7276 *Macromolecules* **1996,** *29,* 7276−7279

On “Pinning” Domain Growth in Two-Phase Polymer Liquids

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Received April 9, 1996; Revised Manuscript Received July 29, 1996⊗

ABSTRACT: What has been reported as “pinning” or severely reduced growth rates of phase-separated domains in off-critical polymer blends is shown to be the normal effect of crossover between two kinetic regimes associated with morphology of the liquid−liquid system. The bicontinuous liquid microstructure formed by spinodal decomposition grows rapidly by hydrodynamic coarsening where size $\bar{\xi} \sim Lt$ until the percolated system dissociates into droplets. The droplets then grow by classical coarsening with radius increasing as $\bar{r}^{\,3} \sim Kt$, where K may be calculated for Ostwald ripening and/or coalescence with no impediments to mobility at any size scale. Apparent pinning persists for the induction period $\Delta t \approx \bar{r}^{\,3}/K$ required for the slower particle growth to be observed, and the characteristic $\bar{r} \propto t^{1/3}$ behavior is not recovered for approximately $10\Delta t$. Numerical simulations of spinodal decomposition in polymer blends, which to date omit hydrodynamics, are unable to capture the change in growth mechanism and rate on switching from percolated to droplet morphology.

Introduction

Coarsening is the process by which domain sizes in a phase-separated system increase with time. Phase separation of the binary mixture has been completed (volume fractions and compositions of phases are very near the equilibrium values) and the system evolves to reduce interfacial energy. Two recent studies[1,2] of coarsening in off-critical liquid−liquid mixtures of polyethylene (PE) and hydrogenated polybutadiene (HPB) showed that the average radius $\bar{r}$ of dispersed HPB-rich droplets increases with time $t^{\,1/3}$ or

$$\bar{r}^{\,3} = \bar{r}_0^{\,3} + K(t - t_0) \qquad (1)$$

Anticipating arguments to follow, coarsening time ($t - t_0$) is measured from an arbitrary reference t_0 after phase separation has been achieved and when the average particle radius is $\bar{r}_0$. Volume fractions of HPB-rich droplets were in the range of 0.1−0.2, and the mean radius $\bar{r}$ was evaluated from stereology of planar sections through quench-solidified structures. Mirabella and Barley[1] measured $K = (1-5) \times 10^{-6}\ \mu\text{m}^3/\text{s}$; which are within 25% of the values calculated for coarsening by Ostwald ripening. Crist and Nesarikar[2] considered a number of PE/HPB blends in which K ranged from 0.05×10^{-6} to $10 \times 10^{-6}\ \mu\text{m}^3/\text{s}$; coarsening was by Ostwald ripening and/or coalescence. Agreement between theory and experiment is excellent for the calculated rate $K_{\text{calc}} = K_{\text{C}} + K_{\text{OR}}$, where K_{C} and K_{OR} are for coalescence and Ostwald ripening, respectively. Figure 1 shows observed (K) and calculated (K_{calc}) results for systems dominated by Ostwald ripening, sometimes called the Lifshitz−Slyozov−Wagner mechanism. Here the particle growth is by diffusive flux of HPB molecules through the PE matrix from small to large droplets. $K_{\text{calc}} \approx K_{\text{OR}}$ involves no adjustable parameters; experimental results on thermodynamics[3] were used to evaluate phase compositions and interfacial energy, and polymer diffusivity was measured independently.[4] It should be noted that many other direct space studies of off-critical polymer blends, cited in refs 1 and 2, indicate that eq 1 is followed. However, no comparison was made of experimental and theoretical rates, so those results are not of direct significance here.

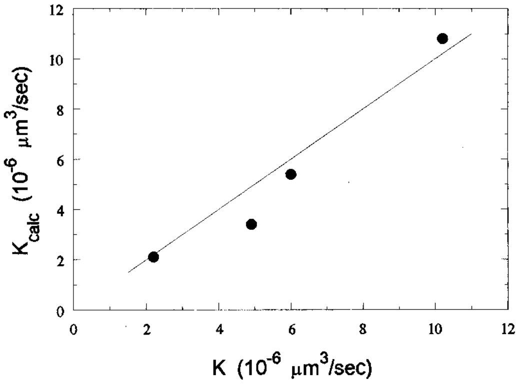

Figure 1. Experimental (K) and calculated (K_{calc}) classical coarsening constants for HPB-rich droplets in PE-rich matrix for melt temperatures 140−160 °C.[2] The solid line is for $K = K_{\text{cal}}$.

The classical coarsening behavior described above appears to be at odds with light scattering studies of spinodal decomposition in blends of poly(styrene-*co*-butadiene) with either polyisoprene or polybutadiene[5−7] or polybutadiene with polyisoprene.[8] For off-critical blends those systems display what has been termed “spontaneous pinning” when the scattering pattern and, by inference, the liquid−liquid structure become independent of time. Both domain size, inversely proportional to the scattering vector at the interference maximum q_{m}, and peak intensity stopped changing for off-critical systems, while those for critical blends evolved continuously over similar time scales. Hashimoto et al. postulated that pinning occurs when the bicontinuous spinodal microstructure is transformed to discrete droplets of the minority phase.[5−7] It was further asserted that dispersed particles coarsen very slowly because large chainlike molecules are subject to enthalpic barriers that retard mass transport. Läuger et al. confirmed that pinning, observed by light scattering, coincides with breakup of the percolated microstructure in polybutadiene/polyisoprene blends.[8] Optical microscopy, however, showed that discrete particles do grow with time, contrary to the light scattering result.

⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1996.

S0024-9297(96)00527-X CCC: $12.00

Thus there are two sets of experiments in which micrometer size droplets of HPB are observed to grow according to eq 1 with rate constant K in excellent accord with theory,[1,2] indicating no impediment to mobility that slows classical coarsening. Other work on off-critical blends indicates that discrete liquid domains grow very slowly or not at all.[5−8] We wish to reconcile the observations to the extent possible. It is shown that "pinning" is a natural consequence of classical coarsening starting after the bicontinuous structure is disrupted. Numerical studies of spinodal decomposition,[9−11] which sometimes indicate pinning at late times in off-critical polymer blends, are considered as well.

Coarsening and Spinodal Decomposition

Spinodal decomposition creates a bicontinuous or percolated microstructure. A distinction should be made between the early and intermediate stages, during which phase separation occurs to establish equilibrium concentrations and volume fractions, and the final stage that describes the growth or coarsening of well-defined phase domains having constant intrinsic properties. The former are driven by chemical potential imbalances, while the latter occurs to reduce the surface energy between coexisting phases. In liquid−liquid systems the bicontinuous regions coarsen by a hydrodynamic viscous flow mechanism driven by local pressure gradients.[13,14] A characteristic feature of this process is that the average domain size $\bar{\xi}$ increases linearly with time:

$$\bar{\xi} = \bar{\xi}_{\rm h} + L(t - t_{\rm h}) \qquad (2)$$

Here $\bar{\xi}_{\rm h}$ is the size at the onset of hydrodynamic growth established at time $t_{\rm h}$. Note that the linear growth rate L is constant, in contrast to $d\bar{r}/dt = K/3\bar{r}^{\,2}$ for classical coarsening in eq 1. It is the size independence of the hydrodynamic mechanism which leads to its dominance in bicontinuous liquids when the diffusion-limited growth rate, which controls early and intermediate stages, invariably drops as the domains (diffusion path lengths) become larger. This size-independent viscous flow process was originally formulated for the final stage of spinodal decomposition, i.e. coarsening of two fully developed interpenetrating phases. Experiments of Hashimoto et al.[5] and Läuger et al.[8] indicate that hydrodynamic coarsening is seen in the intermediate stage, before concentration profiles are fully developed, as well as the final stage.

The bicontinuous morphology established by spinodal decomposition is most stable in symmetric blends having the critical composition $\phi_{\rm c} \approx 0.5$. In off-critical blends the percolated structure invariably converts to particles of the minor phase dispersed in the major phase because the volume fraction of one phase is below the percolation threshold,[9] and/or because hydrodynamic coarsening "pinches off" portions of the structure, disrupting connectivity of the liquid networks.[8,13,14] The percolation-to-cluster (PC) transition occurs at a time $t_{\rm pc}$ that is smaller for blends having overall composition ϕ further from $\phi_{\rm c}$. Of interest here is how domain growth responds to the change from a percolated structure (hydrodynamic coarsening) to a droplet structure (classical coarsening).

A Simple Model

An off-critical blend is quenched into the spinodal region and undergoes phase separation. Hydrodynamic growth proceeds according to eq 2 until the percolation-to-cluster transition at $t_{\rm pc}$, at which time the average domain size is $\bar{\xi}_{\rm pc}$. We assume that phase separation is complete at the PC transition; hence any further growth is by classical coarsening. Two further approximations are invoked: the PC transition is instantaneous, and the resulting particles have average size equal to that of the percolated domains; i.e. $\bar{r}_{\rm pc} = \bar{\xi}_{\rm pc}$. From this time on the dispersed droplets of the minority phase grow according to eq 1, which is rewritten as

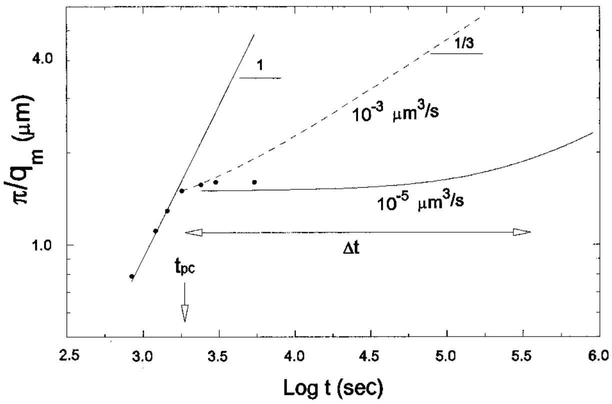

Figure 2. Data of Läuger et al.[8] for domain size in an off-critical PB/PI blend at 82 °C (●). Hydrodynamic coarsening operates on the bicontinuous structure for log $t < 3.25$ (solid line with slope of 1). Following the percolation-to-cluster transition at $t_{\rm pc} = 1800$ s, classical coarsening is calculated for $K = 10^{-3}$ μm^3/s (dashed line with limiting slope of $^1/_3$) and $K = 10^{-5}$ μm^3/s (solid line emphasizing induction period $\Delta t = 3.4 \times 10^5$ s).

$$\bar{r}_{\rm pc} = \bar{r}_{\rm pc}{}^3 + K(t - t_{\rm pc}) \qquad (3)$$

The shift from hydrodynamic coarsening (eq 2) to classical coarsening (eq 3) rescales the time for changes in domain size. Regardless of the linear growth rate L in the percolated structure, the dispersed particles require a time interval $\Delta t = \bar{r}_{\rm pc}{}^3/K$ for $\bar{r}$ to increase by a factor of $2^{1/3} = 1.26$ over the initial size $\bar{r}_{\rm pc}$. If, as is frequently the case, coarsening data are presented in a plot of log $\bar{r}$ versus log t and the initial droplet growth rate is less than L, there will be a crossover period of $\sim 10\Delta t$ before one recovers the expected slope of $^1/_3$, or $\bar{r} \propto t^{1/3}$.

An example of this behavior is given in Figure 2 for the experimental results of Läuger et al.[8] on polybutadiene/polyisoprene (33% PI) at 82 °C. The effective domain size is defined as π/q_m, which is approximately the thickness of one phase in the percolated structure and comparable to the droplet radius at longer times.[15] For $t < t_{\rm pc} = 1800$ s the percolated structure grows at a constant rate ($L = 9 \times 10^{-4}$ μm/s) as expected for hydrodynamic coarsening. Classical coarsening is calculated from eq 3 for the initial droplet size $\bar{r}_{\rm pc} = 1.5$ μm at $t_{\rm pc} = 1800$ s and two rates. $K = 10^{-5}$ μm^3/s is typical of high molecular weight polymers coarsening by Ostwald ripening.[1,2] Note that growth is virtually imperceptible over the induction time $\Delta t = 3.4 \times 10^5$ s. The dashed line for $K = 10^{-3}$ μm^3/s is included to show the return to $t^{\,1/3}$ behavior after lapse of a shorter $10\Delta t$ crossover interval.

Discussion

We concur with Hashimoto et al.[5−7] and Läuger et al.[8] that the percolation-to-cluster transition results in a modification of growth dynamics in phase-separated polymer liquids. When the coarsening of discrete particles is slower than the growth of the bicontinuous structure, log–log plots such as Figure 2 may suggest that the particle size is pinned when it is coarsening as expected according to eq 3. This is a crossover problem exacerbated by different time scales for domain growth before and after t_{pc}. It is not possible to generalize on the magnitude of the induction time after the transition, but the approximate relation $\Delta t \approx (Lt_{pc})^3/K$ is instructive. For a fixed ratio of coarsening constants L^3/K, prolonging the hydrodynamic regime (delaying the PC transition) by a factor of 2 increases the induction time by a factor of 8.

There is no impediment to diffusive mass transport of polymer chains from one liquid phase to another that slows classical coarsening. We base this statement primarily on the equality of experimental coarsening constants K for PE/HPB blends and K_{calc} evaluated with conventional or unrestricted diffusive flux;[1,2] see Figure 1. One must take issue with the proposition of Hashimoto et al.[5,7] that there is a kinetic barrier, derived from molar heat of mixing χN, to the diffusion of polymers between liquid domains; here χ is the Flory–Huggins interaction parameter and N is the degree of polymerization. If one compares a monomer–monomer blend ($N = 1$) and a polymer–polymer blend ($N \gg 1$) at the same quench depth, e.g. at $\chi N \approx 3$, there is no difference in heat of mixing or component miscibilities. High molecular weight polymers do, however, have small interdiffusion coefficients D, thus decreasing $K_{OR} \propto D$. Intrinsic polymer diffusivities are small because of molecular size and shape effects that have nothing to do with enthalpies of mixing. Classical coarsening may be dominated by droplet coalescence when miscibility is very small (χN is large) and/or matrix viscosity η_m is relatively small.[2,12] Here again $\bar{r}^3 \sim K_C\, t$ where the coarsening constant $K_C \propto 1/\eta_m$ is small because of high molecular weight (and entanglements) of polymers. The same induction time $\Delta t = \bar{r}_{pc}{}^3/K$ is expected at the percolation-to-cluster transition.

Three numerical studies of spinodal decomposition and late-stage coarsening of off-critical polymer blends have been reported. In each case the system is composed of two polymers of equal degree of polymerization N and statistical segment length a with repulsive interactions given by the Flory–Huggins parameter χ. Blends were near the upper critical solution temperature, i.e. $\chi \leq 1.2\chi_c$, where $\chi_c = 2/N$. It is important to note that these calculations did not include hydrodynamics (the percolated structure grows as $\bar{\xi} \propto t^{1/3}$), so the crossover effect discussed above does not apply. Kotnis and Muthakumar[9] observed diffusion-controlled domain growth before the PC transition, but no coarsening of droplets after the PC transition. This "freezing" was attributed to entropic barriers opposing diffusion through the polymer–polymer interface. Brown and Chakrabarti[10] found that this type of pinning was absent if thermal fluctuations were added to the model; size was proportional to $t^{1/3}$ before and after the PC transition with no discontinuity. Recent studies by Castellano and Glotzer[11] showed that the pinning observed by Kotnis and Muthakumar was absent, even without thermal noise, if proper attention is paid to length scales represented in the simulation.

Numerical integration of the discretized Cahn–Hilliard equation[16] is done on a lattice, which should have a spatial resolution smaller than the equilibrium interface thickness Z_e between coexisting phases. If this is not the case, the concentration profiles that drive coarsening are represented incorrectly in the late stages and simulated domain growth slows and may cease, an artifact that was recognized in early modeling studies of spinodal decomposition.[17] It is important to remember that equilibrium interface thickness $Z_e \approx a(\chi - \chi_c)^{-1/2}$ is a function of χ (or temperature T) for fixed N, and is independent of overall composition ϕ of the blend.[18] References 9–11 employ a cubic lattice with scaled spacing g that diverges as the spinodal is approached along either the temperature or composition axes of the phase diagram. That scaling relation leads to $g/Z_e \approx 1$ for critical blends ($\phi = \phi_c = {}^1/_2$), which is adequate to prevent freezing or numerical pinning at all relevant quench depths. For off-critical blends ($\phi \neq \phi_c$), however, the scaled grid size increases, while interface thickness is unchanged. It is easy to show that $g/Z_e = 2$ for $\phi \approx 0.4$ (or 0.6) at a representative quench depth of $\chi/\chi_c = 1.1$. The oversize grid indeed causes the domains to stop growing in off-critical simulations,[9,10] but normal $\bar{\xi} \propto t^{1/3}$ growth is recovered when the grid size is reduced by a factor of 2 to reestablish $g/Z_e \approx 1$.[11]

The foregoing analysis confirms the conclusion of Castellano and Glotzer[11] that "pinning" seen with numerical studies of spinodal decomposition in off-critical polymer blends results from improperly scaled grid size. This result is consistent with similar calculations on nonpolymeric systems.[17,19,20] We emphasize that there is no experimental or numerical evidence for hindered diffusive transport in or through polymer liquids. If interfacial barriers of the type proposed by Hashimoto et al[5–7] or Kotnis and Muthakumar[9] did exist, classical coarsening would proceed, albeit slowly, with a $t^{1/2}$ dependence,[21] not the $t^{1/3}$ behavior observed experimentally.[1,2]

While thermally induced concentration fluctuations have, in principle, no effect on the energetics or dynamics of late-stage spinodal decomposition or coarsening, Brown and Chakrabarti[10] found that including a heat bath in the calculation prevented "freezing", even when the grid size was too large. A logical explanation is that the heat bath maintains the interface width at values above Z_e,[22] thus permitting the system to evolve without artificial pinning. Thermal fluctuations here provide a computational mechanism that compensates for inaccurate interfacial profiles resulting from an overly large grid size.

We close this discussion with some observations on the use of scattering methods to follow the evolution of phase separation and subsequent coarsening. When the structure is self-similar, as during hydrodynamic growth of bicontinuous domains at $t < t_{pc}$, changes in the position of the interference maximum q_m are unambiguous measures of the time dependence of the characteristic size $\bar{\xi}$ in the blend. The same statement applies to spherical droplets coarsening by Ostwald ripening; here the particle size distributions are self-similar, and the coarsening mechanism imposes interparticle correlations that result in an interference function peaked at $q_m \approx 2/\bar{r}$.[15] One anticipates difficulty in interpreting scattering patterns when self-similarity is absent, as during the percolation-to-cluster transition. This may be the reason that Läuger et al.[8] see some particle growth by microscopy while the scattering parameter q_m remains constant for $t > 1800$ s (see Figure 2). It is also possible that sampling of relatively small volumes by microscopy leads to atypical results.

Conclusions

There is no fundamental discrepancy between experiments that indicate an apparent cessation of domain growth when the percolated microstructure is disrupted in off-critical polymer blends and studies wherein dispersed droplets coarsen as $\bar{r} \propto t^{1/3}$. The droplets grow according to classical laws to reduce interfacial energy, with no barriers to diffusive transport between or within coexisting phases. What has been described as "spontaneous pinning" of the droplet morphology is a manifestation of the induction time $\Delta t = \bar{r}_{pc}^3/K$ required for classical coarsening to become perceptible after the percolation-to-cluster transition. Because the time scale for hydrodynamic growth is usually much smaller than that for classical coarsening, analysis of both "fast" and "slow" regimes in one experiment has not been reported, to our knowledge. Recent scattering studies by Sung and Han[23] on off-critical, low molecular weight polystyrene/polybutadiene blends do show what appears to be a transition from $\bar{\xi} \propto t$ to $\bar{r} \propto t^{1/3}$ behavior. Given that K would be relatively large in this system because the chains are small, a short crossover period $10\Delta t$, such as indicated by the dashed line in Figure 2, is quite possible.

The percolation-to-cluster transition in off-critical blends is an interesting phenomenon that is not understood in detail. Numerical models without hydrodynamic growth can be used to explore the relevance of equilibrium volume fractions to the percolation threshold, provided the grid size is small enough to permit the system to evolve without artificial constraints. The interesting notion that hydrodynamic coarsening itself contributes to instability of the bicontinuous liquid structure[8,13,14] requires a more sophisticated model. Numerical studies of spinodal decomposition that include hydrodynamics have been done for critical systems of monomeric components.[20,24] It is anticipated that these calculations can be extended to off-critical blends. Such models should capture the crossover, with *apparent* pinning of growth, associated with the percolation-to-cluster transition.

Acknowledgment. This work was supported in part by a grant from the Exxon Education Foundation. The author thanks Sanat Kumar, Monica Olvera de la Cruz, and Peter Voorhees for many helpful discussions.

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MA960527P