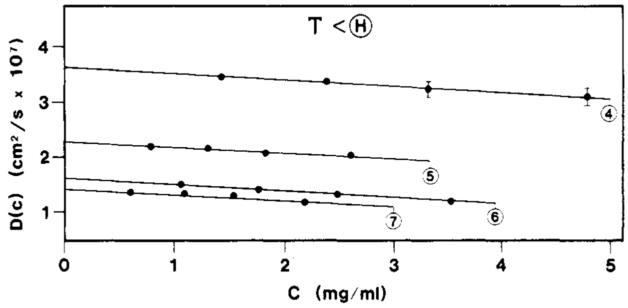

Figure 1. $D(c)$ vs. c.

The focus of the present work was the nature of PαMS coil shrinkage in cyclohexane for solution temperatures 10 °C below Θ. A comparison between PαMS behavior and comparable polystyrene behavior was also of interest. The dependence of coil shrinkage on polymer molecular weight and sample temperature was monitored by PCS measurement of the coil hydrodynamic radius, R_H. The measurement of R_H using PCS is now routine:[41,42] Briefly, polymer z-averaged mutual diffusion coefficients, $D(c)$, were determined from PCS measurements of dilute solutions for temperatures in the range 24.6–27.5 °C and molecular weights in the range 10^5–10^6 using the method of cumulants.[43] Coil self-diffusion coefficients, D_0, were then extracted from least-squares fits to concentration-dependent $D(c)$ data (Figure 1) using the virial expansion

$$D(c) = D_0(1 + k_D c) \qquad (1)$$

with c the polymer concentration and k_D the virial coefficient. Though k_D is not of particular interest here, it is certainly of interest in the more general study, ref 38. R_H

Table I
PαMS Size and Shrinkage Data ($T < \Theta$)

Sample Number	$\bar{M}_w^{TALS}$	$\bar{M}_w^{GPC}$	$\bar{M}_n^{MO}$	D_0 ($cm^2/s \times 10^7$)	R_H ($cm \times 10^7$)	$-\partial D(c)/\partial c$ (cm^3/g)	α_H
4	145000	156000	140000	3.65 ± 0.07	6.66 ± 0.13	11.4 ± 2.2	0.93 ± 0.03
5	395000	425000	314000	2.30 ± 0.02	10.6 ± 0.1	10.3 ± 1.5	0.95 ± 0.01
6	793000	—	661000	1.63 ± 0.02	14.9 ± 0.2	12.0 ± 1.0	0.92 ± 0.02
7	976000	953000	887000	1.44 ± 0.01	16.0 ± 0.1	10.2 ± 0.7	0.94 ± 0.01

Table II
PCS Reduced Second Cumulant ($\mu_2/\bar{\Gamma}^2$) Results ($T < \Theta$)

Sample 4			Sample 5			Sample 6			Sample 7		
C (mg/ml)	$\mu_2/\bar{\Gamma}^2$	T (°C)	C (mg/ml)	$\mu_2/\bar{\Gamma}^2$	T (°C)	C (mg/ml)	$\mu_2/\bar{\Gamma}^2$	T (°C)	C (mg/ml)	$\mu_2/\bar{\Gamma}^2$	T (°C)
4.79	-0.01 ± 0.05	26.5	2.63	-0.01 ± 0.06	27.5	3.56	0.05 ± 0.03	24.7	2.21	0.05 ± 0.04	26.4
3.35	0.00 ± 0.04	26.4	1.84	-0.01 ± 0.03	27.4	2.49	0.03 ± 0.05	24.6	1.55	0.03 ± 0.04	26.1
2.40	0.03 ± 0.03	26.1	1.32	0.03 ± 0.04	26.6	1.78	-0.01 ± 0.05	25.0	1.11	0.03 ± 0.08	26.0
1.44	0.02 ± 0.06	26.7	0.79	0.00 ± 0.08	25.8	1.07	0.00 ± 0.05	25.0	0.66	0.04 ± 0.02	26.4

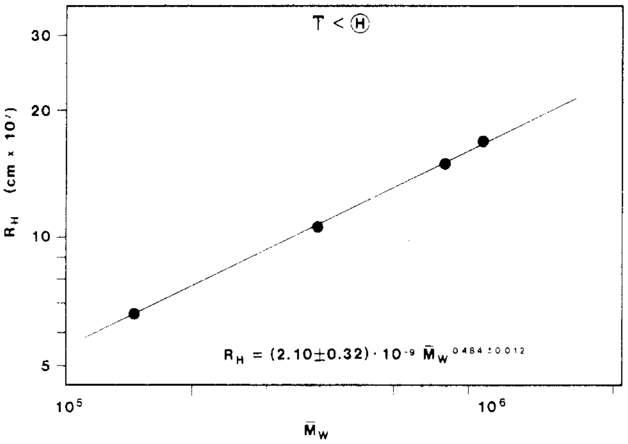

Figure 2. R_H as a function of $\bar{M}_w$.

values were then computed from the Stokes–Einstein relation

$$R_H = k_B T / 6\pi\eta D_0 \tag{2}$$

with k_B the Boltzmann constant, T the abolute temperature, and η the solvent viscosity. Possible polymer aggregation was monitored by using measured values of the relative dispersion in $D(c)$, $\mu_2/\bar{\Gamma}^2$ (often referred to as the reduced second cumulant), provided by cumulants analyses of the data.[43] Small temperature and viscosity corrections were made to standardize R_H values to 25 °C (see Table II) and the dependence of R_H on molecular weight was then determined (Figure 2). Chain hydrodynamic radii at $T = \Theta$, $R_H(\Theta)$, were obtained from the general study[38] and chain shrinkage at 25 °C, as measured by the chain hydrodynamic expansion factor, $\alpha_H = R_H(25\ °C)/R_H(\Theta)$, was determined for each molecular weight (Table I). From the results presented here, the following can be seen:

(1) "Normal" dilute solutions of PαMS in cyclohexane do not aggregate or separate even 10 °C below Θ: Solutions remained clear and reduced second cumulants remained comparable to single-chain values, $\mu_2/\bar{\Gamma}^2 \leq 0.05$ (Table II), at 25 °C. PαMS/cyclohexane solutions are thus well suited to the study of chain sub-Θ behavior without the limitations imposed by the requirement that solutions be extremely dilute.

(2) In contrast to polystyrene, for example, PαMS in cyclohexane does not collapse 10 °C below Θ and, in fact, retains its "Θ character" at that temperature: Values of α_H exhibit a shrinkage of about 5% for PαMS while polystyrene shows substantially greater sub-Θ shrinkage. Examples of polystyrene shrinkage about 10 °C below Θ include approximately 32% shrinkage in ref 37, about 60% shrinkage in ref 32, about 40% shrinkage (1.4 °C below Θ) in ref 29, and about 35% shrinkage in ref 36, though dioctyl phthalate and not cyclohexane was the solvent in this study.

Theoretical treatments (ref 22 and references therein) predict $R_H \sim M^{1/2}$ at $T = \Theta$ while for collapsed chains at sub-Θ temperatures, $R_H \sim M^{1/3}$. Using the three independently determined values of average molecular weight (Table I) and the approach developed in ref 39, it was found here that at 25 °C

$$R_H = (1.76 \pm 0.33) \times 10^{-9} \bar{M}^{0.50 \pm 0.01} \tag{3}$$

Figure 2 illustrates the particular relationship between R_H and $\bar{M}_w$ as determined by time-averaged light scattering (TALS). The failure of PαMS to collapse well below Θ is reminiscent of the behavior of poly(*p*-chlorostyrene) in *n*-propylbenzene:[27] Small-angle X-ray measurements detected only a 10% decrease in radius for gyration 16 °C below Θ. Below this temperature, precipitation occurred. By comparison, recent analytical ultracentrifugation measurements of narrow fractions of high molecular weight, linear polystyrene in both cyclohexane and cyclopentane[37] found that $R_H \sim M^{1/3}$ for $T \lesssim 10$ °C below Θ, illustrating the collapse of polystyrene under those conditions.

Lastly, the retention of Θ-like character for PαMS at 25 °C can be seen in the molecular weight independence of the slopes of plots of $D(c)$ vs. c (Table I, Figure 1). This independence has been predicted for polymer coils in poor solvent[44] and has been observed for polystyrene at $T = \Theta$.[44]

(3) For molecular weights in the decade 10^5–10^6 at temperatures 10 °C below Θ, PαMS does not exhibit an increasing rate of shrinkage with increasing molecular weight (Table I). Even for a molecular weight of 10^6, the shrinkage is still only about 5%. This behavior contrasts with that of polystyrene for which the trend was evident and contradicts theoretical expectations that the general rapidity of chain shrinkage and the sharpness of the corresponding collapse transition increase with increasing molecular weight.

Based on the results presented here and keeping similar polystyrene results in mind, it is seen that methyl substitution into the polystyrene backbone produces distinct,

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if not dramatic, differences in the nature of the dependence of the size change on solution temperature and polymer molecular weight for these two similar linear, flexible polymers. As seen here, this substitution reduced the rate of sub-Θ chain shrinkage and prevented chain collapse. In an earlier study of the behavior of PαMS in toluene,[39] this substitution promoted chain swelling in good solvent, thereby shifting the molecular weight threshold for the Gaussian-to-excluded volume transition from about 10^7 for polystyrene downward to about 10^5 for PαMS.

In conclusion, the observed differences in behavior between PαMS and polystyrene are most easily explained as being due to substituted methyl group steric hindrance effects and indicate the desirability of extending current theoretical treatments of polymer size behavior, e.g., sub-Θ chain shrinkage and collapse, to include such details.

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Registry No. PαMS (homopolymer), 25014-31-7.

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Diffusion of Dye Molecules in Polymers above and below the Glass Transition Temperature Studied by the Holographic Grating Technique

Studies of the diffusion of dye molecules in polymers are important in technological applications. They also provide important information about the effect of the chain relaxation of polymers on the diffusional process. Existing in the literature are data of diffusion of small molecules (such as Ar, CH_4, and hydrocarbons) in polymer glasses.[1] The diffusion coefficients of these small molecules in polymers at temperatures above T_g were measured by radioactive tracer or NMR techniques.[2] The diffusion coefficients obtained are greater than 10^{-10} cm^2/s and upon traversing the glass transition temperature,[1] a change of the apparent activation energy E_A was found in many cases. In all cases, the E_A values determined for the dissolved molecules were far below the corresponding values of the "glass process" governing segmental chain mobility of the polymer in this temperature region. Diluent diffusion above T_g could be combined with some of the scarce data[3] below T_g within the framework of a free volume theory.[4] The holographic grating technique[5–7] provides access to the measurement of very small diffusion coefficients expected for larger molecules dissolved in polymeric glasses. In the present communication, we present the first results obtained in polycarbonate glasses. To our knowledge, this is also the first report which applies the holographic grating technique to the study of the dye diffusion process in the polymer glass.

Poly(bisphenol A carbonate) (PC) with $M_w = 35000$ was obtained from the Bayer Co. Our samples, which contained about 0.5 wt % of the dye, were prepared by precipitation from a dichloromethane solution into petroleum ether. The residue was dried under vacuum for 1 day at 50 °C and an additional 2 days at ~160 °C, where sintering to a dense regulus was avoided. The dried sample was pressed into pellets for the diffusion measurements performed as described elsewhere.[6,7] Using DSC with a heating rate of 10 K min^{-1}, we determined T_g = 150 °C. No effect in T_g could be found on dissolving the dye in PC; neither could the melting peak below 300 °C be detected, suggesting the fact that the sample is amorphous. Poly-

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