Polymer Conformation near the Critical Point of a Binary Mixture

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Conformation of a flexible linear polymer (polyacrylic acid, PAA) in a binary mixture (water + 2,6-lutidine, LW) near the critical point of LW is studied using dynamic light scattering (DLS) by which the diffusivities of the polymer molecules and the critical composition fluctuation of the LW are measured. The DLS measurements, supplemented by viscosity data, show that the PAA molecule in LW shrinks when approaching the critical point of LW. At temperature T close to the critical temperature T_c when the correlation length ξ of LW is comparable to the intermolecular distance of PAA, we find that $\xi \propto (1 - T/T_c)^{-\nu}$ with $\nu = 0.44 \pm 0.03$ which is smaller than $\nu = 0.60$ of pure LW. [S0031-9007(97)05094-1]

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At present, the conformation of a flexible linear polymer chain in a single component solvent can be understood satisfactorily using the two parameter theory and the renormalization group theory [1]. However, if the solvent is a binary mixture, one of the components (presumably the better solvent) may be preferentially adsorbed to the polymer [2]. de Gennes [3] pointed out that such a preferential wetting layer will contribute an indirect attraction among the monomers within the polymer chain, and the indirect attraction will reduce the size of the macromolecule. Obviously, the interaction range of this composition fluctuation driven attraction is the width of the preferential wetting layer which is the solvent correlation length. Since the correlation length diverges at the critical point of the binary mixture, the polymer molecule should shrink and collapse when approaching the critical point of the binary mixture [3]. Although such interesting phenomenon has been observed in computer simulation [4], no experimental confirmation has been reported. It is difficult to study the polymer conformation close to the critical point of the solvent [5] because most polymers become insoluble due to a diverging interaction parameter [4,6]. Nevertheless, after many trials and much testing, we find that the flexible linear polymer polyacrylic acid (PAA) remains soluble in 2,6-lutidine + water (LW) even at the critical point of LW. Presumably, close to the critical point, because of preferential adsorption, the LW concentration inside the PAA molecule is shifted with respect to that of the bulk LW [7] so that precipitation of PAA can be avoided.

In this Letter, we report the first dynamic light scattering (DLS) experiment in which both the conformation of the polymer and the critical dynamics of the binary mixture can be measured simultaneously. The DLS data, together with viscosity measurements, show that the size of the polymer in a critical binary mixture does decrease towards the critical point of the binary mixture. This provides evidence of the indirect attraction due to the critical composition fluctuation of the binary solvent. On the other hand, if we consider the polymer as a random field [8] acting on the binary mixture, the critical behavior of the binary mixture should be affected by the presence of the macromolecules [9,10]. From the DLS measurement, at temperature T close to the critical temperature T_c of LW such that the correlation length ξ of LW is comparable to the intermolecular distance of PAA, we find that $\xi \propto (1 - T/T_c)^{-\nu}$ with the critical exponent ν changed from 0.6 for the pure LW to 0.44 due to the presence of PAA.

In our experiments, samples of polyacrylic acid dissolved in the critical binary mixture 2,6-lutidine + water is studied. LW has an inverted coexistence curve with a lower critical temperature about 33.7 °C at the critical composition of 28.2% lutidine by weight [11]. PAA of molecular weight $M_w = 7.5 \times 10^5$ and polydispersity equal to 1.4 from Aldrich Chemicals is used as purchased. Although PAA is soluble in water it is insoluble in lutidine. We dissolve PAA in critical LW such that the PAA concentration in the sample (LW/PAA) is 0.7 mg/cm^3. The PAA, being a third component of LW, shifts the critical temperature down by 0.2 °C below that of the pure LW without PAA [12]. The LW/PAA sample is then sealed in a 1 mm path length cell made of 1.25 mm thick quartz. Light scattering experiments are performed in a transparent rectangular water bath with a temperature stability of ±0.001 °C. We direct a He-Ne laser beam of wavelength $\lambda = 633$ nm to the sample, and the scattering of the sample is detected by a photon counting photodiode module (EG&G SPCM-100) at the scattering angle of $\theta = 90°$. This corresponds to a scattering vector $q \equiv (4n\pi/\lambda)\sin(\theta/2) = 1.87 \times 10^5$ cm^{-1}, where $n = 1.35$ is the refractive index of LW. The signal from the photodiode is fed to a digital correlator (ALV-5000) for extracting the intensity autocorrelation function $g_2(t)$.

For pure LW, $g_2(t)$ is a simple exponential decay function of the following form: $g_2(t) = 1 + A|g_1(t)|^2$ with $g_1(t) = e^{-\Gamma_0 t}$ and $\Gamma_0 = Dq^2$, where D is the diffusion constant (see the inset of Fig. 1). For the LW/PAA

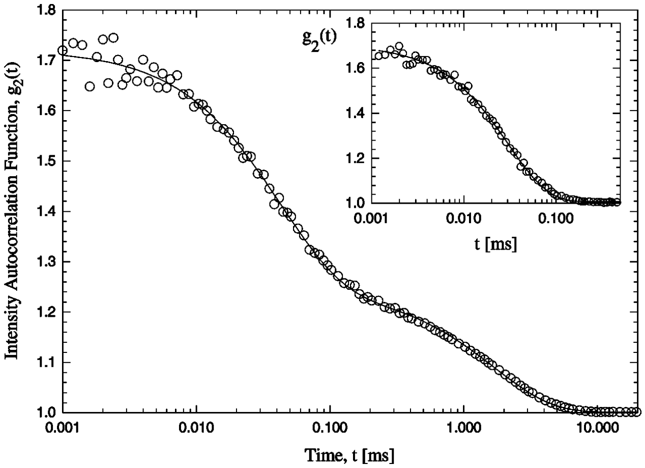

FIG. 1. Intensity autocorrelation function $g_2(t)$ for the LW/PAA sample at 9.45 °C from the critical temperature. The solid line is the least square fit of $g_2(t)$ to the functional form $B + (A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t})^2$. The inset shows the $g_2(t)$ obtained for the pure LW sample at 8.55 °C from the critical temperature. The solid line in the inset is the fit of $g_2(t)$ to the simple exponential form: $1 + Ae^{-2\Gamma_0 t}$.

sample, $g_2(t)$ is no longer single exponential. Nevertheless, at 9.45 °C from T_c, the shape of $g_2(t)$ for the LW/PAA sample (see Fig. 1) suggests two separate relaxation processes. Fitting $g_2(t)$ to the double exponential form, $g_2(t) = B + (A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t})^2$, we obtain $B = 1.00$, $A_1 = 0.39$, $A_2 = 0.42$, $\Gamma_1 = 19.4\ \text{ms}^{-1}$, and $\Gamma_2 = 0.30\ \text{ms}^{-1}$. We identify Γ_1 as the relaxation rate of the composition fluctuation of LW because the decay rate Γ_0 for the pure LW sample measured at this temperature is numerically the same as Γ_1. Then, the slower decay rate Γ_2 is due to the diffusion of the PAA molecules.

Since composition fluctuation of LW relaxes via diffusion and the Brownian motion of the PAA molecules is also diffusive, the above interpretation can be checked by the angular dependence of the decay rates. Thus we measure $g_2(t)$ at other scattering angles ($\theta = 70°$, 80°, 90°, 100°, 110°, and 120°) and extract the decay rates by fitting $g_2(t)$ to the double exponential form. The results, which are plotted in Fig. 2, confirm the linear dependence of Γ_1 and Γ_2 on q^2. From the slopes, the diffusion constant of LW and that of the PAA molecules are $5.2 \times 10^{-7}\ \text{cm}^2/\text{s}$ and $1.1 \times 10^{-8}\ \text{cm}^2/\text{s}$, respectively. The correlation length of LW is found to be $\xi = 1.7$ nm, using the Stoke-Einstein relation, $D = kT/6\pi\eta\xi$, where k, T, and $\eta = 2.3$ cP are the Boltzmann constant, the sample temperature, and the viscosity of LW, respectively. Similarly, we can calculate the hydrodynamic radius $R_h = 106$ nm of the PAA molecule from its diffusion constant. Note that the fraction $A_2/(A_1 + A_2)$, which indicates the contribution of PAA molecules to the scattering intensity, decreases monotonically from 0.62 at $\theta = 70°$ to 0.37 at $\theta = 120°$ as shown in Fig. 2(c). This is because $q\xi < 0.04$ and $qR_h > 1$ within this angular range. So the scattering by the composition fluctuation of LW, which is $1/(1 + q^2\xi^2)$, is practically isotropic [13]. In contrast, the scattering by the PAA molecules, which is $1/(1 + \frac{1}{2} q^2 R_h^2)$, is stronger at smaller scattering angles [14].

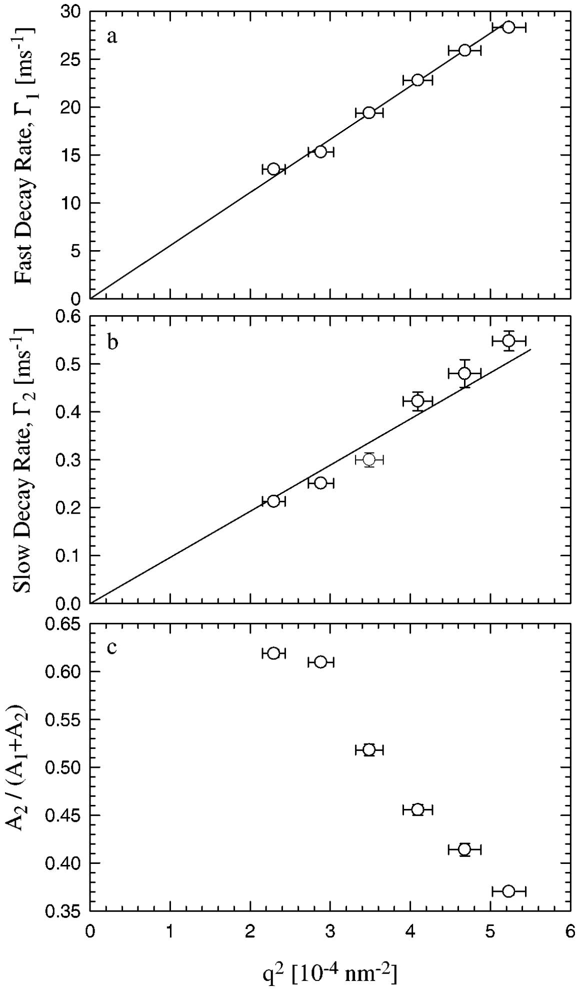

FIG. 2. Angular dependence of (a) the fast decay rate Γ_1, (b) the slow decay rate Γ_2, and (c) the fraction $A_2/(A_1 + A_2)$ for the LW/PAA sample measured at 9.45 °C from T_c.

For the composition fluctuation of LW to have a significant effect on the conformation of the PAA molecule, ξ should be comparable to the average intermonomer distance r within the PAA molecule. Let the volume occupied by a PAA molecule be $\frac{4}{3}\pi R_h^3$. Then, $r = (\frac{4}{3}\pi m/M_w)^{1/3} R_h$, where $m = 72$ is the formula weight of the monomer. At $\Delta T \equiv T_c - T = 9.45$ °C, $R_h = 106$ nm so that $r = 7.4$ nm. At this temperature, $\xi = 1.7$ nm is comparable to, but smaller than, r. To study the effect of increasing ξ on the PAA conformation, we perform the light scattering measurement at temperatures closer to T_c.

Figure 3 shows the variations of the decay rates at a 90° scattering angle with respect to the temperature difference ΔT. One can divide this figure into three temperature regimes. In regime (I) when $\Delta T > 1.5$ °C, the correlation

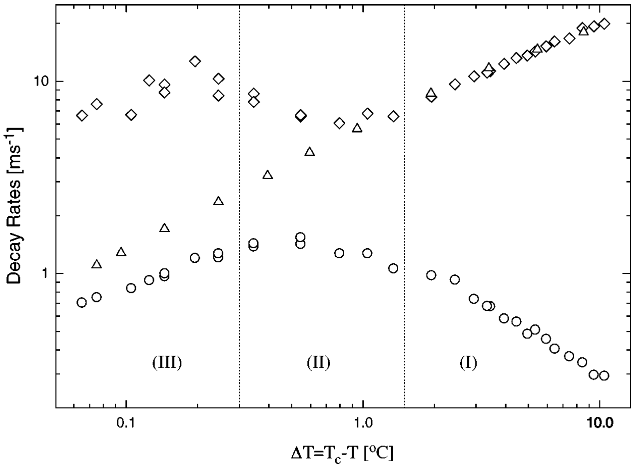

FIG. 3. Variations of the decay rates Γ_1 (◇) and Γ_2 (○) with respect to $\Delta T \equiv T_c - T$. For comparison, the decay rate Γ_0 (△) obtained from the pure LW sample under the same experimental conditions is also plotted in this figure.

length of LW extracted from $\xi = kTq^2/6\pi\eta\Gamma_1$ increases from 1.6 nm at $\Delta T = 10.44$ °C to 3.9 nm at $\Delta T = 1.94$ °C. The change of ξ in this temperature range agrees quantitatively with that of the correlation length calculated from Γ_0 measured for the pure LW sample. On the other hand, the hydrodynamic radius of the PAA molecule obtained from Γ_2 decreases from 109 nm to 32.8 nm when ΔT decreases from 10.44 °C to 1.94 °C. As ΔT decreases below 1.94 °C, Γ_1 starts to deviate from Γ_0 while Γ_2 is nearly constant in regime (II). Presumably, the presence of the PAA molecules starts to affect the critical composition fluctuation of LW. There may be very complicated interaction between LW and PAA in regime (II), and the physics is unclear at this moment.

In regime (III) when $\Delta T < 0.3$°C, as T approaches T_c, Γ_1 fluctuates at about 10 m s^{-1}, while Γ_2 decreases and converges to Γ_0. Therefore, we associate Γ_1 and Γ_2 to the critical composition fluctuation of LW and the diffusion of the PAA molecules, respectively. The size of the PAA molecules estimated from the mean value of Γ_1 in this regime is about 5 nm, which is less than $\frac{1}{20}$ times that at 10.44 °C from T_c. However, it should be pointed out that $A_1/(A_1 + A_2) > 0.9$ in this regime. Thus the observed light scattering is dominated by the critical opalescence of LW, and it is difficult to obtain accurate data for the diffusion of the polymer by fitting $g_2(t)$ to the double exponential form. This explains the large scattering of the data for Γ_1 in this regime. Therefore we need another method to deduce the size of PAA molecules in this regime.

Since the shear viscosity of a polymer solution is an increasing function of the size of the polymer molecule, we can measure the shear viscosity of the LW/PAA sample to check the shrinking of the PAA molecules towards the critical point of LW. Using a video imaging system, we determine the terminal speed u of a small steel ball falling in the sample contained in a 2 cm diameter cylindrical sample cell which is placed in the water bath used in the light scattering experiment. Equating the buoyance force $\frac{4}{3}\pi b^3 \Delta\rho g$ to the drag force $6\pi\eta_s bu\Phi$ on the falling ball, the shear viscosity of the sample is $\eta_s = \frac{2}{9}\,\Delta\rho g b^2 (u\Phi)^{-1}$. Here $b = 0.1$ cm is the radius of the steel ball, $\Delta\rho = 7$ g/cm^3 is the density difference between steel and the LW/PAA sample, $g = 981$ cm/s^2 is the acceleration due to gravity, and $\Phi = 1.21$ is the correction to the drag force due to the finite size of the cylindrical cell [15]. Figure 4 shows the results of the shear viscosity measurement. One can see that η_s decreases from 570 cP at 10.5 °C from T_c to 110 cP at 0.06 °C from T_c. On the other hand, the viscosity η of pure LW varies from 2.60 to 2.47 cP [11] and that of water containing 0.7 mg/cm^3 PAA remains constant at 72 ± 5 cP within this temperature range. Therefore, the decrease in η_s towards T_c is clearly the result of the shrinking of the PAA molecules induced by the criticality of LW.

It should be pointed out that the shear viscosity data for the LW/PAA sample is very different from those measured by Staikos and Dondos [10] for polystyrene (PS) and polyethylene glycol (PEG) in a critical mixture of cyclohexane-methanol (Ch-MeOH). They observed, instead of a decreasing shear viscosity as in our LW/PAA sample, an increasing shear viscosity towards the critical point of the binary mixture. They claimed that the increase of shear viscosity was not due to the change in the size of the macromolecules. Note that the molecular weights ($M_w = 7700$ for PS and $M_w = 6000$ for PEG) of their polymers were much smaller than that ($M_w = 7.5 \times 10^5$) of the PAA used in our experiments. The differences in the molecular weights mean that the molecular sizes of their polymers are much smaller than that of our PAA sample. Then, even if there was contraction or expansion of the macromolecules, the effect would be too small to significantly affect the shear viscosity of

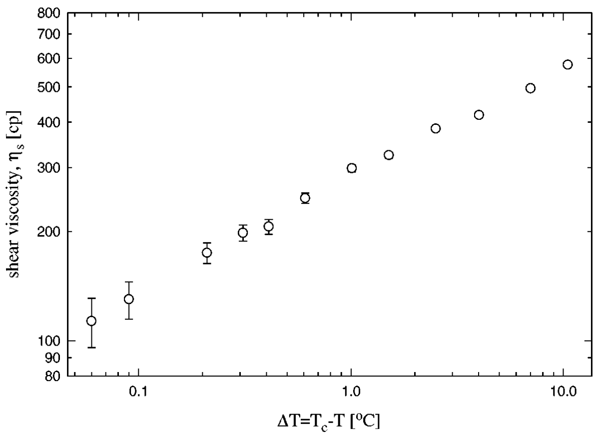

FIG. 4. Variation of the shear viscosity η_s of the LW/PAA sample with respect to the reduced temperature ϵ.

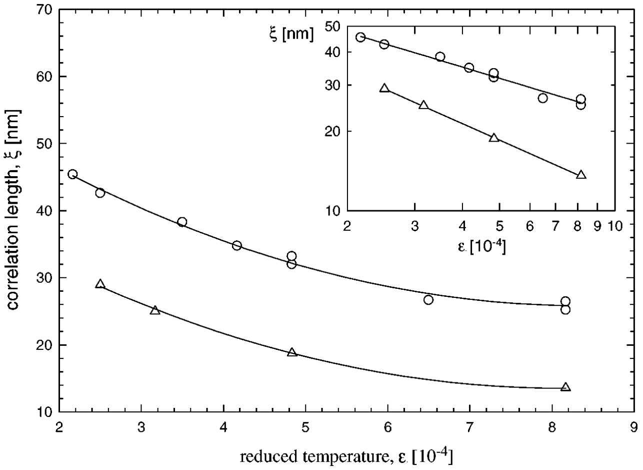

FIG. 5. Variations of the correlation length ξ of the LW/PAA sample (○) and the pure LW sample (△) with respect to the reduced temperature ϵ. The inset is a log-log plot of ξ against ϵ. The curves (and the corresponding straight lines in the inset) are the lines of best fit to the power law $\xi \propto \epsilon^{-\nu}$ with $\nu = 0.44$ and 0.60 for the ○ and the △ points, respectively.

their samples. In fact, the difference in shear viscosity for Ch-MeOH with and without the polymer was less than 40% in their experiments. In contrast, the shear viscosity increases by more than 250 times when PAA is added to LW at 10.5 °C from T_c. Such a large thickening effect is usually observed in a semidilute solution when the macromolecules begin to overlap [14]. This happens when the size of the polymer is comparable to the intermolecular distance a of the polymer molecules. In the LW/PAA sample, with $c = 0.7$ mg/cm^3 being the concentration of PAA and N_A being the Avogadro number, $a = (cN_A/M_w)^{-1/3} = 120$ nm which is indeed larger than R_h at this temperature. Therefore the shear viscosity η_s of the LW/PAA sample becomes very sensitive to the size of the macromolecules, which shrinks and causes η_s to decrease when approaching the critical point.

Staikos and Dondos explained the increased shear viscosity of their samples by the increase of the correlation length of Ch-MeOH due to the presence of the polymer. Clearly such an effect is most significant when the correlation length ξ is comparable to the intermolecular distance a of the polymer. Thus, the effect of a polymer enhanced correlation length should be observable in the LW/PAA sample close to the critical point when ξ can be very large. Indeed, in regime (III) in Fig. 3, ξ calculated from the decay rate Γ_2 of the LW/PAA sample is larger than that calculated from Γ_0 of the pure LW sample. In Fig. 5, ξ is plotted against the reduced temperature $\epsilon \equiv \Delta T/T_c$. Note that ξ for the LW/PAA sample which is larger than 25 nm, is comparable to a. Thus the enhanced correlation length of LW by the polymer is confirmed in this regime. In addition, the inset in Fig. 5 shows that ξ for the pure LW sample follows the usual scaling behavior $\xi \propto \epsilon^{-\nu}$ and the critical exponent ν is found to be 0.6, which agrees with that measured by Gulari *et al.* [11]. On the other hand, fitting ξ for the LW/PAA sample to a power law gives $\nu = 0.44 \pm 0.03$ which is smaller than $\nu = 0.60$ for pure LW. Hence, it is possible that the LW samples with and without PAA may not belong to the same universality class. Currently, more detailed investigation is being carried out to check this speculation.

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[1] H. Fujita, *Polymer Solution* (Elsevier, Amsterdam, 1990); H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971); K. F. Freed, *Renormalization Group Theory of Marcromoleclues* (Wiley, New York, 1987).
[2] I. Katime and J. R. Ochoa, Eur. Polym. J. **20**, 99 (1984).
[3] P. de Gennes, J. Phys. **37**, 59 (1976).
[4] J. Magda, G. Fredrickson, R. Larson, and E. Helfand, Macromolecules **21**, 726 (1987).
[5] K. To, C. K. Chan, and H. J. Choi, Physica (Amsterdam) **221A**, 223 (1995); K.-Q. Xia, Ph.D. dissertation, University of Pittsburgh, 1987.
[6] A. Shultz and P. J. Flory, J. Polym. Sci. **15**, 231 (1955).
[7] F. Brochard and P. de Gennes, Ferroelectrics **30**, 33 (1980).
[8] P. G. de Gennes, J. Phys. Chem. **88**, 6469 (1984); Y. Imry and S. Ma, Phys. Rev. Lett. **35**, 1399 (1975).
[9] K.-Q. Xia and J. V. Maher, Phys. Rev. A **37**, 3626 (1988); J. V. Maher, W. I. Goldburg, D. W. Pohl, and M. Lanz, Phys. Rev. Lett. **53**, 60 (1984).
[10] G. Staikos and A. Dondos, Phys. Rev. A **33**, 4479 (1986).
[11] E. Gulari, A. F. Collings, R. L. Schmidt, and C. J. Pings, J. Chem. Phys. **56**, 6169 (1972).
[12] R. H. Cohn and D. T. Jacobs, J. Chem. Phys. **80**, 856 (1984).
[13] W. I. Goldburg, in *Light Scattering Near Phase Transitions,* edited by H. Z. Cummins and L. P. Levanyuk (North-Holland, New York, 1983), Chap. 9.
[14] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, New York, 1987).
[15] A. Ambari, B. Gauthier-Manuel, and E. Guyon, J. Fluid Mech. **149**, 235 (1984).