

Nonuniversal nature of dynamic critical anomaly in polymer solutions

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Critical anomaly of viscosity has been studied for ideal polymer solutions, focusing on its dependence on the molecular weight of polymer M_w . According to the conventional understanding that polymer solutions should belong to the same dynamic universal class as classical fluids, the critical exponent of viscosity y_c should be a universal constant (~ 0.04). Contrary to this, we find that y_c significantly decreases with increasing M_w . This unusual behavior can be explained by the dynamic coupling of critical concentration fluctuations with an additional slow viscoelastic mode intrinsic to polymer solutions. Our dynamic light scattering measurements support this picture.

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I. INTRODUCTION

Complex fluids such as polymers and surfactant solutions are characterized by their large internal degrees of freedom and the resulting slow dynamics [1–3]. However, it has so far been considered that the only slow mode is the critical concentration fluctuation even in such systems since its spatial correlation length ξ well exceeds the molecular length scale near a critical point T_c and its lifetime is proportional to ξ^3 . This is a heart of the concept of dynamic universality [4,5]. Thus, it has been widely believed that dynamic critical phenomena and phase separation of complex fluids are essentially the same as those of classical fluids, which belong to “model H ” in the Hohenberg-Halperin classification [5].

Recently, however, we proposed that (i) critical phenomena in polymer solutions cannot be described by “model H ” at least in the practical sense [6–8] and (ii) phase separation in any mixture having strong dynamic asymmetry between its components should practically be classified into a new group, which we call “viscoelastic model” [7–10]. The latter claim is based on the experimental findings of viscoelastic phase separation in polymer solutions and dynamically asymmetric polymer mixtures [7,9,10]. It has been revealed that viscoelastic phase separation is caused by the viscoelastic effects produced by slow dynamics intrinsic to the slower component of a mixture. Although the viscoelastic effects on phase separation are rather evident because of the peculiar morphological evolution [10], those on critical concentration fluctuations have not been clarified yet.

Here, we focus our attention on the critical anomaly of viscosity. For classical fluids, Kawasaki [11,12] and Perl and Ferrell [13] predicted that the critical anomaly of viscosity $\Delta\eta$, which is defined as $\Delta\eta = \eta - \eta_b$ (η_b : the noncritical background part of viscosity), is described by a logarithmic divergence as

$$\Delta\eta/\eta_b = x_\eta \ln(q_e \xi) = -x_\eta \nu \ln \epsilon + x_\eta \ln(q_c \xi_0). \quad (1)$$

Here $\xi = \xi_0 \epsilon^{-\nu}$, where ϵ is the reduced temperature given by

$\epsilon = \Delta T/T_c$ ($\Delta T = T - T_c$), ν (~ 0.63) is the critical exponent for ξ , ξ_0 is the bare correlation length, and q_c is the cutoff wave number. x_η is a universal constant and estimated as $8/15\pi^2 \sim 0.054$ [11–13]. Later, Ohta pointed out that the viscosity anomaly is a multiplicative anomaly [14] and predicted that

$$\eta/\eta_b = (q_e \xi)^{x_\eta} \sim \epsilon^{-\nu x_\eta} = \epsilon^{y_c}, \quad (2)$$

where q_e is an effective wave number determining the amplitude of the power law. Mode-coupling theory predicts the critical viscosity exponent y_c to be $y_c^I = 0.033$ with the self-consistent approximation [11–13,15], and to be $y_c^{II} = 0.043$ with vertex correction [16]. Renormalization group theory, on the other hand, predicts $y_c^I = 0.033$ in an ϵ expansion to first order [17] and $y_c^{II} = 0.040$ in an ϵ expansion to second order [18] for three dimensions. The values of y_c estimated carefully from experimental data of various classical fluids support $y_c = y_c^{II} \sim 0.04$ [19,20]. Thus, the critical exponent y_c is concluded to be a universal exponent having the value of ~ 0.04 for classical fluids.

For polymer solutions, there have not been many studies on the viscosity anomaly. Hamano *et al.* estimated y_c^{poly} to be 0.033 ± 0.001 for a critical mixture of poly(dimethylsiloxane) and diethyl carbonate [21]. Izumi, Sawano, and Miyake estimated y_c^{poly} to be 0.029 ± 0.003 for a critical mixture of polystyrene (PS) and cyclohexane [22]. These results were considered to support that polymer solutions belong to the same universality class as classical fluid mixtures since $y_c^{\text{poly}} \sim y_c^I$. The validity of this conclusion will be reconsidered in the following paragraph. Here it should be noted that molecular weights of polymers used in these studies are of the order of 10^5 .

Contrary to the expected universal behavior of critical viscosity, we recently found its nonuniversal behavior, more specifically, the molecular-weight dependence of the critical viscosity anomaly, for polymer solutions [6]. Thus, we pointed out a possibility that viscoelastic effects affect the coupling of critical concentration fluctuations with velocity fields and suppress the critical amplitude of the resulting viscosity anomaly [7]. Unfortunately, however, our previous experimental results are not so conclusive because (i) we

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cannot completely deny the effects of a finite measurement frequency since the lowest frequency accessible by our apparatus was not low enough compared to the terminal relaxation frequency of the polymer solutions (in Ref. [6] the data at 150 Hz were analyzed) and (ii) the accurate estimation of the noncritical background was difficult because of the rather poor signal-to-noise ratio. Later, Berg and Gruner [23] made very careful experiments and obtained the viscosity critical exponent of 0.028 for a mixture of PS ($M_w = 1.02 \times 10^5$) and diethyl malonate (DEM), consistently with the earlier work by Gruner, Habib, and Greer on the same system [24]. They concluded that the critical exponent is considerably smaller for polymer solutions than for classical binary mixtures, in accord with our previous study [6]. They were confident that the difference between 0.042 ± 0.002 and 0.028 ± 0.003 well exceeds the errors and is significant because both of these values are estimated by their own careful experimental studies [19,23]. Their study suggests that the above-mentioned values of y_c^{poly} estimated by the earlier works [21,22] may also be regarded to be smaller compared to the universal one (y_c^{II}) for classical fluids. However, there still remain two possibilities accounting for this. One is the static mechanism: the weaker fluctuation effects in polymer solutions due to the long-range nature of the interaction makes the renormalization effects insignificant, which leads to a smaller value of y_c ($y_c^I \sim 0.03$) calculated only up to the first-order correction. The other is the dynamic one [7]: the dynamic coupling of concentration fluctuations with the slow viscoelastic mode weakens the critical viscosity anomaly.

In this paper, we demonstrate the first unambiguous experimental evidence supporting the above dynamic mechanism. We find that the critical viscosity exponent y_c decreases monotonically with an increase in the molecular weight of polymer M_w . We also show additional evidence supporting the existence of the dynamic coupling between a critical mode and a viscoelastic relaxation mode, which is obtained from dynamic light scattering experiments.

II. EXPERIMENTAL

The systems studied were mixtures of monodisperse PS and DEM. The moisture contained in DEM was carefully removed by using molecular sieves and all sample preparations were made in a dry box to avoid the impurity effects of water on T_c of this mixture [24]. 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. The θ point (a tricritical point [2]) of the mixture was estimated as $T_\theta = 30.1^\circ\text{C}$ by extrapolating T_c as M_w goes to infinity.

The complex shear modulus was measured by a conventional rheometer (RH-600, Rheology co.) mainly using a coaxial cylinder mode. The measurement frequency was ranged from 0.02 to 0.5 Hz, while the amplitude of the oscillation was from 1° to 3° . We confirmed that the terminal relaxation frequency of polymer solutions is much higher than 1 Hz even for a polymer solution whose PS molecular weight is 3.84×10^6 . We always set the measurement frequency to be

TABLE I. Physical characteristics of polymer solutions.

PS	M_w	M_w/M_n	ϕ_c (wt %PS)	T_c ($^\circ\text{C}$)
PS-1	3.79×10^4	1.01	14.8	-9.0
PS-2	9.64×10^4	1.01	10.7	3.8
PS-3	1.90×10^5	1.04	8.49	11.6
PS-4	3.55×10^5	1.02	6.80	16.5
PS-5	7.06×10^5	1.05	4.98	20.8
PS-6	1.09×10^6	1.08	4.11	22.7
PS-7	3.84×10^6	1.04	2.14	25.7
PS-8	8.42×10^6	1.17	1.2	28.5

much lower than the terminal relaxation frequency.

Dynamic light scattering measurements were performed by using the digital correlator ALV-5000. The laser used was a single-mode, continuous wave, frequency doubled Nd:YAG (yttrium aluminum garnet) laser, whose output power and wavelength were 50 mW and 532 nm, respectively.

III. RESULTS AND DISCUSSION

A. Viscosity anomaly

Figure 1 shows a typical example of the critical behavior of the real (G') and imaginary part (G'') of the complex shear modulus. While the imaginary part shows the critical anomaly, the real part does not. The latter fact guarantees that the measurement frequency is low enough compared to the characteristic frequency of concentration fluctuation. Note that in this low frequency range G'' is proportional to the viscosity η as $G'' = \omega \eta$ (ω : angular frequency). The critical temperature T_c can be clearly determined by a sharp rise of the real part of the complex shear modulus and a sharp

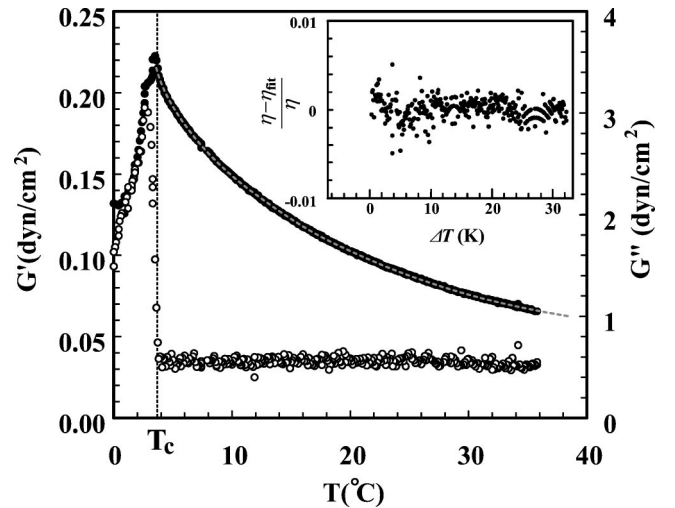


FIG. 1. Temperature dependences of G' (open circles) and G'' (filled circles) at 0.5 Hz in the critical mixture of PS-2 and DEM ($\phi_c = 10.70$ wt %). Note that G'' (dyn/cm^2) = $0.5 \text{ Hz} \times \eta$ (poise). The gray dashed curve is the theoretical fitting curve ($\pi \eta_{\text{fit}}$). In the small inset, the normalized deviation of the data from the fitted curve ($(\eta - \eta_{\text{fit}})/\eta$) is plotted against ΔT .

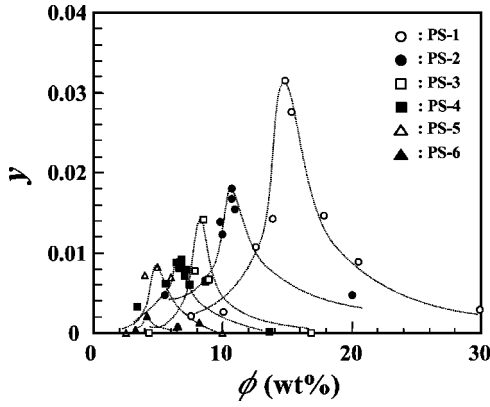


FIG. 2. Composition (ϕ) dependences of the exponent y for solutions of polymers having different molecular weights.

drop of the imaginary part. This behavior may be characteristic of phase separation of mixtures whose components have very different viscoelastic properties. Although this phenomenon itself is interesting to study, we do not dwell into this problem here since it is beyond the scope of this paper. We use this sharp change of G' and G'' as a fingerprint of the phase transition to determine T_c (see Table I). These values of T_c coincide well with those determined by our optical microscopy observation and light scattering experiments.

The fitting result of Eq. (2) to the viscosity data is also shown in Fig. 1. The most delicate problem in studying the critical viscosity anomaly is how to determine accurately the noncritical background. There are many studies on the temperature dependence of the viscosity of usual (noncritical) polymer solutions, and the temperature dependence of the Vogel-Fulcher-type is most widely accepted. Furthermore, Gruner, Habib, and Greer [24] and Berg and Gruner [23] discussed the problem of how we should choose the fitting function to study the critical viscosity anomaly and they concluded that the Vogel-Fulcher-type functional form is most reliable. Thus, we adopt the following temperature dependence of η_b :

$$\eta_b = A \exp[B/(T - T_0)], \quad (3)$$

where A and B are the parameters and T_0 is the so-called Vogel-Fulcher temperature. A nonlinear least-square fitting of Eqs. (2) and (3) to the data is made by using A , B , T_0 , and y as adjustable parameters. The validity of this form is strongly supported by the fact that the behavior of η of strongly off-critical mixtures can be very well described solely by Eq. (3). To perform reliable fitting, we take the temperature range of the viscosity measurement as wide as possible. We also carefully confirm the absence of the systematic errors and the reasonable dependences of the parameters A , B , and T_0 on the molecular weights and polymer concentrations. As an example, the errors of the fitting are shown in the small inset of Fig. 1. There is no systematic deviation from the fitting over the temperature range of 30 K and the error is within 0.5%. This indicates the validity of the fitting and the reliability of the determination of y .

Figure 2 shows the dependences of the exponent y on the

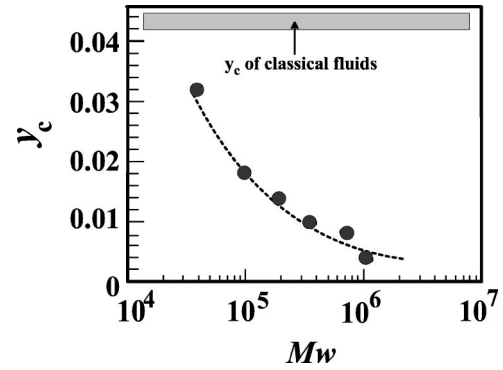


FIG. 3. Molecular-weight (M_w) dependence of the critical exponent y_c . Note that the universal value of y_c for classical fluid mixtures is ~ 0.042 .

polymer concentration for polymer solutions of the six different molecular weights. For every molecular weight, y has a maximum value at the critical polymer concentration ϕ_c . This concentration dependence is quite reasonable, which also indicates the reliability of the viscosity measurement and the functional fitting.

Figure 3 plots the value of the viscosity exponent y at the critical concentration y_c against the molecular weight of polymers M_w . This clearly demonstrates that the value of y_c monotonically decreases with an increase in M_w . If polymer solutions belong to the same dynamic universality class as classical fluids, this exponent y_c should be equal to the universal value of ~ 0.04 , irrespective of the molecular weight of the polymer. Thus, the above results clearly indicate that the viscosity anomaly of critical polymer solutions (especially, of high molecular-weight polymers) cannot be described by “fluid model (model H)” at least in the experimentally accessible temperature range. Note that y_c approaches the universal value of classical fluids as M_w decreases.

We propose that this nonuniversal behavior is due to the existence of an additional slow mode intrinsic to polymer solutions and its dynamic coupling to the critical mode [6,7]. This is a direct consequence of *dynamic asymmetry*. Note that the dynamic universality concept relies on the fact that there exists only one slow mode in a system, which is a critical mode. However, this is not the case for a mixture of strong dynamic asymmetry. For polymer solutions, it is known [25–27] that the viscoelastic relaxation mode is dynamically coupled with the concentration fluctuation mode. The former is characterized by q -independent rheological relaxation time τ_r , while the latter is q dependent and the decay rate of the mode of the wave number q is given by Γ_q . This coupling results in the viscoelastic suppression of the dynamic critical anomaly [28]: The fluctuation modes whose characteristic length is shorter than the magic (viscoelastic) length ξ_{ve} is significantly influenced by the viscoelastic effects. Note that $\xi_{ve} \sim (\xi_b \eta / \eta_s)^{1/2}$ [25,26], where ξ_b is the blob size and η_s is the solvent viscosity.

B. Dynamics of concentration fluctuations under viscoelastic effects

The above physical picture is supported by our dynamic light scattering study. We measure the normalized intensity

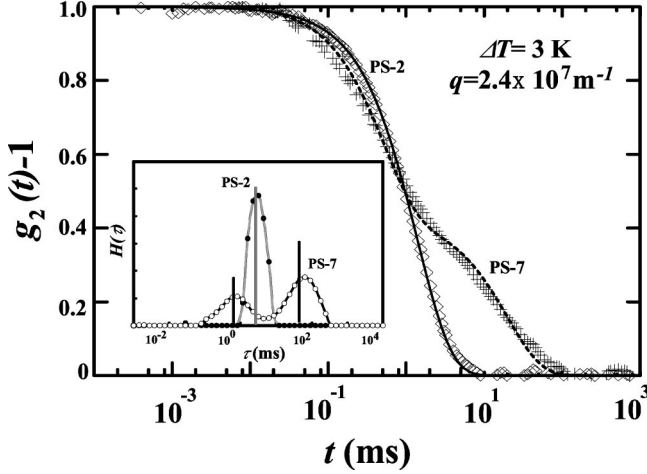


FIG. 4. Normalized correlation functions $g_2(t)-1$ of critical mixtures (PS-2 and PS-7). The distribution function of the correlation time τ , $H(\tau)$, is shown in the inset, where the gray and black vertical lines represent the results of single and double exponential fitting, respectively.

correlation function $g_2(t) = \langle I(t)I(0) \rangle / \langle I(0) \rangle^2$ in (vertical-vertical) polarization by an ALV-5000 correlator, which directly calculates $g_2(t)$ from the intensity of scattered light detected by a photomultiplier. Figure 4 shows the function $g_2(t)-1$ for PS-2 and PS-7 at $\Delta T = 3$ K at $q = 2.4 \times 10^7 \text{ m}^{-1}$. It is well established for classical fluids [12] that $g_2(t)-1$ should decay exponentially as $g_2(t)-1 = \exp(-2\Gamma_q t)$. Indeed, $g_2(t)-1$ for PS-2 is well described by a single decay, as shown in Fig. 4. However, that for the solution of $M_w > 10^6$ it is hardly described by a single decay and the constrained regulation analysis clearly indicates the existence of two modes (see the inset of Fig. 4). The distribution function of the decay time τ initially becomes broader with increasing M_w and the existence of two modes become evident for $M_w > 10^6$. For the same ΔT , the time separation between the two modes increases with increasing M_w . Under the coupling between viscoelastic and critical modes, $g_2(t)$ should be given by

$$g_2(t)-1 = [f_+ \exp(-\omega_+ t) + f_- \exp(-\omega_- t)], \quad (4)$$

where

$$\omega_{\pm} = \frac{1 + q^2 \xi_{ve}^2 + \tau_t \Gamma_q \pm \sqrt{(1 + q^2 \xi_{ve}^2 + \tau_t \Gamma_q)^2 - 4 \tau_t \Gamma_q}}{2 \tau_t}, \quad (5)$$

$$f_{\pm} = \pm \frac{\omega_{\pm} \tau_t - (1 + q^2 \xi_{ve}^2)}{(\omega_+ - \omega_-) \tau_t}. \quad (6)$$

We fit this function to the data of such high M_w solutions, following the pioneering work on the θ solution by Adam and Delsanti [27]. An example is shown in Fig. 4, which is quite satisfactory.

The temperature dependences of ω_+ and ω_- for PS-7 and Γ_q for PS-2 are shown in Fig. 5. Far above T_c where $\tau_t \Gamma_q \gg 1$, the theory [25,26] predicts that $g_2(t)-1$ should be approximated as

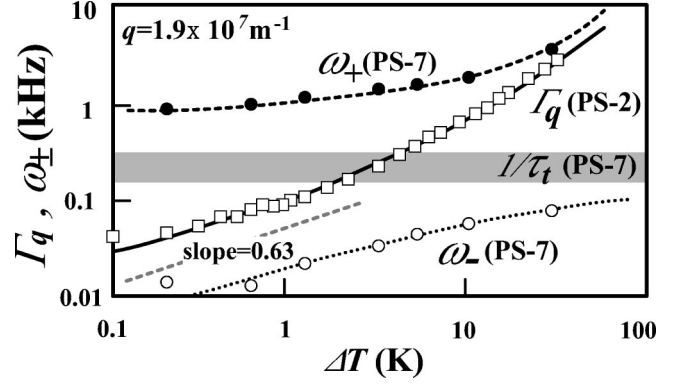


FIG. 5. Temperature dependences of Γ_q (open square) for PS-2 and ω_+ (filled circle) and ω_- (open circle) for PS-7. The viscoelastic relaxation rate $1/\tau_t$, which is estimated by the analysis, is also shown by the thick gray line. The gray dashed line has a slope of $\nu = 0.63$.

$$g_2(t)-1 \equiv \left[\exp(-\Gamma_q t) + \frac{\xi_{ve}^2 q^2}{\Gamma_q \tau_t} \exp(-t/\tau_t) \right]^2. \quad (7)$$

In this limit, $\omega_+ = \Gamma_q$ and $\omega_- = 1/\tau_t$. The value of τ_t , to which ω_- approaches at large ΔT , is estimated from the data analysis as $\tau_t \sim 0.005$ s. This value of τ_t is compatible with our previous rheological measurements [6]. We also estimate ξ_{ve} from the relation

$$f_- \omega_+ + f_+ \omega_- = \frac{1 + \xi_{ve}^2 q^2}{\tau_t}, \quad (8)$$

as $\xi_{ve} \sim 0.1 \mu\text{m}$ for PS-7. It is found that ξ_{ve} only weakly depends on T , which is reasonable. We also note that both τ_t and ξ_{ve} are found to be larger for PS-8 than for PS-7, as expected.

Very near T_c where $\Gamma_q \rightarrow 0$, on the other hand, the slow ω_- branch should become dominant and there we have

$$g_2(t)-1 = \exp \left[-2 \left(\frac{\Gamma_q t}{1 + \xi_{ve}^2 q^2} \right) \right]. \quad (9)$$

The critical mode can be free from the coupling to the viscoelastic mode only very near T_c and at small q . It is expected, thus, that very near T_c ω_- is proportional to $(\Delta T)^\nu$. This is indeed the case for both PS-2 and PS-7. Figure 5 clearly demonstrates that the behavior of the critical mode is strongly influenced by its dynamic coupling to the viscoelastic mode in a wide temperature range for PS-7. This strongly supports our scenario that it is the dynamic coupling of a critical mode with a slow viscoelastic mode that leads to nonuniversal dynamic critical behavior of polymer solution. The detailed analysis of our light scattering study will be described elsewhere.

IV. CONCLUSION

In summary, we demonstrate that the dynamic critical behavior of polymer solution, which is a typical example of dynamic asymmetric fluid mixtures, can be essentially differ-

ent from that of classical fluid and nonuniversal at least in the experimentally accessible temperature region. Here it is worth noting that dynamically symmetric fluid mixtures should belong to model H no matter how slow the elementary dynamics is. The origin of the nonuniversal behavior is *dynamic asymmetry*, and not simply slow dynamics of a system. In principle, if we approach the true critical regime, the critical mode should be the only slow mode even in a dynamically asymmetric system and we should see the universal critical behavior there. However, such a temperature regime may be inaccessible experimentally for a system with

strong dynamical asymmetry. In the limit of $M_w \rightarrow \infty$, the dynamic universality may intrinsically break down. Further studies are highly desirable to clarify on a quantitative level how internal molecular dynamics affects dynamic critical phenomena.

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