Spinodal Decomposition in Isotopic Polymer Mixtures

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Spindol decomposition of a critical binary mixture of perdeuterated and protonated polymers has been examined by light scattering. Reduction of the characteristic composition fluctuation length (i.e., scattering-peak wave vector) and time, based on independently verified scaling parameters obtained from early-stage linear analyses, fails to collapse the intermediate-stage results onto a universal curve. This is the first demonstrated violation of the universal scaling of time and length during spinodal decomposition.

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The discovery[1,2] that binary liquid mixtures of deuterated (D) and protonated (H) polymers are characterized by an upper critical solution temperature makes possible previously infeasible liquid-state experiments on spinodal decomposition, as a consequence of the following unique combination of properties. The very small difference in index of refraction ($\Delta n \approx 0.003$) between H and D polymers eliminates problems associated with multiple scattering, even in the very late stages of spinodal decomposition (domain size ≈ 100 μm); this allows the phase-separation process to be studied by light scattering with use of macroscopic cylindrical samples, which afford access to scattering angles of $0° \lesssim \theta \lesssim 180°$. The self-diffusion coefficient for polymers is typically N^{-2} (N is the degree of polymerization) times smaller than for low-molecular-weight fluids,[3] which slows the spinodal decomposition kinetics to time scales where early and intermediate stages can be studied conveniently, even for deep quenches. A further advantage of working with polymer mixtures is that the phase diagram can be tailored; both the critical temperature and composition can be adjusted by choice of the appropriate magnitude and ratio, respectively, of component N's. In the present study we used nearly symmetric conditions (critical volume fraction $\phi_c = 0.485$), under which it is much easier to follow critical paths, unlike, e.g., in the most widely studied[4,5] critical polymer liquid system, polystyrene-polyvinylmethylether (PS-PVME) with $\phi_c \approx 0.8$. A final advantage worth mentioning is the absence of gravity effects, which become important during late-stage coarsening in low-molecular-weight fluid mixtures.[6]

Monodisperse protonated and perdeuterated 1,4-polybutadiene were synthesized and characterized as previously[7] reported. The polymerization indices were $N_{\mathrm{H}} = 3200$ and $N_{\mathrm{D}} = 3600$, with a corresponding calculated[8] critical volume fraction of deuterated polybutadiene $\phi_c = 0.485$. We determined the critical temperature to be $T_c = 62 \pm 1.5$ °C. Samples were prepared by solution of the polymers in excess cyclohexane with subsequent solvent stripping and drying under vacuum at 75 °C. The cylindrical Pyrex cells (diameter ≈ 0.7 cm) were then torch sealed under vacuum to eliminate possible oxidation problems. The quench temperatures ranged between 25 and 60 °C, corresponding to reduced quench depths $0.006 \lesssim (T_c - T)/T_c \lesssim 0.11$. Under these conditions the range of composition difference between the coexisting phases is $0.16 \lesssim \Delta\phi \lesssim 0.56$, as determined within the Flory-Huggins formalism.[8]

Figure 1 shows the intensity scattered by a sample after it was quenched from 75 to 25 °C, as a function of scattering wave number $q = 4\pi\bar{n}/\lambda \sin(\theta/2)$ at various times, where $\bar{n} = 1.5$ is the average index of refraction of the polymer, $\lambda = 6328$ Å the wavelength of the light, and θ the scattering angle. The temperature equilibration time in the sample is calculated to be approximately 150 sec, and a q scan takes 150 sec; this is short compared to the time scales of the experiment. Temperature control is better than 0.1 °C. The excess light scattered for $q \lesssim 3$ μm^{-1} is attributed to the main beam's being defocused

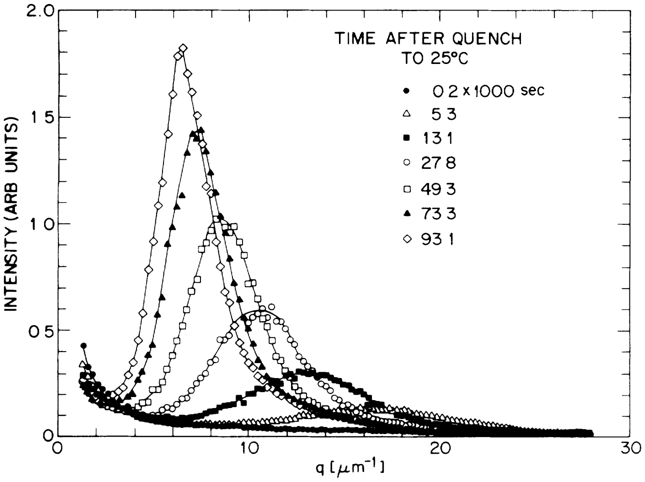

FIG. 1. The scattered intensity as a function of wave number at various times as spinodal decomposition proceeds. The sample was equilibrated in the one-phase region at 75 °C.

by the cylindrical cell; it is time independent and can be easily separated from the relevant signal. Here we note that the accessible q range illustrated in Fig. 1 is 3 times larger than in high-contrast systems,[3-5] where only thin-film specimens can be studied.

In Fig. 2 we plot the wave number q_m at which the intensity peaks, as a function of time for four different quenches. For the shallowest quench shown (54.5 °C) the peak can be observed to grow out of the background only after about 12 h. At earlier times the composition fluctuations are too small to yield measurable signals, primarily because of the proximity of the critical temperature. We also note that regardless of quench depth the peak position moves as a function of time as soon as it can be detected. The linear regime predicted by Cahn,[9] where q_m is time independent, is never observed in these experiments.

Scaling analysis has been very successful in the field of critical phenomena. For spinodal decomposition, linear theory can be expressed in terms of dimensionless units for lengths and time, where the scaling variables are equilibrium and linear-response properties of the one-phase region, respectively. Surprisingly, such scaling analysis has proven successful in low-molecular-weight fluid systems[3] and polymer liquids,[4,5] even at intermediate and late stages, far from the initial linear regime. We will attempt to represent the results of Fig. 2 in a similar fashion, necessitating estimation of the linear scaling variables.

The linear (early stage) spinodal decomposition behavior of polymer systems can be cast into a mean-field formalism, as shown by de Gennes,[10] Pincus,[11] and Binder,[12] based on the original Cahn theory[9] and the Flory-Huggins free energy. This theory predicts that in the unstable region fluctuations with wave number $0 < q < \sqrt{2}q_m$ become spontaneously amplified and grow exponentially. The wave number q_m, at which the growth rate is maximal, depends on the quench depth via

$$q_m(t=0) = \left[\frac{3}{2R_G^2}\left(1-\frac{\chi_s}{\chi}\right)\right]^{1/2}, \qquad (1)$$

where $R_G = a(N/6)^{1/2}$ is the radius of gyration of the polymer, a the Gaussian coil segment length, and χ the segment-segment interaction parameter. $\chi_s = [(\phi_H N_H)^{-1} + (\phi_D N_D)^{-1}]/2$ represents the limit of thermodynamic stability (i.e., the spinodal point), where ϕ_H and ϕ_D are the volume fractions of protonated and deuterated polymers, respectively. Since it has been shown[1,2,7] that $\chi \propto T^{-1}$ for isotopic polymer mixtures, the parenthesis in (1) is simply a reduced temperature with $\chi_s \propto T_s^{-1}$, where T_s corresponds to the spinodal temperature. Values of $q_m(t=0)$ have been obtained from linear analysis of the exponential growth of the scattered intensity at early times for $q < q_m$, and independently through linear regression of $q_m(t \to 0)$, for ten different quenches. These are both self-consistent, and in very good agreement[13] with prediction (1), despite the fact that q_m is time dependent at the earliest measuring times. The analysis yields $R_G = 175$ Å, which is in excellent agreement with $R_G = 164$ Å, calculated with a segment length $a = 6.9$ Å, independently determined from small-angle neutron-scattering measurements in the one-phase region.[7] To our knowledge this is the first time that such agreement has been found in any polymer system undergoing spinodal decomposition. The linear analysis also yields the quench-depth-dependent diffusion coefficient[13] which also shows critical slowing down[10-12] similar to Eq. (1): $D(\chi,T) = D_s(T)(1-\chi/\chi_s)$. The bare mutual diffusion coefficient $(\chi=0)$

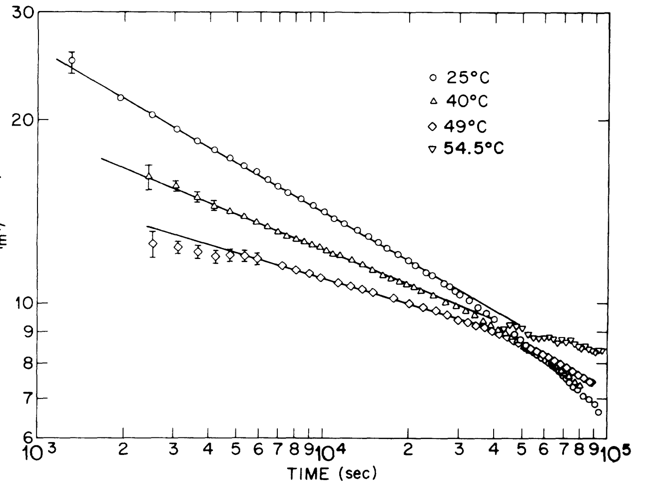

FIG. 2. The peak position as a function of time for four different quenches. The temperature equilibration time is approximately 150 sec.

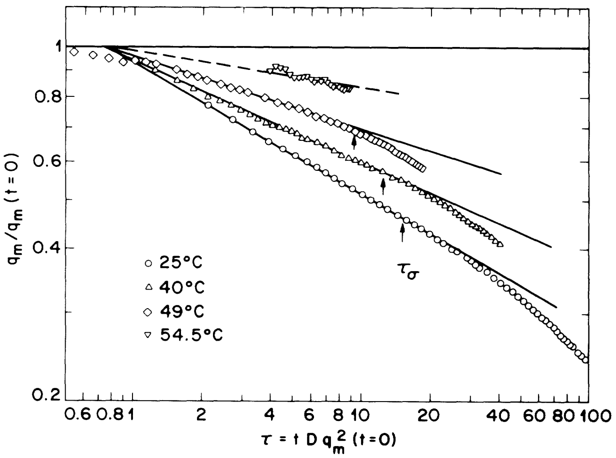

FIG. 3. Reduced plot of the peak position vs time. The scaling variables $q_m(t=0)$ and D were obtained from linear analysis (see text). The arrows indicate the time τ_σ (in reduced units) at which the composition inside the coexisting domains reaches the equilibrium value.

determined from the temperature dependence of D is $D_s = 1.1 \times 10^{-13}$ cm^2/sec (at 25 °C), which again is in excellent agreement with the self-diffusion coefficient $D_s = 1.4 \times 10^{-13}$ cm^2/sec calculated[14] independently from rheological data.[15]

Hence, we are in a position to reduce wave numbers $[q_m/q_m(t=0)]$ and time $[\tau = tDq_m^2(t=0)]$ with well-defined scaling variables obtained from early-stage linear analysis. The results are presented in Fig. 3. Contrary to our expectations based on previous experiments,[3-6] *the data do not superimpose onto a single master curve.* From this we must conclude that *universal scaling of time and length has failed.* The lines in Fig. 3 are guides to the eye and indicate that a departure from the early-stage linear regime (q_m time independent) occurs expectedly around $\tau = 1$. It is noteworthy that the time scales covered in these experiments are substantially earlier than those of other studies, e.g., $10 \lesssim \tau \lesssim 10^5$ for low-molecular-weight fluids[3,6] and $20 \lesssim \tau \lesssim 2000$ for polymeric systems.[4,5]

In order to characterize further the growth process covered by the data in Fig. 3, we analyzed the scaling behavior of the structure factor. During the late stages, where the composition inside the domains has reached the equilibrium value, the dynamic scaling hypothesis[16,17] predicts that the structure factor should obey the following law:

$$S(q/q_m,t) = q_m^{-3} F(q/q_m,t), \qquad (2)$$

where $F(q/q_m,t)$ is a universal scaling function. Figure 4 shows such a plot for a quench to 49 °C. Universal behavior is indeed observed for times greater than $t_\sigma = 53\,500$ sec. The corresponding reduced saturation time τ_σ is indicated for the various quenches by an arrow in Fig. 3. Thus the violation of scaling observed in Fig. 3 occurs during the spinodal decomposition process as the unstable composition fluctuations grow in spatial extent and in composition, i.e., from compositions initially close to the average composition ϕ_c to the final coexistence-curve composition.

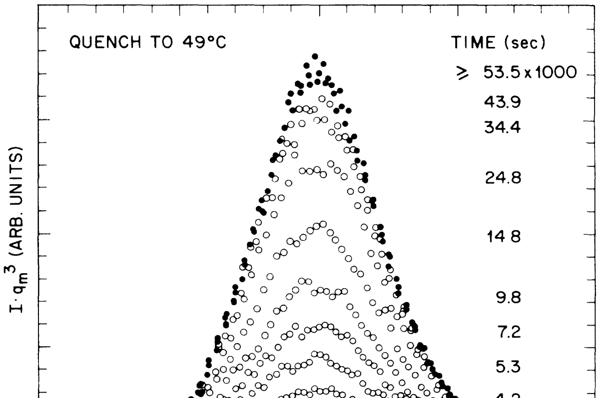

FIG. 4. Dynamic scaling plot of the wave-number dependence of the structure factor. For this quench $t_\sigma = 53\,500$ sec. Longest time shown is 87 000 sec.

It is interesting to note that for $1 \lesssim \tau \lesssim \tau_\sigma$ the temporal evolution of the peak position is governed by a power law $q_m \sim \tau^{-n_{\rm eff}}$ stretching over typically 1 decade in time in Figs. 2 and 3. Such a power-law regime has been predicted, e.g., for Lifshitz-Slyozov–type droplet coalescence mechanisms. Although a number of values for $n_{\rm eff}$ (typically around $\frac{1}{3}$) have been proposed,[16-19] to our knowledge there is no prediction of a quench-depth-dependent $n_{\rm eff}$ for the early to intermediate stages. We find experimentally that $n_{\rm eff}^2 \sim (T_s/T - 1)$.

After the composition inside the domains has reached the equilibrium value, growth is governed by diffusive coalescence. Preliminary results indicate that if we empirically scale time by t_σ and the peak position by $q_m(t_\sigma)$, all the data collapse onto a master curve for $\tau > \tau_\sigma$, whereas the data for $\tau < \tau_\sigma$ are nonuniversal. This further corroborates our analysis that the early to intermediate stages of the decomposition process, traveling from the critical isochore to the coexistence curve, are those which are theoretically unaccounted for.

Why does scaling of time and q_m fail to superimpose the data onto a master curve as it apparently does for all previous experiments on spinodally decomposing fluid mixtures?[3-6] The most serious attempt to push theory beyond the linearization approach by Cahn[9] was undertaken by Langer, Bar-on, and Miller[18] and subsequently by Kawasaki and Ohta.[19] These formalisms predict the shrinking of q_m based on the previously defined scheme for the reduction of variables, i.e., with appropriate parameters from the equilibrium state in the one-phase region. One of the most important assumptions made in these theories is that the free energy has the Ginzburg-Landau form (only terms in ϕ^2 and ϕ^4). This is a poor approximation for the full Flory-Huggins[8] free-energy expression, especially for the deeper quenches, where $\Delta\phi \simeq 0.5$. In addition, recent experiments,[20] have shown that concentration fluctuations in isotopic polymer mixtures have to be taken into account via additional terms in the Flory-Huggins expression, which lead to a significant composition- and temperature-dependent interaction parameter $k_B T \chi$. It thus appears that a possible reason for the failure of scaling is the approximation made in ϕ^4 theories. Unfortunately, we are not able to predict even qualitatively whether a more complete treatment of the free energy describes the behavior of Fig. 3. Nevertheless, it is our opinion that scaling works in low-molecular-weight fluids[3,6] because the quenches are necessarily very shallow. The coexistence curve diameter is typically $0.01 \lesssim \Delta\phi \lesssim 0.05$ allowing the spinodal decomposition process to stay within the linear regime as the domains form. In our deeper quench experiments, nonlinearities must play an important role. The disparity between our results for polymer (scaling violation), and those[4,5] for PS-PVME (scaling) may be related to the local structural symmetry and asymmetry, respectively, characterizing these mixtures, which has been shown to lead to qualitative differences in the excess free energy of mixing.[20]

In summary, we have examined the dynamics of spinodal decomposition for a critical binary mixture of perdeuterated and protonated 1,4-polybutadiene by light scattering. Because of a combination of low contrast (no multiple-scattering effects) and very slow processes (small diffusion coefficients) characterizing isotopic polymer mixtures, these measurements have extended previously attainable reduced spatial and temporal ranges by factors of 3 and $\frac{1}{20}$, respectively. At early and intermediate times, our results, obtained for relatively deep quenches ($2 \lesssim T_c - T \lesssim 37\,^\circ\mathrm{C}$), clearly demonstrate a violation of universal time and length scaling. These experiments are not feasible with low-molecular-weight fluids.

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