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Dimensions of Ultrahigh Molecular Weight Polystyrene in Cyclohexane below the Θ Temperature

IL HYUN PARK,[†] LEWIS FETTERS,[‡] and BENJAMIN CHU*[†]

Department of Chemistry, State University of New York at Stony Brook, Long Island, New York 11794-3400, and Exxon Research and Engineering Company, Annandale, New Jersey 08801.

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The transition of a flexible polymer chain from a random coil at the Θ temperature to a collapsed globule in a poor solvent has attracted a great deal of attention both theoretically[1-4] and experimentally.[5] The coil-to-globule transition is closely related to attractive interactions and is a phenomenon of fundamental importance.

The change from an ideal chain behavior to a collapsed globular behavior may be introduced by varying the temperature or the composition of solvent (e.g., by adding a nonsolvent). In the neighborhood of the upper critical solution temperature, as the polymer solution is cooled down below the Flory Θ temperature the polymer chain will begin to contract. Based on the mean-field theory[1,6] or the temperature blob theory,[1,7] polymer size $R(T)$ (either radius of gyration, R_g, or hydrodynamic radius, R_h) scales as $|\tau|^{-1/3}M^{1/3}$ at a given temperature T in the collapsed regime where τ [$\equiv(T-\Theta)/\Theta$] is the reduced temperature and M is the molecular weight of the polymer chain.

In previous papers,[8,9] we studied the coil-to-globule transition of polystyrene (PS) (M_w ranging from $\sim 2\times10^6$ to $\sim 20\times10^6$ g/mol) in cyclohexane (CY) and in methyl acetate. As a polymer chain contracts with increasing scaled reduced temperature, $|\tau|M_w^{1/2}$, a high molecular weight PS sample is more effective than a low molecular weight PS sample in being able to let the polymer chain reach the collapsed regime over the same temperature drop, ΔT [$\equiv|T-\Theta|$]. However, although we can take light scattering measurements at lower polymer concentration with a higher molecular weight polymer sample without decreasing the signal-to-noise ratio, a steeper slope in the low concentration side of the cloud-point curve could introduce practical experimental difficulties for the ultrahigh molecular weight PS sample because of the polydispersity effect.[10]

In this work, we investigated the temperature dependence of dimensions of a very high molecular weight ($M_w \sim 41\times10^6$ g/mol) PS sample in cyclohexane below the Θ temperature by means of laser light scattering.

Experimental Section

Details of experimental conditions and methods of data analysis have already been described in ref 8. Dust-free solutions of this PS sample were prepared as follows. As the mother solution with $C\sim10^{-4}$ g/g was being diluted with dust-free solvent, the number of dust particles in the polymer solution also decreased. Finally, only a few dust particles exist at very dilute concentrations ($C\sim10^{-6}$ g/g). Dust-free solutions could be obtained by centrifugation at ~100*g* for less than 30 min, without changing the polymer molecular weight observed by light scattering. The polymer solution should never be filtered and precautions were taken to reduce shear during solution transfer. The specifications of this PS sample measured by laser light scattering[11] are as follows: $M_w\sim41\times10^6$ g/mol and $M_w/M_n\sim1.7$ with M_w and M_n being the weight-average molecular weight and the number-average molecular weight, respectively. The index of polydispersity M_w/M_n was estimated by means of the Fujita plot.[12] The *z*-average characteristic line width ($\bar{\Gamma}$) and the variance were obtained by analyzing the intensity–intensity time correlation function by using a second-order cumulants fitting method.[13] Another index of polydispersity, M_z/M_w was computed according to the relation $M_z/M_w = 1 + 4$ variance as reported by Brown et al.[14], with M_z being the *z*-average molecular weight. M_z/M_w was estimated very approximately to be ~1.3. Earlier calibration of the same PS sample showed $M_w = 4.37\times10^7$ g/mol, $M_z = 4.88\times10^7$ g/mol, and $M_z/M_w = 1.12$. Thus, the PS sample could have some slow degradation taking place when compared with the essentially atactic polystyrene sample first prepared by anionic polymerization circa 1969.

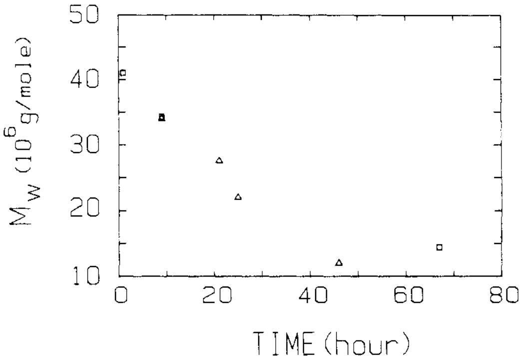

Figure 1. Degradation of high molecular weight polystyrene ($M_w\sim41\times10^6$ g/mol) in cyclohexane with time. (□) $C = 2.1\times10^{-6}$ g/g with 1 wt % antioxidant (2,6-di-*tert*-butyl-4-methylphenol) at $T\sim32.7$ °C. Values are listed in Table II at time = 0, 9, and 67.5 h. (△) $C = 9.5\times10^{-7}$ g/g without antioxidant at $T\sim35.0$ °C. Addition of 1 wt % antioxidant was not very helpful in preventing the polymer from degrading.

Table I
Radii of Gyration of High Molecular Weight PS in Cyclohexane with 1% Antioxidant below the Θ Temperature at $C = 7.3\times10^{-5}$ g/g

$M_w\times10^{-6}$, g/mol	T, °C	R_g, nm	α_s	$\lvert\tau\rvert M_w^{1/2}$ [c]	$\alpha_s^3\times\lvert\tau\rvert M_w^{1/2}$ [c]	symbol
40.3	32.7[a]	230	1.00	0	0	
42.8[b]	32.0	177	0.770	14.5	6.62	-•-
49.4[b]	31.8	166	0.722	19.7	7.41	-•-
50.0[b]	31.5	152	0.661	24.5	7.08	-•-

[a] Θ temperature of PS/CY system with 1 wt % antioxidant (2,6-di-*tert*-butyl-4-methylphenol). [b] Apparent molecular weight measured at each temperature. The change in the measured PS molecular weight at temperature below the Θ temperature and sufficiently high concentrations (e.g., $C\sim7\times10^{-5}$ g/g) could imply that the high molecular weight fraction of the PS polymer had reached the metastable state in the two-phase region. [c] Unit: g$^{1/2}$ mol$^{-1/2}$.

One weight percent of antioxidant (2,6-di-*tert*-butyl-4-methylphenol) was added to PS solutions in order to prevent polymer degradation.[15] Nevertheless, the molecular weight in the PS/CY system with and without 1 wt % antioxidant decreased continuously with increasing time as shown in Figure 1. It seems that the antioxidant was not helpful in preventing degradation for extremely high molecular weight PS samples at very dilute concentrations. The Θ temperature of PS/CY systems with 1 wt % antioxidant was 32.7 °C as reported in ref 8.

Results and Discussion

Radii of gyration of the high molecular weight PS in CY with 1 wt % antioxidant at various temperatures are listed in Tables I and II, and the hydrodynamic radii in Table III. We observed that the static size R_g of the polymer chain contracted very rapidly with decreasing temperature. From Table I, for example, at 31.5 °C ($\Delta T = 1.2$ °C) and $C = 7.3\times10^{-5}$ g/g (~5.5×10^{-5} in units of g/mL), contraction of the static size from an ideal unperturbed size

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[†] State University of New York at Stony Brook.
[‡] Exxon Research and Engineering Co.

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Table II
Time Dependence of R_g and M_w of High Molecular Weight PS at $C = 2.1 \times 10^{-6}$ g/g

time, h	T, °C	$M_w^{app} \times 10^{-6}$ (A),[a] g/mol	$M_w \times 10^{-6}$ (B), g/mol	A/B[c]	R_g, nm	$R_g(\Theta)$,[d] nm	α_s	symbol
0	32.7[e]	40.9	40.9	1.00	255	255	1.00	
2	32.0	40.5	39.6[b]	1.02	232	250	0.928	ϕ
4	31.5	37.3	37.8[b]	0.99	196	244	0.803	●[f]
6	31.0	34.9	36.6[b]	0.95	140	241	0.581	●[f]
8	30.5	38.7	35.4[b]	1.09	124	236	0.525	●[f]
9	32.7[e]	34.3	34.3	1.00	231			
19	31.0	36.4	31.8[b]	1.14	115			
43	31.0	31.7	25.9[b]	1.22	136			
43.5	30.5	31.0	25.9[b]	1.20	126			
67	30.5	26.9	14.4[b]	1.87	93.7			
67.5	32.7[e]	14.4	14.4	1.00	160			

[a] Apparent molecular weight measured at each temperature from absolute excess scattered intensity extrapolated to zero scattering angle. [b] Interpolated from the values of M_w measured at the Θ temperature (time = 0, 9, and 67.5 h). [c] The ratio indicates the degree of aggregation. [d] Calculated from M_w by using $R_g^2(\Theta) = 1.58 \times 10^{-17} M_w$ cm^2. [e] Θ temperature of PS/CY system with 1 wt % antioxidant. [f] Filled symbols suggest measurements in the metastable region.

Table III
Hydrodynamic Radii of High Molecular Weight PS in Cyclohexane with 1% Antioxidant below the Θ Temperature at $C = 2.1 \times 10^{-6}$ g/g

$M_w \times 10^{-6}$, g/mol	T, °C	R_h, nm	$R_h(\Theta)$,[a] nm	α_h	$\lvert\tau\rvert M_w^{1/2}$ [e]	$\alpha_h^3\lvert\tau\rvert M_w^{1/2}$ [e]	symbol
40.9	32.7[c]	164	164	1.00	0	0	
39.6[b]	32.0	141	161	0.876	15.4	10.3	ϕ
37.8[b]	31.5	125	158	0.791	25.1	12.6	●[d]
36.6[b]	31.0	116	155	0.748	34.6	14.6	●[d]

[a] Calculated from $R_h^2(\Theta) = 6.57 \times 10^{-18} M_w$ cm^{-2}. [b] Interpolated value (see Table II). [c] Θ temperature of PS/CY with 1 wt % antioxidant. [d] Filled symbols suggest measurements in the metastable region. [e] Unit: g$^{1/2}$ mol$^{-1/2}$.

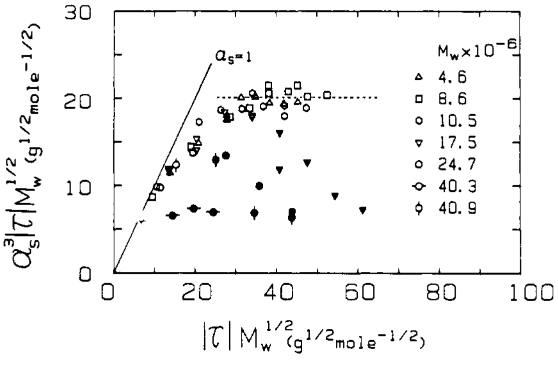

Figure 2. Variation of scaled expansion factor $\alpha_s^3\lvert\tau\rvert M_w^{1/2}$ of static size as a function of scaled reduced temperature $\lvert\tau\rvert M_w^{1/2}$. Data points (-○-) of the high molecular weight samples are plotted in Figure 10 of ref 8 for comparison. Filled symbols indicate "metastable" collapsed regime: (-●-) $M_w = 40.3 \times 10^6$ g/mol, $C = 7.3 \times 10^{-5}$ g/g, values listed in Table I; (ϕ and ●) $M_w = 40.9 \times 10^6$ g/mol, $C = 2.1 \times 10^{-6}$ g /g, values listed in Table II.

is about 34% ($\alpha_s = R_g(T)/R_g(\Theta) \sim 0.66$) even with an apparent molecular weight increase of about 20%. Thus, if the PS molecular weight were to remain constant, the contraction should have been even greater. The increase in the apparent molecular weight, on the other hand, suggested a problem with such data, as the PS molecular weight should remain constant during the coil-to-globule transition. From the static size change, it is worthwhile to note the following observations. (i) When comparing our data, as listed in Table I, with results ($\alpha_s \sim 0.58$ at $\Delta T = 1.4$ °C and $C \sim 2 \times 10^{-5}$ g/mL) reported by the Akron group,[16] we could find good agreement between the two sets of experiments. The Akron group used the same polystyrene sample prepared by Fetters. (ii) In a plot of the scaled expansion factor $\alpha_s^3\lvert\tau\rvert M_w^{1/2}$ of static size versus the scaled reduced temperature $\lvert\tau\rvert M_w^{1/2}$, as shown in Figure 2, the results at $C \sim 7.3 \times 10^{-5}$ g/g (denoted by -●-) correspond to the "metastable" collapsed regime as discussed in detail in ref 8.

In the metastable region between the coexistence curve and the spinodal curve, the homogeneous polymer solution will phase separate into two phases, one at dilute concentration and the other in the semidilute (or concentrated) solution regime. As we approach the phase separation from the very dilute homogeneous solution regime using a relatively polydisperse polymer sample, the high molecular weight fractions will separate out into droplets of polymer solutions in the semidilute regime leaving a polymer solution of lower molecular weight in the dilute homogeneous phase. However, the equilibration time is very long because of the dilute polymer concentration. Therefore, we tried to prepare a polymer solution which was ~30 times more dilute ($C \sim 2.1 \times 10^{-6}$ g/g) in order to avoid the rapid contraction of the polymer chain due to the fact that the high molecular weight fraction of the PS polymer has reached the metastable collapsed regime. However, as shown in Figure 1 (or Table II), polymer degradation appeared to be a serious problem in very dilute polymer solutions of our extremely high molecular weight PS sample. At a very dilute polymer concentration ($C \sim 2.1 \times 10^{-6}$ g/g), the true molecular weight at each temperature was interpolated from two values of M_w measured (without any aggregation) at the Θ temperature: one in the beginning of the experiment (time = 0 h in Table II), i.e., we started our experiment at the Θ temperature; another at the end of the experiment (time = 9 h in Table II), i.e., after completing the measurements at time = 2, 4, 6, and 8 h. The Θ sizes corresponding to the interpolated molecular weight could be estimated by the scaling relations $R_g(\Theta)^2 \sim 1.58 \times 10^{-17} M_w$ and $R_h(\Theta)^2 \sim 6.57 \times 10^{-18} M_w$ with R and M_w expressed in units of cm and g/mol, respectively. Values of expansion factors (denoted by ϕ and ●; α_s for the static size as listed in Table II and α_h for the hydrodynamic size as listed in Table III) after correction due to the effect of polymer degradation by the abovementioned method are shown in Figures 2 and 3. As shown in Figures 2 and 3, almost all the data points of PS ($M_w = 40.9 \times 10^6$ g/mol) at $C \sim 2.1 \times 10^{-6}$ g/g never

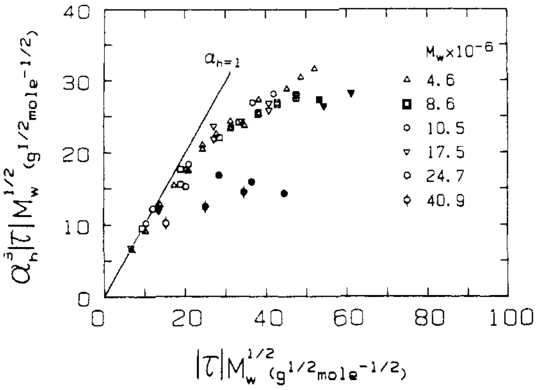

Figure 3. Variation of scaled expansion factor $\alpha_s^3|\tau|M_w^{1/2}$ of hydrodynamic size as a function of scaled reduced temperature $|\tau|M_w^{1/2}$. Data points (♁ and ⧫) of the high molecular weight PS sample, as listed in Table III, are plotted in Figure 17 of ref 8 for comparison. Filled symbols denote "metastable" collapsed regime.

reached the asymptotic height and belonged to the metastable collapsed regime (emphasized by the filled symbols).

In summary, (1) degradation of very long polymer chains occurs readily at very dilute polymer concentrations ($C \leq 10^{-6}$ g/g) for our high molecular weight PS sample. (2) In coil-to-globule transition studies, the polydispersity effect becomes a critical issue. As it is difficult to prepare ultrahigh molecular weight PS samples with a very narrow molecular weight distribution, the advantage of this ultrahigh molecular weight PS sample was overshadowed by its unexpectedly broad polydispersity. (3) Most of the experiments suggested measurements in the metastable collapsed regime at finite concentrations.

The present experiment simply demonstrates polymer solution behavior in the metastable region and conforms to problems associated with earlier results in the literature. As the low polymer concentration (left) side of the cloud-point curve is not only very steep but also occurs at very low polymer concentrations, it becomes essential that the only accessible path to reach the globule state is to use a ultrahigh molecular weight polymer with a very narrow molecular weight distribution.

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Registry No. PS, 9003-53-6.

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Communications to the Editor

Time-Resolved SAXS on Crystallization of a Low-Density Polyethylene/High-Density Polyethylene Polymer Blend

Small-angle X-ray scattering (SAXS) has been used successfully to study the structure of polymer blends.[1-5] A natural extension is to use synchrotron radiation for measurements of time-resolved structural changes during early stages of crystallization.[6-8] In this paper, we report our time-resolved SAXS patterns of a blend of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) and of the respective homopolymers.

HDPE has $M_w = 1.60 \times 10^5$ g/mol, $M_w/M_n = 7.1$, ca. one short chain branching per 1000 carbon atoms, and a density of 0.957 g/mL. The LDPE has $M_w = 2.86 \times 10^5$ g/mol, $M_w/M_n = 16$, ~26 short chains branching per 1000 carbon atoms, and a density of 0.920 g/mL. The blend is 50/50 of HDPE and LDPE by weight percentage. These are the same materials as used in a previous study.[5]

SAXS measurements were carried out by using a modified Kratky collimator[9] adapted for synchrotron radiation at the SUNY beamline, NSLS, Brookhaven National Laboratory (BNL). The wavelength of X-ray used was 0.154 nm. We used a photodiode array of ~2.5-cm window length as the linear position sensitive detector, which was mounted at a distance of 548 mm from the sample.

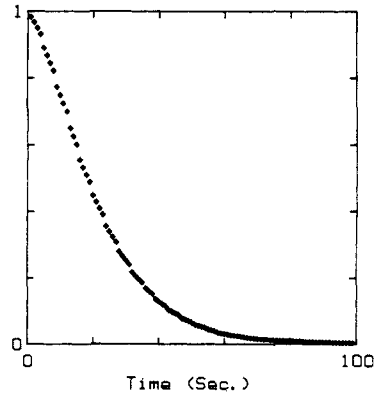

Figure 1. Cooling curve during a temperature jump ΔT of 70 °C. The temperature was normalized by $(T - T_2)/(T_1 - T_2)$. T_1 and T_2 denote the temperatures of the thermal blocks.

In order to achieve rapid cooling during the SAXS measurements, the copper cell containing the polymer sample was quickly moved from one thermal block ($T = T_1$) to the other block ($T = T_2$) by use of a pneumatic piston. The cooling rate depends on the temperature difference between the two thermal blocks ($\Delta T = T_1 - T_2$). For example, as shown in Figure 1, the cooling rate achieved during the first 30 s, after a temperature jump