Dimensions of Polymer Chains in Critical Semidilute Solutions

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In this Letter we present first measurements of the radius of gyration (R_g) for polystyrene in deuterocyclohexane at the critical concentration of the polymer over a temperature range $\Theta \geq T \geq T^c$ using small-angle neutron scattering and the high-concentration labeling methodology. We do not observe a reduction of $R_g(T^c)$ at the critical temperature of phase demixing T^c as compared to $R_g(\Theta)$ in the Θ region, which indicates that the critical polymer solution cannot be considered as an ensemble of partially collapsed noninterpenetrating coils. [S0031-9007(96)02248-X]

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The conformation of polymer chains depends crucially on the quality of the solvent [1], and at high temperatures ($T \gg \Theta$) the chain dimensions are expanded due to the excluded volume interactions between monomers. In the Θ region, excluded volume effects are annulled by the attractive solvent-monomer interactions. Hence, the conformation of chains is described by Gaussian statistics and the radius of gyration R_g varies with the molecular weight M_w as $R_g(T \cong \Theta) \sim M_w^{\nu_F}$, where $\nu_F = 0.5$ is the Flory exponent. In the poor solvent regime $T < \Theta$ the dominating attractive interactions between monomers are believed to collapse the chains into compact polymer globules. The transition from the ideal Gaussian to the compact state of individual coils in the *dilute concentration domain* $\phi < \phi^*$ (where ϕ^* is the overlap concentration) is now well understood and documented experimentally [2]. Much less is known about the conformation of chains at $T < \Theta$ in the *semidilute domain* $\phi > \phi^*$, where the coil dimensions can be substantially affected by the interchain interactions and the critical fluctuations (see, e.g., Sanchez [3] and references therein). The different theoretical approaches that have been applied so far for calculating R_g at the critical point of phase demixing (T^c, ϕ^c) led to conflicting conclusions. Starting from de Gennes' assumption that, *at the critical point polymer chains just begin to overlap and do not interpenetrate significantly* [1] and using scaling arguments, Izumi and Miyake [1] have shown that

$$R_g(T^c, \phi^c) \sim M_w^{(r+1)/3} \sim M_w^{\nu_F'}. \qquad (1)$$

Substituting in Eq. (1) the well established experimental value $r = 0.38$ [5] yields an exponent ($\nu_F' \equiv \nu_F(T^c) = 0.46) < 0.5$, implying that the chains should be partially collapsed at $T \cong T^c$ [3,4]. In attempting to justify this semi-intuitive finding, Lhuillier [6] arrived at $\nu_F' = 0.471$ and Cherayil [7] found that $\nu_F' = 0.462$ using the mean-field and the canonical partition function formalisms, respectively. Conversely, in their molecular theory, Raos and Allegra [8] demonstrated that conformation of a single chain in a "Gaussian cluster" below the Θ temperature remained unperturbed over the whole poor solvent regime, and the collapse to the globular state should occur only at $T < T^c$. A similar conclusion may be derived from the theory of Muthukumar [9], which accounts for three-body interactions between monomers in polymer solutions at $T < \Theta$.

Providing definitive experimental data on the size of polymer chains at the critical point to resolve this issue has remained a challenge for the past decade. In this Letter we address the effect of temperature on the size of polystyrene coils in deuterocyclohexane at the critical concentration of phase demixing $\phi^c \sim \phi^*$ [1]. For this purpose we apply the small-angle neutron scattering (SANS) and make use of high-concentration labeling [10] to increase the signal-to-noise ratio. This methodology allows us to follow the radius of gyration of the few labeled chains in both the Θ region and the critical region of phase demixing of semidilute polymer solutions.

Following the high-concentration methodology [10,11], the coherent intensities of scattering for solutions of identical protonated and deuterated polymer coils can be represented as follows:

$$I(Q,T,x) = I_S(Q,T,x) + I_t(Q,T,x), \qquad (2)$$

$$I_s(Q,T,x) = KnN^2 S_s(Q,T), \qquad (3)$$

$$I_t(Q,T,x) = LnN^2 S_t(Q,T), \qquad (4)$$

where

$$K \equiv (b_H - b_D)^2 x(1-x),$$
$$L \equiv [b_D x + (1-x) b_H - b_s']^2.$$

Subscripts s and t correspond to the scattering from a single chain and the total scattering, respectively, x is the molar ratio of labeled chains, b_D and b_H are the scattering lengths of deuterated and protonated monomers, b_s' is the normalized scattering length of a solvent molecule, n and N are the total number of polymer molecules and the degree of polymerization, respectively, and S_s and S_t are the single-chain and the total scattering structure factors, respectively. It follows from Eqs. (2)–(4) that one can directly observe $S_s(Q,T)$ by making the prefactor (L) vanishingly small. Similarly, $x = 1$ makes the prefactor

(K) zero, and thus $S_t(Q)$ can be obtained directly in the experiment. If the magnitude of (L) is not precisely zero, as is the case for (HPS-DPS) + DCH solutions with $x = 0.1$, the single-chain structure factor can be obtained by subtracting the normalized intensity of total scattering $I_t(Q,T,x = 1)$ from $I(Q,T,x = 0.1)$ via

$$I(Q,T,x = 0.1) - \frac{L(x = 0.1)}{(b_H - b_s')^2} I_t(Q,T,x = 1) = nN^2(b_H - b_D)^2 x(1 - x) S_s(Q,T). \quad (5)$$

Calculations yield 0.018 for the prefactor of the second term in Eq. (5). The effect of a 1.8% correction for $I(Q,T,x = 0.1)$ is negligible in the Θ region, though it can become finite near T^c due to the divergence of $I_t(0) \sim (T - T^c)^{-1.24}$ (Melnichenko *et al.* [12]).

Hydrogenated and deuterated polystyrene standards (HPS and DPS, respectively) were purchased from Polymer Laboratories. Solutions of HPS and HPS-DPS pairs with similar M_w were prepared in deuterocyclohexane (DCH, 99.5% deuterium, sigma). Characteristics of the polymer species and solutions are given in Table I. Each solution was contained in a 5 mm thick quartz cell and the temperature was controlled to better than ±0.1 K. The appearance of the meniscus at $T = T_{\mathrm{menisc}}$ (phase demixing) was detected visually. The temperature step in the vicinity of T_{menisc} was 0.5 K, and the critical temperature was assigned to be $T^c = (T_{\mathrm{menisc}} + 0.25\ \mathrm{K}) \pm 0.25$ K.

Measurements were performed on the 30-m SANS spectrometer at the Oak Ridge National Laboratory. The neutron wavelength was $\lambda = 4.75$ Å $(\Delta\lambda/\lambda = 0.06)$ and the range of scattering vectors was $0.006 < Q = 4\pi\lambda^{-1}\sin\theta < 0.09$ Å^{-1}, where 2θ is the scattering angle. The data were corrected for scattering from the empty cells, detector sensitivity, and beam-blocked background and placed on an absolute scale using precalibrated secondary standards after radial averaging to produce functions of the intensity I vs Q. Procedures for subtracting the incoherent background have been described previously (Wignall and Bates [13], Dubner, Schultz, and Wignall [14]). After phase demixing, the lower half of the cells was covered by cadmium mask, and the scattering from the upper diluted phase of the solution was measured at several temperatures below T^c. The functions $S_s(Q,T)$ were obtained using Eq. (5) and used to extract the (z-averaged) R_g by fitting the Debye form factor for Gaussian chains [15],

$$F_D = (2/y^2)(y - 1 + e^{-y}), \qquad y = Q^2R_g^2. \quad (6)$$

Magnitudes of $R_g(\Theta)$ for all M_w (Table I) agree well with our previous results as well as with the data of other workers [16] for the unperturbed dimensions of polystyrene molecules. As seen from Fig. 1, the radius of gyration for HPS in all solutions studied does not decrease over the whole temperature range below the Θ temperature. The abrupt decrease of R_g is revealed only at $T < T^c$.

TABLE I. Molecular weight M_w (10^{-5} g/mol), polydispersity index $P = M_w/M_N$, critical volume fraction ϕ^c, and critical temperature T^c of the $[x\mathrm{HPS} + (1 - x)\mathrm{DPS}]$-DCH and HPS-DCH solutions studied. R_g is the average experimental radius of gyration of the HPS chains over the Θ region.

HPS		DPS			SOLUTION		
M_w	P	M_w	P	ϕ^c	x	T^c/K	R_g/Å
1.15	1.05	1.19	1.09	0.0860	0.1	297.4	90
					1.0	298.4	
2.00	1.03	2.05	1.04	0.0697	0.1	300.4	117
					1.0	301.15	
5.15	1.08	5.20	1.05	0.0485	0.1	304.65	189
					1.0	306.9	

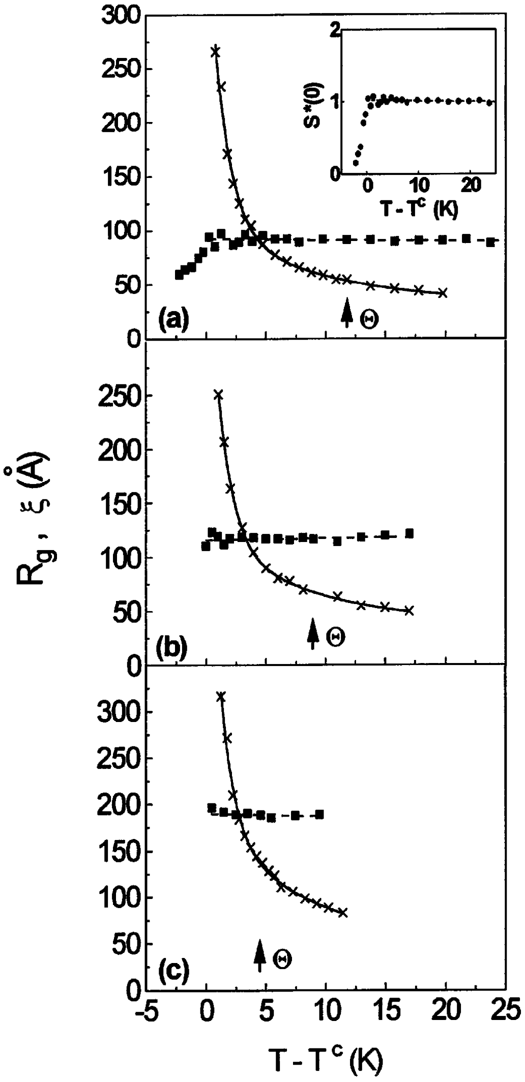

FIG. 1. Temperature dependence of the radius of gyration (■) and the correlation length (X) for the solutions of polystyrene with $M_w \sim 1 \times 10^5$ (g/mol) (a), $M_w \sim 2 \times 10^5$ (g/mol) (b), and $M_w \sim 5 \times 10^5$ (g/mol) (c). The inset in (a) shows the temperature variation of the normalized intensity of forward scattering $S^*(0) = S_s(0,T)/S_s(0,\Theta)$. Arrows indicate the Θ temperature ~309 K [17] for DPS-DCH solution.

This is the central result: Instead of the anticipated [1,4,6,7] reduction of R_g induced by the possible change of the value ν_F from 0.5 to 0.46 [which would have corresponded to the decrease, e.g., from $R_g(\Theta) \approx 190$ Å to $R_g(T^c) \approx 110$ Å for PS of $M_w = 5.15 \times 10^5$], we find that the radius of gyration remains unperturbed below the Θ temperature down to T^c. In Fig. 1 we also show the temperature variation of the correlation length ξ of the concentration fluctuations containing information on both intermolecular and intramolecular correlations between monomers, irrespective of their belonging to a given polymer chain. The magnitude of ξ was extracted from the total scattering structure factor $S_t(Q,T)$ for HPS-DCH solutions by fitting the low-Q region to the Ornstein-Zernike formula,

$$S_t(Q,T) = S(Q = 0)/(1 + Q^2\xi^2), \qquad (7)$$

which yields ξ as the fit parameter at each temperature. As seen in Fig. 1, the magnitude of ξ dramatically increases from about several tens of Å at $T \approx \Theta$ [$\xi < R_g(\Theta)$] to up to several hundreds of Å at $T \approx T^c$ [$\xi > R_g(T^c)$]. This finding, in conjunction with the observed constancy of $R_g(T)$, indicates that deterioration of the solvent quality leads to the formation of distinct microdomains, representing undisturbed, strongly interpenetrating polymer coils [18].

In summary, we have presented the first results of the SANS measurements of the radius of gyration of polystyrene in deuterocyclohexane at the critical concentration in the poor solvent regime down to the critical temperature of phase demixing. We did not find any reduction of chain sizes at $T \Rightarrow T^c$, in agreement with the theoretical predictions of Muthukumar [9] and Raos and Allegra [8]. The abrupt shrinkage of the chains is revealed at $T < T^c$ along the dilute branch of the binodal. We thus conclude that the Flory exponent ν_F remains unchanged down to T^c, the critical polymer solution cannot be considered as an ensemble of shrunken, noninterpenetrating coils, and Eq. (1) does not hold at $T = T^c$. Our results are in qualitative agreement with recent experimental observations of Yoshikawa *et al.* [19], indicating substantial "softening" of the coil-globule transition in solutions of long DNA with the concentration of the biopolymer.

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