Critical Anomaly of Complex Shear Modulus in Polymer Solutions: Viscoelastic Suppression of Order Parameter Fluctuation due to Dynamic Asymmetry

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The critical anomaly of the complex shear modulus has been studied for ideal polymer solutions in the frequency range from 1 Hz to 400 Hz. The logarithmic critical divergence is observed for both the real and imaginary parts of the complex shear modulus. It is found that the strength of the critical anomaly decreases with an increase in the degree of polymerization N, while the noncritical background increases with N, indicating the significance of the viscoelastic effect. The critical anomaly is likely suppressed by the viscoelastic effects through the spontaneous coupling between the stress field and the order parameter fluctuation.

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Dynamic critical phenomena have been extensively studied in the past three decades from both the experimental and the theoretical viewpoints, and the concepts of dynamic scaling and dynamic universality have been established [1]. The behavior has been classified in terms of the types of Hamiltonian, order parameter, and kinetic effects [1,2]. Binary polymer mixtures and polymer/liquid mixtures have so far been believed to belong to the same dynamic universality class as classical fluids (the so-called *model H*) [2]. It is well known that entangled polymer solutions behave like elastic gels when the characteristic deformation time is shorter than the rheological time, while they behave like viscous fluids for slower deformation. Thus we would like to raise the following question: How is the order parameter fluctuation affected by the viscoelastic properties or slow molecular dynamics? All the previous theories assume that elementary molecular dynamics is much faster than critical dynamics, or diffusion is a limiting process. This assumption is true for *dynamically symmetric mixtures*; however, it could be violated by the slow molecular dynamics of a component for *dynamically asymmetric mixtures.* In polymer solutions and polymer blends, viscoelasticity likely plays an important role when the critical dynamics is comparable to or faster than the characteristic rheological time. In this Letter we demonstrate that the slow polymer dynamics strongly affects the critical fluctuation of the order parameter and causes the suppression of the critical anomaly in the complex shear modulus of a polymer solution.

The systems studied were critical mixtures of monodisperse polystyrene (PS) and diethyl malonate (DEM). The weight-average molecular weight (M_w) of PS, the polydispersity ratio (M_w/M_n, M_n: number-average molecular weight), and the critical polymer composition (ϕ_c) and temperature (T_c) of the mixture are listed in Table I. Since the densities of the components are matched, there is little effect of gravity [3]. The θ point (tricritical point [4]) of the mixture is estimated as $50 \pm 5\,^\circ$C by extrapolating T_c for $N = \infty$ from all the existing data of ϕ_c and T_c for various N [3,5,6] including our data. The large error bar of θ is likely due to the significant impurity effect of water to T_c for this mixture [6].

The complex shear modulus of a mixture was measured by an instrument developed by us [7]. A sample was sandwiched by two piezoelectric transducers through two parallel glass plates having optically flat surfaces. The complex mechanical transfer function $Z^*(f)$ was measured as a function of an excitation frequency f. The spacing between the two glass plates (i.e., sample thickness) d was set to 100 μm. The frequency spectrum of the complex shear modulus $G^*(f)$ should be proportional to $Z^*(f)$ when the decay length of the shear wave is much longer than d. We used a multifrequency excitation method to obtain a whole spectrum from 1 Hz to 400 Hz within a short time. The excitation signal used was $\sum_n A \sin(2\pi f_n t)$ (A denotes amplitude, $f_n = 4n+1$, n = 0–100). The temperature was controlled within ± 0.03 K by circulating the temperature-controlled water inside the cell. The details of the instrument will be described elsewhere [8]. In the experiment, the temperature of the sample having a critical composition was scanned from far above T_c to T_c. Since the phase diagram of the polymer solution can be scaled by $t_c = (T_c - \theta)/\theta$ and ϕ_c in the plane of $t = (T - \theta)/\theta$ and ϕ (polymer composition) into the universal phase diagram [9], the experimental paths for our four critical mixtures can be drawn as a single line ($\phi/\phi_c = 1$) in the scaled $t - \phi$ phase diagram. Thus the paths are identical irrespective of N and the critical behavior could be directly compared among the critical mixtures having different N.

Figures 1(a) and 1(b) show the temperature dependences of the real and imaginary parts of $G^*(f)$, respectively, for PS-2/DEM (7.0 wt% PS). We can clearly see

TABLE I. Physical characteristics of polymer solutions

PS	M_w (10^5)	M_w/M_n	ϕ_c (wt% PS)	T_c (°C)
PS-1	1.02	1.02	9.5	4.8
PS-2	1.80	1.06	8.7	15.8
PS-3	3.55	1.02	7.0	21.0
PS-4	12.6	1.05	4.0	28.8

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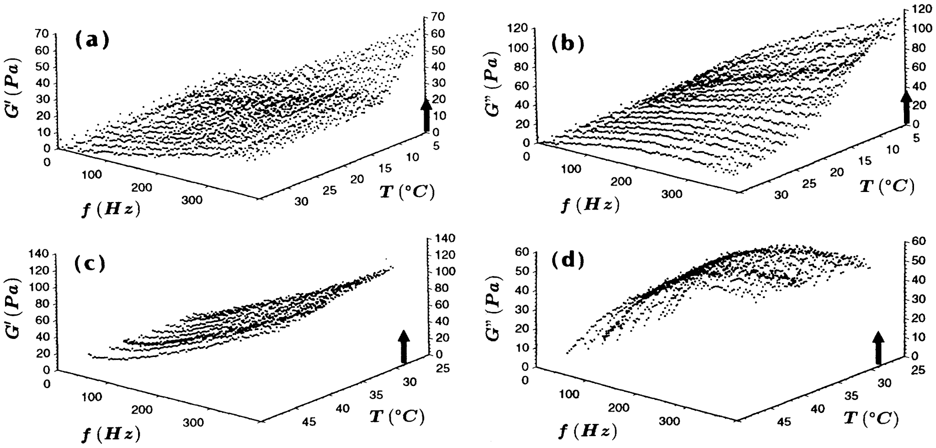

FIG. 1. Temperature dependence of complex shear modulus spectra for PS-2/DEM [(a) and (b)] and for PS-4/DEM [(c) and (d)]. Arrows indicate T_c of each mixture.

the increases in both real and imaginary parts with approaching T_c. In this mixture $G''(f)$ [the real part of $G^*(f)$]$\propto f^2$ and $G''(f)$ [the imaginary part of $G^*(f)$] $\propto f$, although there are slight deviations from the relations. This indicates that the characteristic rheological time τ_t is likely shorter than 1 ms. Figures 1(c) and 1(d) show the temperature dependences of the real and imaginary parts of $G^*(f)$, respectively, for PS-4/DEM (4.0 wt% PS). Here no critical anomaly is observed. We can clearly see the deviation of $G'(f)$ and $G''(f)$ from the f^2 and f dependences, respectively. This relaxational behavior suggests that τ_t is longer than 1 ms for this mixture. Figures 2(a) and 2(b) summarize the dependences of $G'(f)$ and $G''(f)$ on temperature at $f = 150$ Hz, respectively, for the four different molecular weights. This frequency is close to the upper frequency limit satisfying $G''(f) \propto f$. The striking feature is that the critical anomaly in both $G'(f)$ and $G''(f)$ decreases with an increase in the degree of polymerization N. In particular, for the mixture of PS-4/DEM, we cannot see any critical anomaly even at the critical composition in the measurement temperature range. It should also be noted that the background parts of $G^*(f)$ steeply increase with an increase in N. This suggests stronger viscoelastic effects for larger N. Figure 3 indicates the N dependence of the critical anomaly of $G^*(f)$, $\Delta G^*(f)$. In the figure, $\Delta T = T - T_c$. Although the critical anomaly can be well described by the logarithmic divergence [10], the strength of the anomaly decreases with an increase in N beyond the prediction of conventional theories for critical binary fluids [10,11].

Here we discuss the physical mechanism for the decrease in the critical amplitude with N. The characteristics of long chainlike molecules can be summarized by the large molecular size (spatial characteristics) and the slow dynamics (dynamic characteristics). First we consider the former effect. Critical fluctuation is suppressed for large N by the constraints that (i) the correlation length should be comparable to the chain size at the θ point and (ii) $\theta - T_c$ is proportional to $N^{-1/2}$. Thus the static correlation length ξ has the following dependence on N [4]: $\xi = R_g[(\theta - T_c)/(T - T_c)]^\nu = R_g N^{-\nu/2}\epsilon^\nu$ and $\xi_0 = R_g N^{-\nu/2}$. Here $\epsilon = \Delta T/T_c$, ν is the critical exponent of ξ ($\nu \sim 0.63$), and R_g is the radius of gyration. However, this static suppression is much weaker than the following dynamic one: It does not cause the change in the amplitude of the logarithmic divergence since the critical anomaly of viscosity is proportional to $\ln \xi$ according to the conventional theories [10]. The temperature distance between T_c and θ is also important from another aspect; i.e., revealing how to understand the competition between critical and tricritical effects [4,12–14]. This might be significant for a critical polymer solution in the

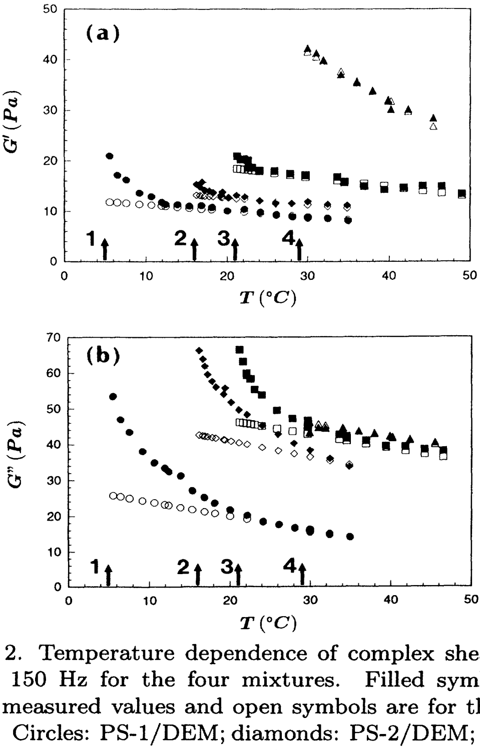

FIG. 2. Temperature dependence of complex shear modulus at 150 Hz for the four mixtures. Filled symbols are for the measured values and open symbols are for the background. Circles: PS-1/DEM; diamonds: PS-2/DEM; squares: PS-3/DEM; and triangles: PS-4/DEM. Arrows 1–4 indicate T_c's for PS-1–4/DEM, respectively.

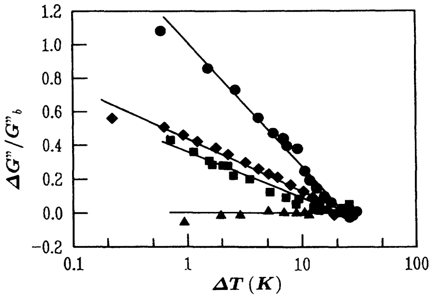

FIG. 3. Temperature dependence of the anomalous part of G'' ($\Delta G''$) scaled by the background part G''_b. Note that $\Delta G''/G''_b \sim \Delta\eta/\eta_b$. Circles: PS-1/DEM; diamonds: PS-2/DEM; squares: PS-3/DEM; and triangles: PS-4/DEM.

limit of large N; however, in our case tricritical effects likely play few roles in critical dynamics of concentration fluctuation as in usual cases [1,3,6]. It should be noted that the above static effect likely causes the drastic suppression of the critical anomaly of the bulk viscosity since its critical amplitude is proportional to ξ_0^{-3} [15].

Next we discuss the dynamic effect. The striking dynamic effect comes from the viscoelastic effect, which reflects the topological characteristics of chains. The critical composition $\phi_c \sim N^{-1/2}$ where chains are closely packed is located in the crossover region from the dilute (Rouse) regime to the semidilute (reptation) regime (see, e.g., Fig. 3 in Ref. [12]). The quantitative treatment of viscosity in this regime has never been established [4], but the rheological behavior at ϕ_c can be estimated at least qualitatively as follows. The characteristic rheological time τ_t at $\phi = \phi_c$ is related to the viscosity η as $\eta \propto \phi_c \tau_t k_B T/N$. On the other hand, the characteristic decay time of concentration fluctuation free from the viscoelastic effect is estimated by $\tau_\xi = \xi^2/D_\xi$ ($D_\xi = k_B T/6\pi\eta\xi$). By using the relation $\phi_c \sim N^{-1/2}$, $\tau_\xi/\tau_t \sim (N^{1/2}\epsilon)^{-3\nu}$. When τ_ξ is comparable to or shorter than τ_t (for large N or large ϵ), the concentration fluctuation could be severely suppressed by the elastic effect [16]. This is a kind of relaxational phenomenon between the two internal frequencies (τ_ξ^{-1} and τ_t^{-1}) characterizing the system. In the following, we consider this problem on a more quantitative basis.

The coupling between stress field and diffusion was first noticed and studied by Brochard and de Gennes [17] for a polymer solution far from the critical point. Recently the problem has been extensively studied by many researchers in connection with shear-induced phase separation from the theoretical viewpoints [18–20]. Very recently Doi and Onuki [20] have derived the following general diffusion equations including the dynamic coupling between stress and composition, on the basis of the two fluid model:

$$\frac{\partial \phi}{\partial t} = -\nabla\cdot(\phi \boldsymbol{v}) + \nabla\cdot\left[\frac{\phi^2(1-\phi)^2}{\zeta}\left(\nabla\frac{\delta F}{\delta\phi} - \frac{\nabla\cdot\boldsymbol{\sigma}^{(n)}}{\phi}\right)\right], \tag{1}$$

$$\boldsymbol{v}_p - \boldsymbol{v}_s = -\frac{1-\phi}{\zeta}\nabla\cdot[\pi\boldsymbol{I} - \boldsymbol{\sigma}^{(n)}], \tag{2}$$

$$\rho_0\frac{\partial \boldsymbol{v}}{\partial t} = \nabla\cdot[-(\pi+p)\boldsymbol{I} + \boldsymbol{\sigma}^{(n)}] + \eta_0\nabla^2\boldsymbol{v}. \tag{3}$$

Here $\boldsymbol{v}_p(\boldsymbol{r},t)$ and $\boldsymbol{v}_s(\boldsymbol{r},t)$ are the average velocities of polymer and solvent at point $\boldsymbol{r}$ and time t, and $\boldsymbol{v} = \phi\boldsymbol{v}_p + (1-\phi)\boldsymbol{v}_s$. $\phi(\boldsymbol{r},t)$ is the composition of polymer. ρ_0 is the average density and p is the pressure. ζ stands for the friction constant per unit volume and is of order $\eta_s\xi_b^{-2}$, where η_s is the solvent viscosity and ξ_b is the so-called blob size. The essential point is that the stress in entangled polymer systems is supported by chains; thus a gradient in the stress causes a net force on the chains as well as a gradient in the osmotic pressure π and leads to the motion of the chains relative to the solvent [see Eq. (2)]. Near a critical point, the free energy F is given in the Ginzburg-Landau form as follows:

$$F = \int d\boldsymbol{r}\left[-\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{K}{2}(\nabla\phi)^2\right].$$

In the linear response regime $\boldsymbol{\sigma}^{(n)}$ is generally given by

$$\sigma_{ij}^{(n)} = \int_{-\infty}^{t} dt' G(t-t')\left[\frac{\partial v_{pj}}{\partial x_i} + \frac{\partial v_{pi}}{\partial x_j} - \frac{2}{3}(\nabla\cdot \boldsymbol{v}_p)\delta_{ij}\right].$$

The $G(t)$ is the stress relaxation function that is related to the complex shear viscosity $\eta^*(\omega)$ by

$$\eta^*(\omega) = \frac{G^*(\omega)}{i\omega} = \int_0^\infty dt\, e^{-i\omega t}G(t).$$

Equations (1)–(3) naturally coincide with the equations for hydrodynamic systems if we put $\nabla\cdot\boldsymbol{\sigma}^{(n)} = 0$. Here $G(t)$, or $\boldsymbol{\sigma}^{(n)}$, is strongly dependent on ϕ and N, although it is not explicitly written in Eqs. (1)–(3). This fact should play a crucial role in unstable states [21]. However, it is probably not so important near equilibrium, which simplifies the problem of a stable state.

The complex shear modulus $G^*(\omega)$ is given by [22]

$$\frac{G^*(\omega)}{i\omega} = \int_0^\infty dt \int d\boldsymbol{r}\, e^{-i\omega t}\langle\sigma_{xy}(\boldsymbol{r},t)\sigma_{xy}(0,0)\rangle.$$

For a usual fluid system the mechanical stress σ_{xy} can be calculated from the expression for the osmotic pressure tensor coming from the critical fluctuation. In the viscoelastic system, however, it should be expressed as follows:

$$\sigma_{xy} = \pi_{xy} - \sigma_{xy}^{(n)}.$$

$$\pi_{xy} = K(\partial\phi/\partial x)(\partial\phi/\partial y).$$

The critical anomaly likely originated from the osmotic pressure tensor π_{xy}. The network stress $\sigma_{xy}^{(n)}$ causes the noncritical background in a direct way, while the diagonal parts of $\boldsymbol{\sigma}^{(n)}$ cause the suppression of critical fluctuation in an indirect way. By using the decoupling approximation and the relation

$$\langle\phi(\boldsymbol{r},t)\phi(0,0)\rangle = (2\pi)^{-3}\int d^3q\, e^{iq\boldsymbol{r}}S(q,t),$$

we get the following expression for the critical part of $G^*(\omega)$ [10,11]:

$$\frac{\Delta G^*(\omega)}{i\omega} = \frac{8K^2}{\pi^2 k_B T}\left\langle \frac{q_x^2 q_y^2}{q^4}\right\rangle_a \int_0^\infty dt \int dq\, e^{-i\omega t} q^6 S(q,t)^2, \tag{4}$$

where $\langle\ \rangle_a$ means the angular average and q_x and q_y are the x and y components of wave number vector $\boldsymbol{q}$, respectively. Thus the complex shear modulus can be calculated from $S(q,t)$. Here it should be noted that K is independent of N.

Although the general expression for $S(q,\omega) = \int_0^\infty dt\, e^{-i\omega t} S(q,t)$ is given in Ref. [20], it is not straightforward to analytically calculate $G^*(\omega)$ from $S(q,\omega)$. Thus here we focus our attention on the simplest cases: (i) the limit of $\Gamma_q \to 0$, where Γ_q is the usual thermal decay rate without the viscoelastic effect and $\Gamma_q = k_B T q^2 (1+q^2\xi^2)^{1/2}/16\eta\xi$ [10] and (ii) $\tau_t \Gamma_q \gg 1$. The functional forms of $S(q,t)$ are given by [20]

$$S(q,t) \sim \chi_q \exp[-\Gamma_q t/(1+\xi_{ve}^2 q^2)] \quad \text{[case(i)]}, \tag{5}$$

$$S(q,t) \sim \chi_q \left[\exp(-\Gamma_q t) + \frac{\xi_{ve}^2 q^2}{\Gamma_q \tau_t} \exp\left(-\frac{t}{\tau_t}\right)\right] \quad \text{[case(ii)]}, \tag{6}$$

where χ_q is the static correlation function of the Ornstein-Zernike type.

The critical anomalies in viscosity for cases (i) and (ii) are roughly estimated from Eq. (4) by using Eq. (5) or (6), respectively, as follows:

$$\Delta\eta/\eta_b \sim \left(1 - \frac{5\xi_{ve}^2}{2\xi^2}\right) \ln(q_c\xi) \quad \text{[case(i)]}, \tag{7}$$

$$\sim \left(1 - \frac{32\eta\xi_{ve}^2\xi}{k_B T \tau_t}\right) \ln(q_c\xi) \quad \text{[case(ii)]}. \tag{8}$$

Here q_c is the cutoff wave number, η_b is the noncritical normal viscosity, and ξ_{ve} is the viscoelastic length defined as $\xi_{ve} \sim \xi_b(\eta/\eta_s)^{1/2}$. Since the critical anomaly in the viscosity is given by $\ln(q_c\xi)$ for simple liquid mixtures [10,11,22], the prefactors in Eqs. (7) and (8) can be regarded as the modifications coming from the viscoelastic effect. Since $\xi_{ve} \sim N$, $\xi \sim N^{(1-\nu)/2}$, and $\eta/\tau_t \sim N^{-3/2}$, the critical part of the viscosity, $\Delta\eta$, is expected to decrease with N for the same values of ΔT or ϵ for both cases (i) and (ii). This result [especially on case (ii)] is at least qualitatively consistent with Fig. 3. For the very critical regime we should see the critical divergence even for large N since the correction $(-5\xi_{ve}^2/2\xi^2)$ becomes negligible in the limit of $\xi \gg \xi_{ve}$. Detailed theoretical calculation of $\Delta\eta^*(\omega)$ in the whole temperature and frequency regime is a future problem and now under investigation.

In summary, it has been found that critical concentration fluctuation in polymer solutions could be suppressed by the viscoelastic effect. The kinetic effects caused by the coupling between the order parameter and the stress fields should be considered. It is known that in fluid mixtures the hydrodynamic interaction significantly affects the critical fluctuation through the coupling between the velocity and the concentration fields. Similarly to this hydrodynamic effect, the viscoelastic effect never appears in the Hamiltonian, while it appears only in the kinetic equations. The difference between these two effects likely comes from the fact that there is an intrinsic characteristic time scale for the viscoelastic effect, but no such time scale for the hydrodynamic effect. The suppression effect increases with an increase in the degree of *dynamic asymmetry*. It should be stressed that only when there is a strong asymmetry in molecular dynamics, critical fluctuation does not always become the slowest process in the system. Polymer solutions and polymer blends are expected to belong to a new dynamic universality class based on Eqs. (1)–(3) [21]. Similar phenomena are expected to exist for any system having an asymmetry in elementary molecular dynamics. The possible candidates for *dynamic asymmetry* are (1) slow dynamics due to the internal degree of freedom in complex fluids and (2) slow dynamics near the glass transition.

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