Dynamic Scaling in Spinodally Decomposing Isotopic Polymer Mixtures

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ABSTRACT: A symmetric critical isotopic mixture of protonated and deuterated poly(ethylene–propylene) (PEP) has been quenched from the homogeneous state (T_c = 93 °C) to temperatures ranging from 45 to 89 °C. As reported for a previous isotopic polybutadiene mixture, the classical light scattering results from this sample fail to reduce to a universal curve by the scaling of time and length based on scaling parameters extracted from linear analysis. The light scattering results confirm the mean-field nature of the thermodynamic aspect of the Cahn theory, producing initial temperature-dependent heterogeneity lengths that are quantitatively anticipated by the de Gennes–Pincus–Binder modifications. Calculation of the effective diffusion coefficient based on independent measurements of the cooperative diffusion coefficient leads to an order of magnitude greater value than is obtained from the linear analysis of the time-dependent light scattering data. This disparity calls into question the conventional assumption of mean-field van Hove dynamics, which ignores hydrodynamic interactions, in the treatment of spinodal decomposition in polymer mixtures. Rheological measurements also demonstrate that, within the limits of our equipment, spinodal decomposition is not discernible through dynamic–mechanic experimentation.

Introduction

Nearly three decades ago, on the basis of his study of binary metallic systems, Cahn[1] first proposed that spinodal decomposition proceeded by the exponential growth of the amplitude of unstable concentration fluctuations. Since then, much theory and experimentation has been devoted to further description of this process. Because polymer mixtures are composed of high molecular weight, and therefore highly entangled, molecules, phase separation is drastically slowed relative to simple mixtures, which allows for the experimental investigation of the entire spinodal decomposition process from early to late stages. A description of the current understanding of the concentration and amplitude growth accompanying the various stages of spinodal decomposition was first presented by Hashimoto et al.[2] and later modified by Bates and Wiltzius[3] to include four distinct stages: (a) the early stage in which the amplitude of the composition fluctuations changes but the wavelength remains stationary; (b) the intermediate stage during which both the amplitude and the wavelength of the composition profile change; (c) the transition stage where the amplitudes of the fluctuations have reached equilibrium values but the interfacial profile and heterogeneity length continue to develop; and (d) the late or final stage during which only the heterogeneity length changes.

The salient feature of Cahn's work,[1] which is based on a linear stability analysis of the equations of motion, is the discovery that in an unstable binary mixture there is a characteristic length scale, L_m, and a characteristic time scale, $t_m = L_m^2/D_{eff}$, where D_{eff} is an effective cooperative diffusion coefficient. Both L_m and t_m depend on quench depth. Cahn's work deals with the early-stage regime (a) mentioned above, where the length scale L_m is time independent. A linearized treatment of the equations of motion will fail, however, as soon as nonlinearities become important (regimes b–d). A common feature of nearly all current theories that deal with spinodal decomposition dynamics is the concept of universal scaling. The time-dependent heterogeneity length, L_m, is predicted to evolve following a single function of time, t, for all systems that belong to a particular dynamical class. For example, binary fluid mixtures are characterized by a conserved order parameter with a long-time ($t \rightarrow \infty$) limiting growth law[4] given by $L_m \sim t^1$. Universal scaling should collapse all spinodal decomposition results onto a unique master curve by rescaling the heterogeneity length, $L_m(t)$ with its value at $t = 0$ and plotting it against a scaled time $\tau = tD_{eff}q_m^2(t = 0)$. Here $q_m(t) = 2\pi/L_m(t)$ is the wavenumber of the characteristic length scale, which is typically measured in a scattering experiment. Recently we reported[3] that a symmetric binary isotopic polymer mixture failed to conform to this universal dynamic scaling hypothesis where D_{eff} and $q_m(0)$ were determined from the linear analysis of early-time light scattering data. In this paper we examine a second isotopic system and provide evidence that indicates the origins of the effect.

Experimental Section

The materials used in this study were protonated and deuterated poly(ethylene–propylene) (PEP), each with a molecular weight of 1.6 × 10^5. (The weight-average degrees of polymerization are $N_{h\text{-PEP}}$ = 2140 and $N_{d\text{-PEP}}$ = 2360.) These relatively monodisperse ($N_W/N_N < 1.05$) polymers were prepared by, respectively, hydrogenating and deuterating anionically polymerized perdeuterated and normal 1,4-polyisoprenes. Elastic light scattering measurements on solutions and calibrated size exclusion chromatography were used to determine N_W to within 5%.

Light scattering and rheological measurements were made using a nearly critical composition, ϕ = 0.5, which is very close to the calculated critical value,[5,6] ϕ_c = 0.49. The critical temperature is T_c = 93 °C. The mixture was prepared by dissolving the polymers in hexane and precipitating with methanol, followed by drying in a vacuum oven at 115 °C for several days; complete evaporation of the solvent was established by weighing.

Light scattering experiments were performed on a classical elastic light scattering apparatus using a computer-controlled motorized goniometer. A cylindrical sample cell of 10-mm

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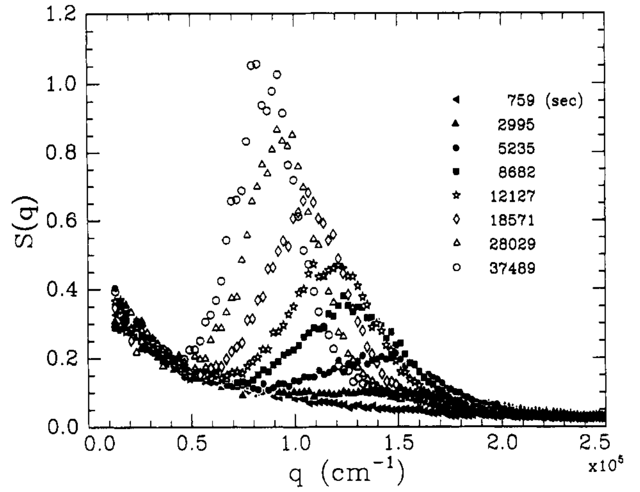

Figure 1. Representative light scattering data for a quench of a symmetric isotopic PEP mixture to 83.25 °C. The peak intensity is seen to increase with time while $q_{\rm m}$ decreases, indicating growth of spatial and compositional amplitude fluctuations.

diameter was placed in a cylindrical vat with index matching oil that was temperature controlled to better than 20 mK. The scattered light was measured with a photomultiplier tube at scattering angles ranging between 5 and 139°. The incident laser light had a wavelength of 632.8 nm, affording an accessible range of wavevectors, q, from 1.30×10^4 to 2.79×10^5 cm^{-1} ($q = 4\pi n\lambda^{-1} \sin(\theta/2)$, where n is the average medium refractive index, λ is the radiation wavelength, and θ is the scattering angle). The sample was annealed in the one-phase region at 105 °C for 3 days between quenches. Temperature equilibration was estimated to be achieved less than 3 min after a temperature quench.

Rheological measurements were made on two rheometers, a Rheometrics solid analyzer RSA II using a shear sandwich geometry and a Rheometrics RMS800 using a circular plate geometry. Data were obtained both in the one-phase region at 110 °C and after quenching to 75 °C using a temperature controller stable to ±0.5 °C. On the solids analyzer, the frequency of oscillations was varied from 100 to 0.01 rad/s with a 5% strain amplitude, and measurements were conducted over a 5-day period. On the RMS800, the sample moduli were monitored for 2 days as a function of frequency between 2×10^{-3} and 2×10^{-2} rad/s and using a strain amplitude of 10%. To obtain these low-frequency data, the RMS800 was operated in a Fourier data acquisition mode that provides for the simultaneous analysis of eight separate frequencies.

Using the protonated homopolymer alone, a separate set of frequency scans was made on the RMS800 from 100 to 0.01 rad/s with a 10% strain amplitude. These scans were conducted from 30 to 110 °C at 10 °C intervals with a 15-min temperature equilibration time between each run. A scan was also conducted at 35 °C to be used as a reference.

Results

Figure 1 shows representative light scattering data for a quench to 83.25 °C. The peaked structure function characteristic for spinodal decomposition is seen to emerge from the background after typically a few thousand seconds. The upturn at q values below 5×10^4 cm^{-1} is due to stray light and large impurities in the sample. It is *not* a function of time and thus not part of the dynamic processes that we are interested in here. It can be treated as a q-dependent, time-independent background and subtracted from the data during data analysis. The portion of the data around the peak is fitted to a squared-Lorentzian function yielding peak position $q_{\rm m}$, peak intensity, and width. The intensity is observed to increase as a function of time while $q_{\rm m}$ decreases, both indicating growth in spatial and compositional amplitude fluctuations as explained in an earlier paper.[3]

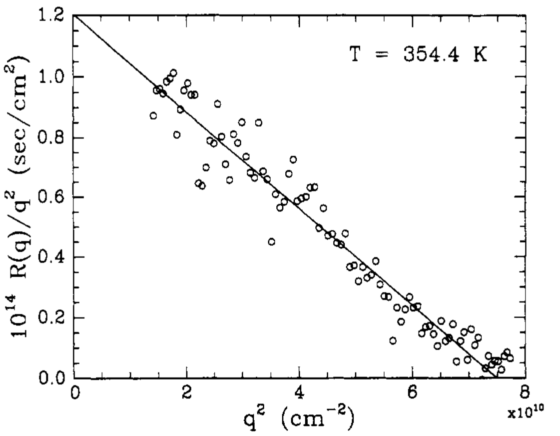

Figure 2. Results of a representative linear analysis on early-time spinodal decomposition light scattering data based on eq 2. $q_{\rm m}(0)$ and $D_{\rm eff}$ are obtained from the q^2 and $R(q)/q^2$ intercepts, respectively.

We performed linear stability analysis using two different procedures[3] to obtain the maximally unstable wavenumber $q_{\rm m}$ at time $t = 0$. The first procedure is an extrapolation using polynomial fits of $q_{\rm m}$ vs time. This method worked well for all quenches. The second procedure is the more involved analysis of the amplification factors in the linear regime as originally proposed by Cahn.[1] In this case, the rate at which the intensity scattered by unstable wavenumbers grows must be evaluated. During the early stages this intensity grows exponentially

$$I(q,t) \cong I(q,0)e^{2R(q)t} \tag{1}$$

with a q dependence described by the so-called amplification factor[7-9]

$$R(q) = D_{\rm eff}q^2\left[1 - \frac{1}{2}\left(\frac{q}{q_{\rm m}(t = 0)}\right)^2\right] \tag{2}$$

which contains two parameters, $q_{\rm m}(t = 0)$ and an effective diffusion coefficient $D_{\rm eff}$.

We were able to obtain a viable set of $R(q)$ values from the linear portion of $\ln[I(q,t)]$ vs t (see ref 3) for quenches between 78.5 and 90.5 °C. A representative plot of $R(q)/q^2$ vs q^2 is presented in Figure 2, from which $q_{\rm m}(0)$ and $D_{\rm eff}$ were determined. In all cases $q_{\rm m}(0)$ obtained by this approach was in excellent agreement with that determined by the extrapolation method; a comparison of the two techniques is given in an earlier publication.[3] For quenches below 78.5 °C we were not able to access a time regime in which eq 1 is valid. Figure 3 shows the values of $q_{\rm m}^2$ $t = 0$) obtained using both procedures as a function of the inverse of the quench temperature T. The larger error bars for deeper quenches are indicative of the difficulties in the extrapolations to time zero. Except for a few quenches close to the critical point, the data follow a straight line as expected from mean-field theory (see below). The deviations from the mean-field behavior will be the subject of a future publication.[10]

The Cahn-Cook[1,11] theory for the spinodal decomposition of metal alloys has been extended to polymer blends by de Gennes,[7] Pincus,[8] and Binder.[9] These authors developed the following prediction

$$q_{\rm m}^2(t = 0) = \frac{3}{2R_{\rm g}^2}\left(\frac{\chi}{\chi_{\rm c}} - 1\right) \tag{3}$$

where $R_{\rm g}$ is the unperturbed radius of gyration of the polymer chains and χ is the Flory-Huggins segment-segment interaction parameter. Within mean-field theory the critical point is given by $\chi_{\rm c} = 2/N$.[5,6,12] Here, the factor

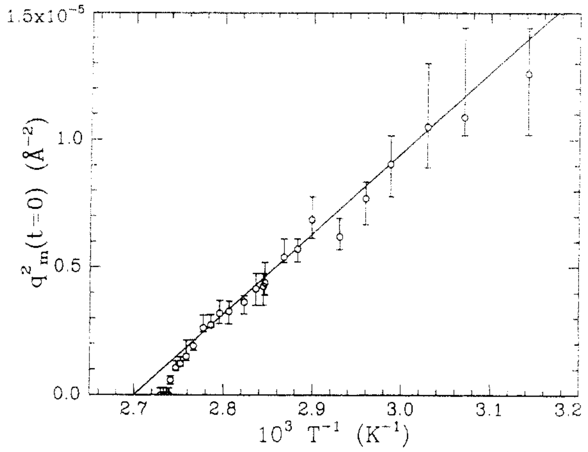

Figure 3. Maximum initial-time wave vector plotted vs inverse temperature for quenches ranging from 45 to 89 °C. Using mean-field theory, the data fall onto the expected straight line except for a few quenches near the critical point. The slope of the line yields a radius of gyration R_g = 165 Å, in good agreement with the SANS value of 155 Å. Likewise, the $q_m^2 = 0$ intercept, which provides an estimate of the mean-field critical temperature T_c = 97 °C, agrees well with the SANS-determined value of 93 °C.

$(3/2R_g^2)^{1/2}$ plays the role of a reciprocal bare correlation length. For the PEP mixture used in this study, the temperature dependence of χ was measured in the one-phase region with small-angle neutron scattering[12] (SANS) and found to be

$$\chi = a/T + b = 0.568/T - 6.62 \times 10^{-4} \tag{4}$$

These same experiments also yielded the radius of gyration R_g = 155 Å. Combining eqs 3 and 4 yields

$$q_m^2(t=0) = \frac{3}{2R_g^2}\left(\frac{T_c}{T} - 1\right)\frac{a}{a + bT_c} \tag{5}$$

which accounts for the axes used in Figure 3. From the slope of the straight line in Figure 2, we calculated R_g = 165 Å, which is in good agreement with the results obtained from SANS in the one-phase region. Here we note that setting the entropic part of the χ parameter to zero (b = 0) results in a radius of gyration of 125 Å. This underscores the importance of knowing and using the temperature dependence of χ in comparing temperature quenches to the theoretical predictions.

The $q_m^2 = 0$ intercept of the linear fit in Figure 3 provides an estimate of the mean-field value for the critical temperature T_c = 97 °C. Using $\chi_c = 2/N$ and N = 2250, eq 4 yields T_c = 93 °C. This is a reasonable agreement between the critical temperatures determined from mean-field analyses in the two-phase and one-phase regions.

To analyze the coarsening of the spinodally decomposing mixtures for dynamic scaling behavior, we need a natural time scale τ in addition to the above-described natural length scale $q_m^{-1}(t = 0)$. Here we follow two separate procedures for estimating τ and compare the results under Discussion. The conventional approach[2,3] is to use the values of D_{eff} that were obtained from the early-stage analysis (i.e., Figure 2). A reduced plot of $q_m/q_m(0)$ vs $\tau = tD_{\text{eff}}q_m^2(0)$ is presented in Figure 4. (This plot contains only those data that exhibited a measurable early-stage regime, ln $I(q,t) \sim t$.) Clearly, the light scattering data fail to collapse onto a single reduced curve. A similar result was obtained in our earlier study of protonated and deuterated polybutadienes,[3] although there the order was inverted, i.e., the smallest quench produced the largest τ.

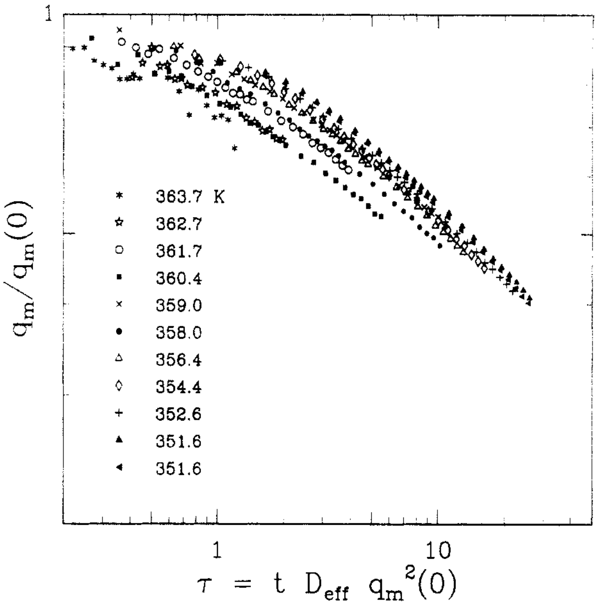

Figure 4. Universal scaling plot of light scattering data based on length and time scaling parameters obtained from the linear Cahn analysis. Failure of these data to collapse onto a single, universal curve can be attributed to deficiencies in the definition of D_{eff} since $q_m(0)$ is quantitatively accounted for by eq 3 (see Figure 3).

Two factors contribute to the temperature dependence of the effective cooperative diffusivity in the typical treatment of polymer mixtures[6,9]

$$D_{\text{eff}} = D(\chi/\chi_c - 1) = D\epsilon \tag{6}$$

where D is the cooperative diffusion coefficient and $\epsilon = \chi/\chi_c - 1$ provides the familiar critical slowing down as $T \to T_c$. (Equation 6 represents the $q \to 0$ limit as discussed below.) For polymer melts D is generally characterized by a much stronger temperature dependence than that found with low molecular weight liquids. Neglecting minor variations in density, the temperature dependence of D can be related to that of the zero-shear viscosity η_0,

$$\frac{D(T)\eta_0(T)}{T\rho} = \frac{D(T_0)\eta_0(T_0)}{T_0\rho_0} \tag{7}$$

where[13]

$$\eta_0(T) = a_T\eta_0(T_0) \tag{8}$$

in which the WLF shift parameter a_T obeys the empirical law

$$\log(a_T) = \frac{-c_1(T - T_0)}{c_2 + (T - T_0)} \tag{9}$$

Using the time–temperature superposition principle with a reference temperature of T_0 = 35 °C, the rheological data obtained for the h-PEP specimen over the temperature range 30–110 °C can be reduced to the master curve illustrated in Figure 5. The value of a_T at each temperature can be determined from[13]

$$G(T_0,\omega) = \frac{T_0}{T}\frac{\rho_0}{\rho}G(T,\omega a_T) \tag{10}$$

where G is either the storage (G') or loss (G'') modulus. Fitting the values of a_T to eq 9, the WLF parameters were determined to be $c_1 = 5.52 \pm 0.36$ and $c_2 = 148.6 \pm 13.2$ °C; errors derive from the estimated uncertainties in superimposing the dynamic–mechanic data. This WLF fit is displayed in the inset of Figure 5.

It is appropriate here to mention that these rheological measurements are not noticeably affected by spinodal

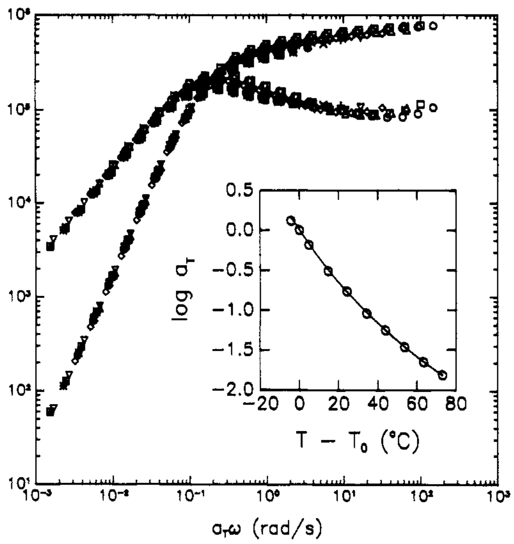

Figure 5. Single-component h-PEP rheological data for temperatures ranging from 30 to 110 °C at 10 °C intervals plotted using time–temperature superposition with a 35 °C reference temperature. Using the shift factors from the superimposed data, the inset displays the WLF fit with parameters $c_1 = 5.52 \pm 0.36$ and $c_2 = 148.6 \pm 13.2$ °C.

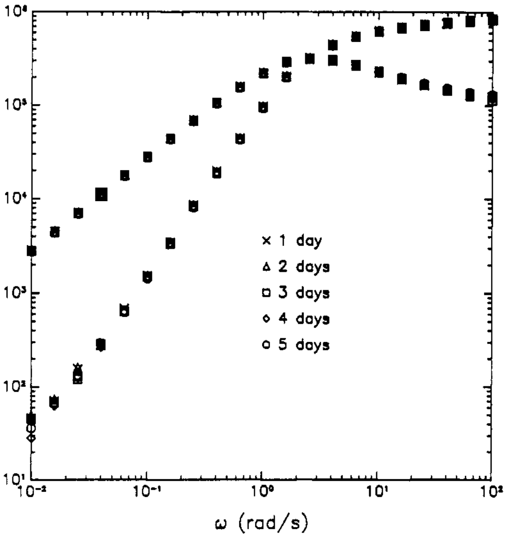

Figure 6. Isotopic PEP mixture was allowed to spinodally decompose for 5 days at 75 °C while rheological measurements were conducted. Although calculations indicate the development of a coarse-grained structure by approximately 12 h, the data reveal no changes with time and maintain terminal-like ($G' \sim \omega^2$, $G'' \sim \omega$) behavior throughout.

decomposition. In our laboratory, rheological data were obtained at a quench depth of 75 °C over a 5-day period after the isotopic PEP mixture was quenched from 110 °C (single phase), and no detection of spinodal coarsening was observed for this critical mixture (see Figure 6). Note that the sample exhibited the expected[13] terminal behavior at low frequencies for both the storage modulus ($G' \sim \omega^2$) and the loss modulus $G'' \sim \omega^1$) and that the moduli values are the same as for the single-component sample (at the appropriate temperature as shown in Figure 5). Figure 7 shows the results of a more sensitive lower frequency experiment, and again no time-dependent change in the mechanical properties of the spinodally decomposing mixture is observed. Although we expect that with a sufficiently sensitive transducer and at low enough frequencies the measured moduli might reflect the presence of spinodal structure, with the equipment available this was not possible.

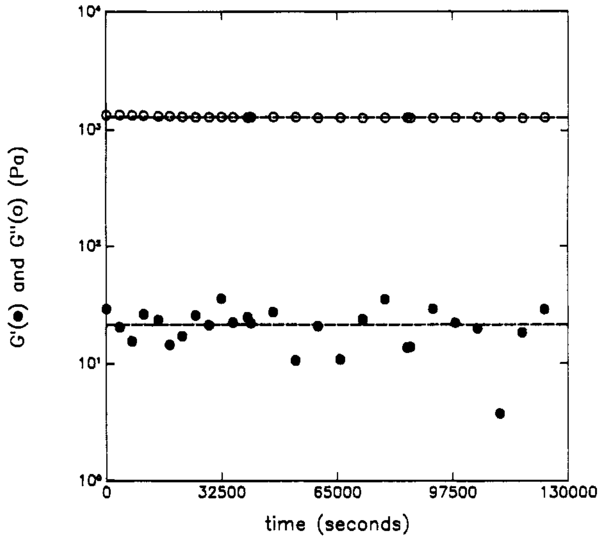

Figure 7. Results of a more sensitive viscoelastic experiment conducted at a frequency of $\omega = 6 \times 10^{-3}$ rad/s. As in Figure 6, no rheological change is observed over a 1.5-day period.

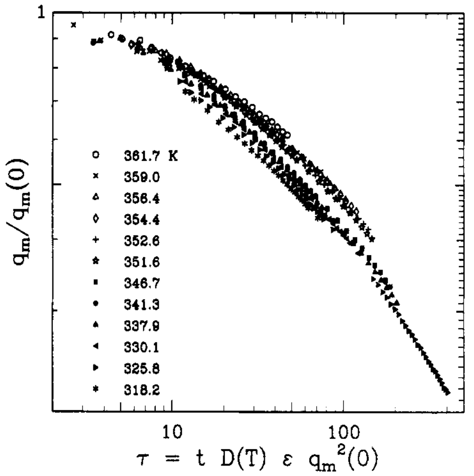

Figure 8. Light scattering data for quenches ranging from 45 to 89 °C plotted after normalizing for time and length based on the independently determined cooperative diffusion coefficient $D(T)$. These data fail to reduce onto a universal curve, and the reduced time scale is an order of magnitude greater than that obtained from the Cahn analysis (see Figure 4).

We are now in a position to scale the light scattering data for quenches to 12 different temperatures with the natural scaling variables in a second way. The cooperative diffusion coefficient $D(T)$ has been determined for the PEP mixture by Norton and Kramer;[14] $D(T = 35\ °\text{C}) = 4.8 \times 10^{-14}$ cm^2/s and $D(T = 70\ °\text{C}) = 6.0 \times 10^{-13}$ cm^2/s. These values are consistent within experimental error with eqs 7–9: $D(70\ °\text{C})/D(35\ °\text{C}) = 12.5$, while $(T\rho/T_0\rho_0)a_T^{-1} = 12.3$, where $T = 70$ °C, $T_0 = 35$ °C, and $(\partial \ln\rho/\partial T) \cong (-7 \times 10^{-4})C^{-1}$. Using $D(T) = D(T_0 = 35\ °\text{C})a_T^{-1}(T\rho/T_0\rho_0)$, we have prepared another "universal" scaling plot based on $q_m/q_m(0)$ and $\tau = tD(T)\epsilon q_m^2(0)$ as illustrated in Figure 8. Our first observation is that the data still do not fall onto a single master curve. There are significant and systematic deviations, well outside the precision of our measurements, indicating that coarsening is seemingly faster for deeper quenches than for shallow quenches. Even more striking is the reduced time scale, which is roughly 10 times greater than that found in Figure 4.

In Figure 9 we demonstrate that it is possible to force the data onto a universal curve (using the measurement at 341.3 K as the reference curve). To do this, it is necessary to use an additional temperature-dependent shift factor,

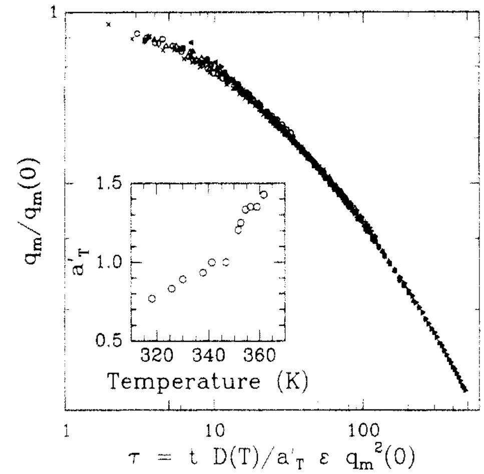

Figure 9. Light scattering data from Figure 8 forced to collapse onto a single curve by additional horizontal shifting. The inset portrays the additional shift factors a'_T necessary to accomplish this superposition.

a'_T, that is plotted vs temperature in the inset of Figure 9. If we simply (and incorrectly) apply the WLF relationship to the raw light scattering data, we obtain $c_1 = 1.99$ and $c_2 = 41.1$ °C for a reference temperature of 35 °C. These values are well beyond the error limits of the rheologically determined values (see inset of Figure 3). Here we note that the absolute value of a'_T is arbitrary (depending on the choice of reference temperature); only the temperature dependence is significant.

Discussion

Our experiments on spinodal decomposition with the critical isotopic PEP mixture have produced two sets of results: time-dependent light scattering data that make contact with the concept of dynamic scaling and rheological measurements that address the issue of macroscopic property changes during this phase separation process. These issues are addressed individually in this section.

Time-Dependent Light Scattering. Two parameters, $q_m(0)$ and D_{eff}, are associated with both linear spinodal decomposition analysis and the nonlinear dynamic scaling hypothesis. Our results conclusively show that the failure of dynamic scaling in spinodally decomposing critical isotopic mixtures derives from shortcomings in the treatment of D_{eff} and not $q_m(0)$. The length scale at which fluctuations grow most rapidly in the early stages of spinodal decomposition is controlled thermodynamically. Since relatively high molecular weights are required to produce phase separation in isotopic polymer mixtures, $q_m(0)$ should be governed by eq 3, a mean-field expression, except very close to T_c.[12] Both symmetric isotopic mixtures that we have studied[3] support this expectation. Linear analysis at early times, coupled with a quantitative knowledge of $\chi(T)$, leads to values for R_g that agree within experimental error with those determined independently by small-angle neutron scattering measurements in the one-phase regime.[12] This firmly establishes the thermodynamic aspect of the Cahn theory[1] as applied to symmetric polymer mixtures.[7-9]

This unambiguous agreement with theory does not extend to the dynamic part of the analysis. Using the established[2,3] procedure for reducing time, we fail to collapse the light scattering data onto a universal curve (Figure 4). Moreover, if we accept the definition of D_{eff} provided by eq 6 and naively use the experimentally determined cooperative diffusion coefficient $D(T)$, the results still fail to superimpose satisfactorily (Figure 8) and the reduced time scale is shifted higher by roughly an order of magnitude relative to that associated with the Cahn analysis. From this we must conclude that $D_{\text{eff}} \neq D(\chi/\chi_c - 1)$.

There are a variety of fundamental reasons why eq 6 could or should fail during spinodal decomposition. A complete assessment of these issues is beyond the scope of this publication. We will only offer several qualitative observations here, deferring a more complete discussion to the future.

Equation 6 represents the $q \rightarrow 0$ limit of the general expression for the relaxation time of a liquid mixture[9]

$$\tau_q^{-1} \equiv D_{\text{eff}} q^2 = q^2 \Lambda(q)/S(q) \qquad (11)$$

where $\Lambda(q)$ is a wavevector-dependent Onsager coefficient and $S(q)$ represents the static structure factor. de Gennes,[7] Pincus,[8] and Binder[9] each recognized the significance of including the q dependence in D_{eff} when treating the spinodal decomposition problem, particularly where $qR_g \gtrsim 1$. Only in the limit $qR_g \ll 1$ can we expect eq 11 to approach eq 6. Our experiments have been conducted over $0.1 \lesssim qR_g \lesssim 0.5$ (see Figure 3 with $R_g = 155$ Å), which certainly does not justify use of the asymptotic, q-independent, relationship, particularly for the deeper quenches. However, this line of reasoning leads us to expect better agreement between Figures 4 and 8 for shallow quenches where $q_m(0)R_g$ is smallest, contrary to what we find.

Equation 11 represents conventional van Hove theory[15] for binary liquid mixtures, which is adapted to binary polymer mixtures by relating collective relaxation to single-chain relaxation.[9] This mean-field approach ignores hydrodynamic interactions ("mode-coupling") that become important as the critical point is approached. Binder[9] has pointed out the potential impact of such fluctuation effects on spinodal decomposition dynamics, although these effects were expected to be relatively small with high molecular weight polymer mixtures. Recently we have shown[16] that mode-coupling dynamics[17-19] extend well beyond the crossover point from non-mean-field to mean-field static behavior as described by the static Ginzburg criterion[20,23] in single-phase binary polymer mixtures. This leads to a rather complex set of dynamical scaling regimes, beginning with Ising-like and mode-coupled dynamics close to T_c and eventually extending to a mean-field and non-mode-coupled (van Hove) regime when $T \gg T_c$. A theoretical description of this behavior has been presented by Fredrickson.[24]

Around a critical point we expect qualitatively similar dynamic scaling above and below T_c, although the magnitudes of certain scaling coefficients may differ.[25] Hence, we presume that the hydrodynamic interactions documented above T_c will be present following an instantaneous quench into the unstable region of phase space. If our findings in the single-phase polymer mixtures are reflected below T_c, then mode-coupled dynamics could influence the initial spinodal decomposition process leading to a failure of eq 6. (Here we note that Douglas[26] has recently considered such effects in a related publication on phase separation and shear flow.) According to the single-phase analysis,[16,24] the mean-field van Hove limit is approached when $\xi \ll R_g N^{1/2}$, where ξ is the static fluctuation correlation length. For the mixture studied here $R_g N^{1/2} = 7350$, while $L_m(0) = 2\pi/q_m(0)$ ranges from 1800 to 8200 Å, placing the (single-phase) dynamical crossover condition within the range of our results. Therefore, a second possible source of discrepancy lies with hydrodynamic interactions. Figure 9 lends some support for this conjecture. As $T \rightarrow T_c$ we notice an increase in the temperature dependence of a'_T, while the required additional shift necessary to superimpose the data (after being time-reduced by $D\epsilon q_m^2(0)$ diminishes with deeper quenches. In the one-phase region hydrodynamic interactions become less important when $T \gg T_c$,[16] and this behavior appears to be consistent with what we observe when $T \ll T_c$.

A final observation should be made regarding our previous findings with an isotopic polybutadiene mixture. There we found a similar reduced time plot based on a Cahn analysis as reported in Figure 4. However, the order in τ with respect to temperature was reversed; i.e., the longest reduced times were obtained with the shallowest quenches. We cannot identify any obvious differences in this mixture that should influence the dynamic scaling behavior. Poly(ethylene–propylene) is characterized by an entanglement molecular weight of $M_e = 1660$, while for 1,4-poly(butadiene) (PB) (approximately 40% *cis*, 50% *trans*, and 10% *vinyl*) $M_e = 1900$ and $M_C = 5900$,[13] where the latter represents the crossover molecular weight for steady-flow viscosity. In the present case involving relaxation time scaling M_C is the appropriate entanglement parameter. Unfortunately, an exact relationship between M_e and M_C has not been developed, although in general $M_C \cong (2\text{–}3)M_e$.[13] Since $M_C/M_e = 3.1$ for the 1,4-polybutadiene material, we can safely assume that $M_{C,PB}/M_{C,PEP} \geq M_{e,PB}/M_{e,PEP} = 1.14$. Considering that this difference will appear to the power 3.4 in the time scales and represents a conservative lower limit, it may influence the dynamics of spinodal decomposition. We believe entanglement effects, and possibly the molecular relaxation mechanism itself, must be considered in addressing the disparity between D_{eff} as determined by the Cahn analysis and $D(\chi/\chi_c - 1)$.

Clearly the only firm conclusion that can be drawn from our results is that the conventional approach to reducing time during spinodal decomposition in binary polymer mixtures should be examined more carefully.

Rheological Measurements. Now we return to the results presented in Figures 6 and 7 and comment on the feasibility of using rheology as an alternate or complementary technique to light scattering with which to observe the growth of spinodal structure. Figures 6 and 7 display rheological data for the h-PEP/d-PEP mixture as it spinodally decomposes for 5 days at 75 °C. Because of the relatively high molecular weight of this sample, it was necessary to choose the quench temperature that maximized the rate at which the spinodal structure evolved such that the various separation stages (described below) could be accessed in a reasonable experimental time window. An examination of eq 6 shows that at shallow quenches the thermodynamic driving force expressed through $(\chi/\chi_c - 1)$ becomes small, while at deeper quenches the viscosity increases due to the lower temperatures and the cooperative diffusion becomes small; that is, as $T \rightarrow T_c$, $D_{eff} \rightarrow 0$, and as $T \rightarrow 0$, $D_{eff} \rightarrow 0$. Our calculations show that these opposing forces produce a maximum D_{eff} at about 75 °C. Using the crossover characteristic times determined by Bates and Wiltzius[3] for the various stages of spinodal decomposition, we estimate that at this temperature the mixture attains a well-defined coarse structure characteristic of the final stage in roughly 12 h. Therefore, we expected that rheological effects due to interfacial tension between the two phases would be most evident within 1 day and would certainly have been observed well before the rheological measurements were discontinued at 5 days after quenching.

Here we note that the literature does contain examples where rheology has been shown to be sensitive to high-amplitude concentration fluctuations. For example, in the block copolymer case,[27] as the sample passes into an ordered (e.g., lamellar) state, the large concentration gradient between the microdomains produces a deviation from terminal behavior of the dynamic modulus. Ajji et al.[28] have also observed a deviation from terminal-like behavior in a spinodally decomposing binary mixture. Given these examples, we sought to explain the absence of rheological changes in our sample. One explanation suggests a low interfacial tension between the PEP isomers. An alternate hypothesis proposes that the bicontinuous spinodal structure does not lend itself to rheological effects and that the observations made by Ajji et al. are due to other physical phenomena.

There are several reasons why the second explanation seems likely. First, calculations were made using the theory of Joanny and Leibler[29] for the interfacial tension, σ, of a phase-separated polymer mixture

$$\sigma = \frac{2}{3}k_B T/l^2 \left[\epsilon\left(\frac{1}{N_A\phi_c} + \frac{1}{N_B(1-\phi_c)}\right)\right]^{3/2}\left(\frac{1}{\phi_c} + \frac{1}{1-\phi_c}\right)^{1/2} \left[\frac{1}{N_A\phi_c^3} + \frac{1}{N_B(1-\phi_c)^3}\right]^{-1} \quad (12)$$

where k_B is Boltzmann's constant, l is the statistical length, ϵ is the reduced temperature, ϕ_c is the critical composition, and N_A and N_B are the degrees of polymerization of polymers A and B, respectively. These calculations indicate that the interfacial tensions for the PEP system quenched to 75 °C and the PS/PVME system in ref 28 quenched to 146 °C (lower critical solution temperature $T_c \approx 137$ °C) are of the same order of magnitude but somewhat higher for the PEP mixture. Note also that the storage moduli values are of the same order of magnitude for both systems. Therefore, it seems unlikely that a lower interfacial tension of the isomeric system is the reason for the lack of rheological effects.

Second, the rheological interactions between the PEP system homopolymers are less complicated than the interactions between the PS and PVME components in the mixture reported by Ajji et al. The PEP system has a symmetric phase diagram and contains components with the same molecular weights and virtually identical rheological properties, while the PS/PVME system has components that differ in molecular weight and dynamic response. Therefore, the nonterminal behavior observed for the PS/PVME systems may be due to a complicated interaction between these different viscoelastic components as the compositions of the two phases vary with quench depth and separation time. The explanation by these authors that the rheological effects are due to concentration fluctuations similar to those in the block copolymers seems unlikely. In the case of block copolymers, it is the large amplitude of the concentration fluctuations (resulting from the block microstructure) that restricts the relaxation of the individual chains and causes the nonterminal G' and G'' behavior observed. In the case of binary mixtures, although the length scale of the fluctuations may be large, the amplitude of those fluctuations is very small when the sample is initially quenched and remains infinitesimal in the one-phase region where Ajji et al. also observe nonterminal behavior.

We should note, however, that in the absence of entanglements the time-dependent effects of a spinodal structure can be observed. For example, Krall et al.[30] have demonstrated for a critical mixture of isobutyric acid and water that the elastic modulus increases sharply upon quenching and decays gradually as the mixture spinodally decomposes. Because Krall et al. observe this effect at moduli values around 1 mPa, we are not surprised that measurements of structural evolution in polymeric systems, in which moduli values are approximately 4 orders of magnitude greater (see Figure 5), do not produce noticeable results due to masking by the large bare viscoelastic properties.

Conclusion

A model symmetric binary mixture of deuterated and protonated poly(ethylene–propylene) has been studied by static light scattering and rheological measurements following a series of quenches from the one-phase into the unstable region of phase space. Linear analysis of the evolution of two-phase structure at early times following these quenches produced initial heterogeneity lengths that vary with temperature and in magnitude in quantitative agreement with mean-field theory. The initial rate of structure evolution was estimated in two independent ways. Using the Cahn analysis, an effective diffusion coefficient was extracted from the light scattering data. This quantity was also calculated on the basis of separate measurements of the cooperative diffusion coefficient with rheologically determined temperature corrections. The calculated reduced time scale is found to be about 1 order of magnitude greater than that associated with the Cahn analysis of the light scattering data, indicating a failure of the conventional assumption of mean-field, van Hove dynamics for spinodal decomposition in polymer mixtures. In addition, we failed to detect evidence of spinodal decomposition in the terminal viscoelastic properties, contrary to a previous paper. This is attributed to the large bare rheological response of the noninteracting polymers that masks the subtle mechanical effects associated with spinodal decomposition.

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