Partial Collapse and Reswelling of a Polymer in the Critical Demixing Region of Good Solvents

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Using small-angle neutron scattering, we explored the conformational behavior of a polymer in a mixture of good solvents near their critical demixing temperature T_C. Experiments at full and zero average neutron contrast were used to study the correlation length of concentration fluctuations ξ and the radius of gyration R_g of individual polymer coils as a function of temperature T. The results confirm a theoretically predicted partial collapse followed by reswelling of polymer coils to the original dimensions as $T \rightarrow T_C$. Reswelling begins when ξ becomes comparable to the R_g of the polymer.

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As pointed out by Flory [1]: “the better the solvent the greater the swelling of the molecule. Conversely, the poorer the solvent the smaller the molecule” captures all essentials of the polymer conformation transitions in solvents of different quality. In a good solvent the chain dimensions are expanded due to the excluded volume (repulsive) interactions between monomers. In a poor solvent the monomer-monomer interactions are attractive and a polymer chain collapses into a compact polymer globule. In a Θ solvent the attractive and repulsive forces compensate and the conformation of chains is “unperturbed” and described by Gaussian statistics. Solvent quality-induced swelling and contraction of polymers in individual solvents is now well understood and documented experimentally [2–7]. An even more rich conformational behavior is expected when a polymer is dissolved in a binary solvent where the components have different solvent qualities and affinities. The solvent quality of mixtures of poor solvents may become “good” and cause polymer swelling (cosolvency). Conversely, the solvent quality of a mixture of good solvents may become poor and induce polymer contraction (co-non-solvency) (see, e.g., [8] and references therein).

In this Letter we address the effect of temperature on the radius of gyration R_g of polymer coils in a mixture of good solvents near their critical demixing temperature T_C. Conformation of a polymer chain immersed in a binary critical mixture of good solvents near T_C was first considered theoretically by Brochard and de Gennes who predicted that a polymer chain should first contract and then resume its original dimension as $T \rightarrow T_C$ [9]. The counterintuitive polymer contraction in a mixture of good solvents is predicted to occur due to preferential adsorption of the “better” solvent on polymer segments that creates a molecular “cloud” attracting other polymer segments. The size of the cloud is of the order of the temperature dependent correlation length of concentration fluctuations ξ that diverges in the critical region. Hence, at a given temperature around T_C, ξ should become comparable to the R_g. At this point, the coils are effectively immersed in a “droplets” highly enriched by the better solvent, which should result in their reswelling and resuming the original dimensions found at $T \gg T_C$. The scaling arguments presented in [9] were later confirmed theoretically [8,10–12] and also by computer simulations [13]. Experimental investigations of this effect have been much less successful and currently only three studies have been reported in the literature. First, a ~30% contraction of polyethylene oxide (PEO) chains near T_C of tetrahydrofuran + water (THF + W) solutions was revealed in [14] using shear viscosity measurements. Second, dramatic ~300% reduction of the hydrodynamic radius R_H of polyacrylic acid (PAA) in the critical region of 2,6 lutidine + water (LW) mixture has been reported using dynamic light scattering [15]. In both studies no polymer reswelling was observed as $T \rightarrow T_C$. Experiments with the PAA + LW mixtures were later continued at much lower total polymer concentration using fluorescence correlation spectroscopy [16]. Contrary to [15], a significant reswelling of PAA chains was reported in [16]: R_H near T_C was claimed to exceed by ~300% R_H in the fully collapsed state and by ~70% R_H of the polymer far away from the critical temperature. This result leaves open a question on the physical reasons for the dramatic reswelling of PAA far beyond noncritical dimensions. Water is known to be a good solvent for PAA and a scaling relation between its molecular weight M_W and R_g reads $R_g = 0.215 M_W^{0.583 \pm 0.031}$ [17]. Using the relation between R_H and R_g for good solvents $R_H = 0.537\ R_g$ [18], we calculate the hydrodynamic radius of the studied in [16] PAA with $M_W = 134\,000$ in water to be $R_{H,\mathrm{H_2O}} \approx 113$ Å. The dimensions of PAA in LW mixture at $T \gg T_C$ reported in [16] ($R_H = 300$ Å) are almost by a factor of 3 larger than $R_{H,H2O}$ that may be explained by cosolvency of water and 2,6 lutidine. However, it is not obvious what might cause additional swelling when PAA coils become immersed in water as $\xi \rightarrow \infty$ in the critical region if water is a poorer solvent compare to the LW mixture.

Solutions of PEO in a partially miscible mixture of good solvents acetonitrile and water were chosen in this study. SANS experiments were conducted at full and zero average neutron contrast condition with a combination of five different solutes. (i) Polymer-free mixtures of 0.639 $H_2O + 0.361$ deuterated acetonitrile (DAN, CD_3CN) at the critical volume fraction of DAN $\phi_C = 0.361$ [19] were studied to explore the temperature variation of ξ. (ii) Polymer-free contrast-matched mixtures of 0.639 $(0.21H_2O + 0.79D_2O) + 0.361$ DAN were measured to demonstrate that contrast matching eliminates critical neutron opalescence. (iii) Dilute solutions of *h*-PEO (volume fraction 0.0019) in $(0.21H_2O + 0.79D_2O)$ and in (DAN) were explored to determine polymer dimensions in each solvent. (iv) Dilute solutions of *h*-PEO (volume fraction 0.0019 and 0.0038) in the contrast-matched critical mixture 0.639 $(0.21H_2O + 0.79D_2O) + 0.361$ DAN were studied to check for possible aggregation. (v) SANS from dilute solutions of (0.182 *h*-PEO + 0.818 *d*-PEO) with the total volume fraction 0.01 in the contrast-matched critical mixture 0.639 $(0.21H_2O + 0.79D_2O) + 0.361$ DAN were used to monitor R_g of individual polymer coils as a function of temperature.

Samples of a fully hydrogenous (*h*-PEO), $M_W = 35\,000$, $M_W/M_N = 1.09$ and deuterated (*d*-PEO), $M_W = 35\,000$, $M_W/M_N = 1.08$, were supplied by Polymer Source, Inc. The DAN and heavy water (D_2O), both with a degree of deuteration of 99.95% were obtained from Cambridge Isotope Laboratories. Each solution was contained in a thin-wall 2 mm quartz cell. The temperature was controlled to better than ±0.01 K and the critical demixing temperature T_C of each solution was detected visually by monitoring the appearance of the meniscus. SANS experiments were conducted at ORNL on the GP-SANS instrument [20] with a neutron wavelength of $\lambda = 6$ Å, $\Delta\lambda/\lambda \sim 0.13\%$. The overall covered range of scattering vector Q was 0.005 Å$^{-1} < Q < 0.1$ Å^{-1} ($Q = 4\pi\lambda^{-1}\sin\theta$, where 2θ is the scattering angle). The data were corrected for instrumental background as well as detector efficiency and put on absolute scale [neutron cross section $I(Q)$ in units of cm^{-1}] by means of precalibrated secondary standards.

For polymer-free solutions, $I(Q)$ is proportional to the difference between the scattering length densities (SLDs) of the components:

$$I(Q) \sim \left(\frac{\bar{b}_W}{v_W} - \frac{b_{\mathrm{DAN}}}{v_{\mathrm{DAN}}}\right)^2 \qquad (1)$$

where $\bar{b}_W = \phi_{D_2O} b_{D_2O} + (1 - \phi_{D_2O}) b_{H_2O}$ is a weighted scattering length of the mixture of light and heavy water; b_{DAN} is the scattering length of DAN; and v_W, v_{DAN} is the monomer volume of water and DAN molecule, respectively. The difference between the SLDs in Eq. (1) is proportional to the neutron contrast [3,21] that is maximal if $\phi_{D2O} = 0$. At this condition (full neutron contrast) SANS provides information on the correlation length ξ that enters the Ornstein-Zernike (O-Z) formula [3]:

$$I^{-1}(Q) = I^{-1}(0)(1 + Q^2\xi^2) \qquad (2)$$

It is known that ξ and $I(0)$ are both divergent functions of temperature as it approaches the critical temperature of phase demixing T_C [22]. For the purpose of monitoring the conformation of dilute polymers in the critical demixing region, the strong scattering signal from fluctuating solvent (critical neutron opalescence) should be minimized. This may be achieved by choosing ϕ_{D_2O} such that $\frac{\bar{b}_W}{v_W}$ is equal to $\frac{b_{\mathrm{DAN}}}{v_{\mathrm{DAN}}} = 4.92 \times 10^{10}$ cm^{-2} in Eq. (1) and thus $I(Q) \sim 0$. Using SLDs of light and heavy water (-5.6×10^{10} cm^{-2} and 6.37×10^{10} cm^{-2}, respectively) we calculate that this zero average contrast (ZAC) is reached at $\phi_{D_2O} = 0.79$. The SANS curves from critical solutions of 0.639 $H_2O + 0.361$ DAN (full neutron contrast) and 0.639 $(0.21H_2O + 0.79D_2O) + 0.361$ DAN (ZAC) are shown in Fig. 1. The inset in Fig. 1 shows the variation of ξ obtained by fitting $I(Q)$ to the O-Z Eq. (2). As may be seen, in the limit of low Q the scattering intensity from 0.639 $H_2O + 0.361$ DAN solution increases by more than 2 orders of magnitude as $T \rightarrow T_C (T_C = -1.175 \pm 0.010\,^\circ\mathrm{C})$. At the same time, $I(Q)$ from the contrast-matched solution remains constant and independent of temperature within experimental error in the critical region.

SANS data from dilute solutions of *h*-PEO with the volume fraction $\phi_H = 0.0019$ in DAN are shown in Fig. 2. Qualitatively similar scattering patterns (not shown) were obtained for dilute solution of *h*-PEO in $(0.21H_2O + 0.79D_2O)$. As is seen in Fig. 2, the scattering intensity is temperature independent between $T = 20\,^\circ$C and $5\,^\circ$C. The radius of gyration R_g of the polymer was determined by fitting the data to the model-independent Guinier formula [23]:

$$\ln I(Q) = \ln I(0) - \frac{Q^2 R_g^2}{3}, \qquad Q \rightarrow 0 \qquad (3)$$

and a representative fit to the Guinier formula for *h*-PEO + DAN solution is shown in the inset in Fig. 2. The measured R_g is temperature independent within the experimental error (see Fig. 4) and the average $R_g = 70.8 \pm 2.5$ Å in DAN and $R_g = 72.5 \pm 2.4$ Å in $(0.21H_2O + 0.79D_2O)$ also coincide within the uncertainties of the measurement, which points out to a similar quality of both solvents. Approximately equal dimensions of PEO in DAN and H_2O were reported previously in [24]. The measured R_g is larger than unperturbed dimension in melt $R_g(\Theta) = 0.35\sqrt{M_W} = 65.5$ Å [25] or in a theta solvent $R_g(\Theta) = 0.34\sqrt{M_W} = 63.6$ Å [26], which indicates a better than Θ

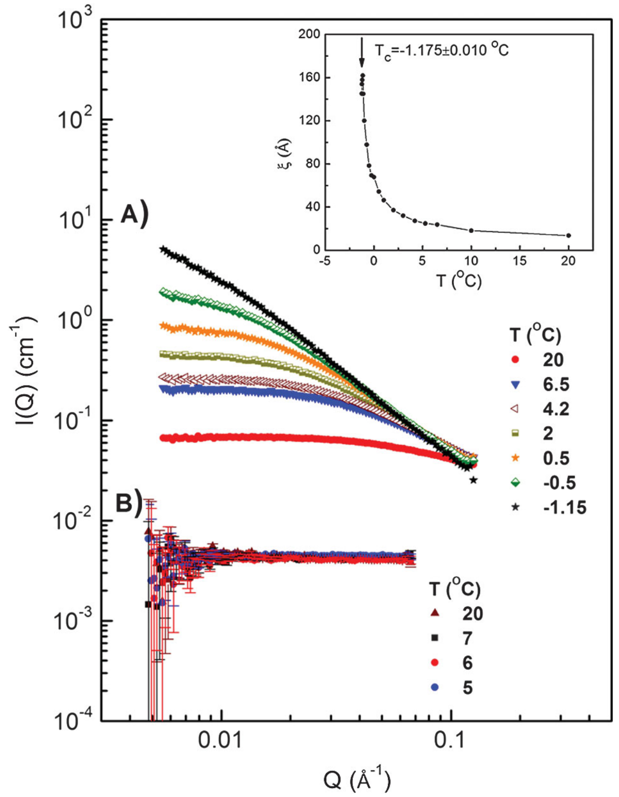

FIG. 1 (color). SANS intensities from A) 0.639 H_2O + 0.361 DAN solution (full neutron contrast) and B) 0.639 ($0.21H_2O$ + $0.79D_2O$) + 0.361 DAN solution (zero average contrast) as a function of temperature. Every second data set is shown for clarity. Critical temperature of solution A) is $T_C = -1.175 \pm 0.010\,^\circ\mathrm{C}$ and critical temperature of solution B) is $T_C = 4.25 \pm 0.010\,^\circ\mathrm{C}$. The inset shows the variation of ξ vs T-T_C for solution A).

solvent quality of both DAN and ($0.21H_2O + 0.79D_2O$) for PEO.

SANS data from h-PEO ($\phi_H = 0.0019$ and $\phi_H = 0.0038$) in a contrast-matched critical solution 0.639 ($0.21H_2O + 0.79D_2O$) + 0.361 DAN are shown in Fig. 3, which demonstrates a significant variation of $I(Q)$ with temperature in the low-Q region. The results of the Guinier fits to the data (the apparent R_g^*) are shown in the inset in Fig. 3. It may be seen that for $T > 10\,^\circ\mathrm{C}$ the apparent R_g^* (68–73 Å) is similar to the radii of gyration measured in DAN and in ($0.21H_2O + 0.79D_2O$) (71–73 Å). This indicates absence of the chain aggregation at $T \gg T_C$. Upon approaching the critical temperature, R_g^* increases by a factor of 2 ($\phi_H = 0.0019$ solution) and by a factor of 3 ($\phi_H = 0.0038$ solution) near corresponding T_C (4.30 °C and 4.65 °C, respectively). In the critical region R_g^* corresponds to the size of the polymer aggregates that are progressively growing as $T \rightarrow T_C$.

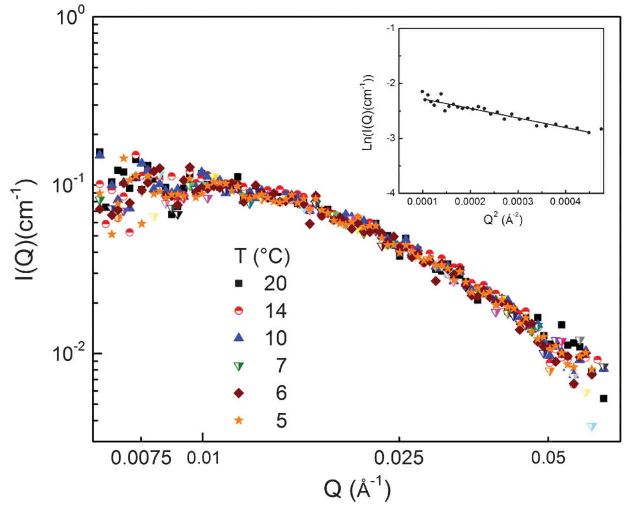

FIG. 2 (color). SANS from h-PEO ($\phi_H = 0.0019$) in DAN at various temperatures. The inset shows a representative Guinier plot for $T = 20\,^\circ\mathrm{C}$.

Information on the R_g of individual polymers in aggregating polymer solutions may be assessed using high concentration isotope labeling that is the method of choice for determining polymer dimensions in solutions of strongly interacting chains [5–7]. $I(Q)$ for solutions of identical protonated and deuterated polymers in a solvent is given by

$$\frac{I(Q)}{nN^2} = (b_H - b_D)^2 \phi_H (1 - \phi_H) P(Q) + v_P^2 \left[\frac{\bar{b}_M}{v_M} - \frac{b_S}{v_S} \right]^2 S(Q), \tag{4}$$

where $P(Q)$ is the single-chain (intramolecular) form factor which contains information on R_g; $S(Q)$ is the total scattering structure factor which embodies information on the total (both intra- and intermolecular) correlations between monomer units and is related to ξ; n and N are the number density and degree of polymerization of the polymer molecules; ϕ_H is the volume fraction of all chains that are protonated; b_H, b_D are the scattering lengths of the protonated and deuterated monomer unit; $\bar{b}_M = b_H \phi_H + b_D(1 - \phi_H)$ is a weighted scattering length of the mixture of protonated and deuterated monomers; and $\frac{b_S}{v_S}$ is the SLD of a solvent, which in our experiments is equal to that of DAN. The SLD of h-PEO (0.64×10^{10} cm^{-2}) and d-PEO (5.87×10^{10} cm^{-2}) monomers are such that at $\phi_H = 0.182$ the solution satisfies zero average contrast condition $\frac{\bar{b}_M}{v_M} = \frac{b_S}{v_S}$. Under this condition the second term in the right-hand side of Eq. (4) is zero, so the contribution of total scattering structure is eliminated, allowing R_g the individual chains to be determined using the Guinier Eq. (3).

Scattering curves from solutions of (0.182 h-PEO + 0.818 d-PEO) in the contrast-matched critical solution 0.639 ($0.21H_2O + 0.79D_2O$) + 0.361 DAN at total volume fraction of the polymer in solution 0.01 were measured in the vicinity of $T_C = 7.15 \pm 0.05$ and fitted to the Guinier formula. As may be seen in Fig. 4, the radii of gyration of individual PEO at $T > 10\,^\circ\mathrm{C}$ chains are independent of temperature and are ~25% larger than R_g of

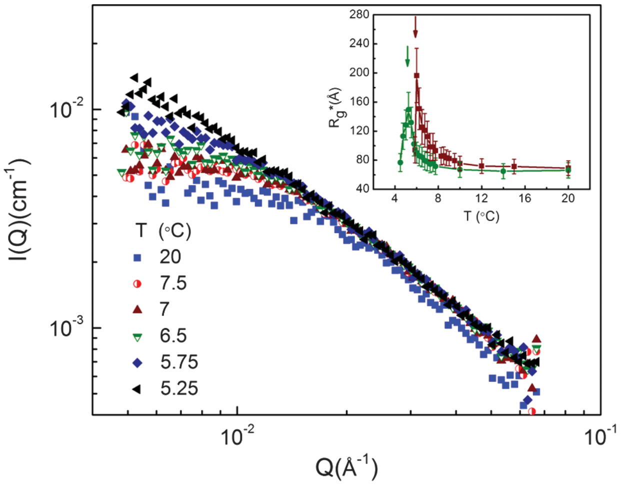

FIG. 3 (color). SANS from h-PEO ($\phi_H = 0.0038$) in 0.639 ($0.21H_2O + 0.79D_2O$) + 0.361 DAN solution (zero average contrast) as a function of temperature at various temperatures. The inset shows the variation of the apparent $R_g{}^*$ (the size of the aggregates) as a function of temperature for volume fraction of h-PEO $\phi_H = 0.0038$ (■) and $\phi_H = 0.0019$ (●) with the critical temperatures $T_C = 4.65 \pm 0.010\,°\mathrm{C}$ and $T_C = 4.30 \pm 0.010\,°\mathrm{C}$, respectively, marked with arrows.

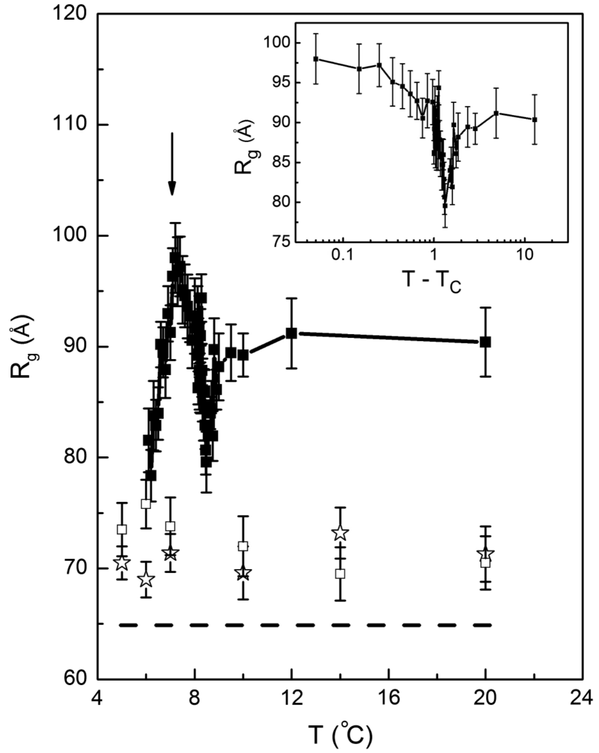

FIG. 4. The variation of R_g of individual PEO polymers as a function of temperature in DAN (\star) and in ($0.21H_2O + 0.79D_2O$) (□). R_g in each individual solvent is larger than unperturbed dimensions shown as a dash line. (■) represents the variation of R_g in the contrast-matched critical solution of (0.182 h-PEO + 0.818 d-PEO) in 0.639 ($0.79D_2O + 0.21H_2O$) + 0.361 DAN at total volume fraction of the polymer in solution 0.01. The inset shows the variation of R_g as a function of T-T_C on a semilog scale in the homogeneous region $T > T_C$. Critical temperature of this solution is $T_C = 6.9 \pm 0.010\,°\mathrm{C}$ (marked as an arrow).

PEO in DAN and ($0.21H_2O + 0.79D_2O$). In view of the fact that no aggregation of polymers was detected in this temperature range, the observed partial swelling PEO in DAN-water mixtures may be attributed to cosolvency of DAN and H_2O already documented in [24]. Below ~10 °C, i.e. ~3 degrees above T_C, the coils begin to gradually contract and the minimum size (~ 79.6 ± 2.5 Å) is reached at 8.48 °C, i.e. ~1.3 degree above T_C. At $T < 8.48\,°\mathrm{C}$ coils reswell and the largest R_g (98 ± 3 Å) is observed at $T \approx T_C$. Comparing the temperature variation of $\xi(T$-$T_C)$ (inset in Fig. 1) and $R_g(T$-$T_C)$ (Fig. 4) we conclude that the polymer conformation remains unaffected by concentration fluctuations in the mixed solvent with the characteristic sizes $\xi < 30$ Å. The contraction occurs in the range of the correlation length values 30 Å ≤ ξ ≤ 70 Å and reswelling begins when $\xi > 70$ Å, i.e., when the correlation length of the concentration fluctuations becomes comparable to the dimension of polymer chains.

In summary, we applied contrast-matching SANS to explore the temperature variation of R_g of individual polymer coils in the critical demixing region of good solvents. Far away from the critical temperature PEO coils are free from aggregation and partially swollen due to cosolvency of water and acetonitrile. Polymer contraction and aggregation begins 3–5 degrees above the critical temperature. Both effects are due to the higher affinity of water and PEO that induces attractive interactions between the monomers of the same polymer as well as between different polymers if they come into contact in course of thermal motion. The degree of the observed partial collapse (~ 25%) is similar to that of PEO in THF + W mixtures [14]. At the same time, the amplitude of the PEO conformational changes observed in this work is about an order of magnitude lower than previously reported collapse and swelling of PAA chains in LW [15,16]. Concentration fluctuations with $\xi < 30$ Å do not affect polymer conformation and contraction is observed in the range of $30 < \xi < 70$ Å. Reswelling of polymers begins as ξ becomes of the order of the radius of gyration of the polymer chains and terminates near the critical temperature where $\xi \gg R_g$. The R_g of the swollen PEO ($R_g = 98 \pm 3$ Å) is close to the original dimensions $R_g = 90 \pm 3$ Å at $T \gg T_C$. All of these conclusions are in agreement with the theoretical predictions [9–12].

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