Domain Growth and Wetting in Polymer Mixtures

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The influence of wetting forces exerted by an interface on the coarsening mechanism of two coexisting liquid phases is studied. Experiments show that in a polymer mixture undergoing spinodal decomposition domains of characteristic length l coarsen with time t according to the power law $l \sim t^{3/2}$ in the direction parallel to a quartz interface. This is in contrast to the bulk behavior, where $l \sim t$. Although a preliminary argument suggests that wetting effects driven by van der Waals forces are responsible for the growth exponent, a proper hydrodynamic theory is not yet available.

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The study of spinodal decomposition and nucleation in binary systems has enjoyed great experimental and theoretical interest in recent years.[1] Our understanding of the various stages of the evolution of the coexisting phases has grown considerably. Most studies to date have concentrated on the behavior of mixtures in the bulk, but it is natural to ask how the presence of a third phase would influence the growth mechanisms. Cahn, in a seminal paper,[2] analyzed the final equilibrium situation for a binary system in the unstable two-phase region in contact with a third phase, e.g., a glass wall. He predicted that close enough to the critical point one of the fluid phases preferentially wets the third phase with a macroscopic layer. This has indeed been observed experimentally in a variety of systems.[3] The kinetics of the formation of the wetting layer, however, are largely unexplored. In this Letter we report on light-scattering and microscopy experiments on a critical polymer mixture quenched into the unstable region. The measured structure factor yields two length scales with a vastly different time dependence. We identify two different growth modes; a slow mode, corresponding to the bulk behavior, and a fast mode, where the length scale l grows with time t like $t^{1.5}$. This fast mode occurs parallel to the interface of the polymer mixture with a quartz window. The observed power law differs from that observed in bulk,[1,4-6] which asymptotically approaches $l \sim t$. The latter result has been explained by Siggia[7] using dimensional analysis of the Navier-Stokes equations. Unfortunately this kind of analysis breaks down, as soon as additional driving forces like gravity or wetting forces are added to the hydrodynamic equations. The observed power-law relationship between time and length scale and the exponent of 1.5 of the fast growth have yet no theoretical explanation. Our results are in apparent disagreement with recent observations by Guenoun, Beysens, and Robert.[8] We believe this is because the fast growth occurs at earlier reduced times than were experimentally accessible by Guenoun, Beysens, and Robert.

The system studied is a blend of polyisoprene (PI) and poly(ethylene-propylene) with molecular weights of 2000 and 5000, respectively. The phase diagram has been published elsewhere.[9] The sample was prepared at the critical composition of 0.605 volume fraction PI and had a critical temperature of $T_c = 38\,°\mathrm{C}$. The sample was sealed between two quartz plates and had a thickness of 1 mm. The quench depth ranged between 0.15 and 0.95 °C below T_c, with temperature equilibration times shorter than 80 sec. The light-scattering apparatus described elsewhere[10] used a 14-bit 512×512 charge-coupled device to measure the intensity of the scattered light for scattering wave vectors q ranging between 0.05

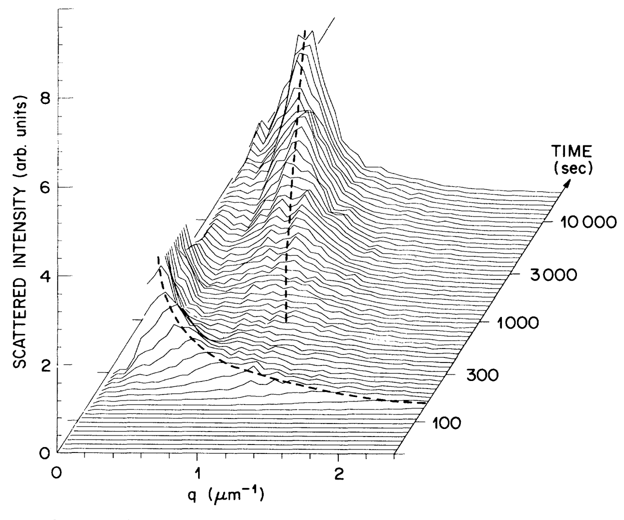

FIG. 1. The scattered intensity as a function of wave vector q at various times after a 0.65 °C quench below the critical temperature T_c. The locus of the maxima of the fast-mode peak and the slow-mode peak are indicated by dashed lines. The maximum peak intensities for the two peaks displayed are 2 and 3.4 for the fast and slow modes, respectively.

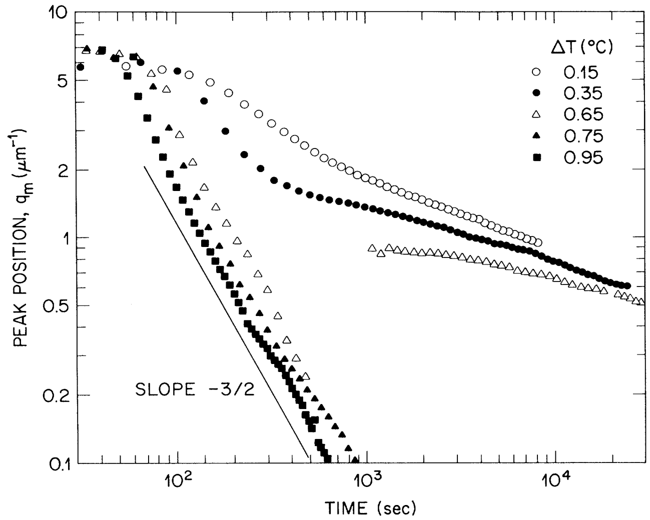

FIG. 2. The peak position of the fast and the slow mode for five different quenches as a function of time.

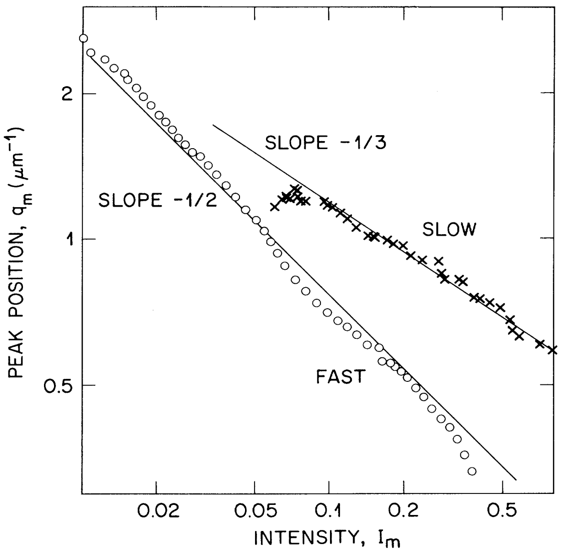

FIG. 3. The peak position of the fast (○) and the slow (×) mode as a function of the peak intensity. The peak intensity is measured in arbitrary units.

and 7.6 μm^{-1}. The incident light beam was perpendicular to the quartz windows. A typical set of data is shown in Fig. 1, where the scattered intensity is plotted as a function of q for a 0.65 °C temperature quench at time $t=0$. Note that the time axis is logarithmic. A peaked structure factor characteristic[11] of spinodal decomposition grew out of the background within 50 sec. The earliest peak emerged at $q_m=6.8$ μm^{-1}, which is within the q range stated above. Prior to 150 sec the peak intensity was too weak to be visible on the linear intensity scale of Fig. 1. The peak position q_m moved very rapidly to smaller q indicating coarsening of the evolving structure, and at the same time its intensity grew. After 1000 sec a second peak became detectable. It also moved to smaller q, but much more slowly. Meanwhile, the fast peak had disappeared into the beam stop, which is at $q=0.05$ μm^{-1}, corresponding to a length of approximately 120 μm. The locus of the maxima is indicated for both peaks by dashed lines. In Fig. 2 the peak positions are plotted as a function of time for a number of quenches. The data corresponding to the 0.65 °C quench clearly exhibit the two different mechanisms. The fast mode grows to length scales large enough that the scattering is completely in the forward direction after less than 1000 sec. For shallower quenches there is only an indication of the fast mode, but because its intensity is too weak it cannot be resolved at later times. The reverse holds for deeper quenches, where only the fast mode is resolved in the scattered intensity. The most striking result to note at this point is that the fast mode has a well-defined power-law dependence $q_m \sim t^{-3/2}$.

To further characterize the physical origin of the observed scattering we plot in Fig. 3 the peak position as a function of the peak intensity. If we assume that the coarsening process preserves the self-similarity of the growing structures and that hence the dynamic scaling hypothesis[12,13] prevails, the scatterd intensity should obey the law

$$I(q,t) \sim q_m^{-d}(t) F(q/q_m(t)) , \qquad (1)$$

where F is a universal scaling function and d is the dimensionality of the scattering structure. Equation (1) implies that $q_m \sim I_m^{-1/d}$. The data in Fig. 3 show that the scattering corresponding to the slow and the fast mode is due to a three-dimensional and a two-dimensional structure, respectively. We thus attribute the slow mode to the coarsening process in the bulk, whereas the fast mode is the coarsening in a two-dimensional boundary layer parallel and adjacent to the polymer-glass interface.

We also directly visualized the phase-separation dynamics using an optical microscope. Figure 4 shows a series of pictures taken during the rapid growth phase. The pictures at times greater than approximately 500 sec confirm that there is coexistence of the rapidly coarsening structure and a fine-grained structure, with much shorter length scale, which on the time scales of the figure does not change noticeably. An interesting observation is that the fast-growing structure disappears after 10000 sec, as the system establishes the equilibrium wetting layer predicted by Cahn.[2]

Siggia[7] has shown that the dominant length scale l of bicontinuous phases grows linearly with time in the regime where the surface tension drives the coarsening. This has indeed been observed[4-6] under the condition that effects of gravity could be avoided. In early studies[14] of the late-stage coarsening, gravity was found to

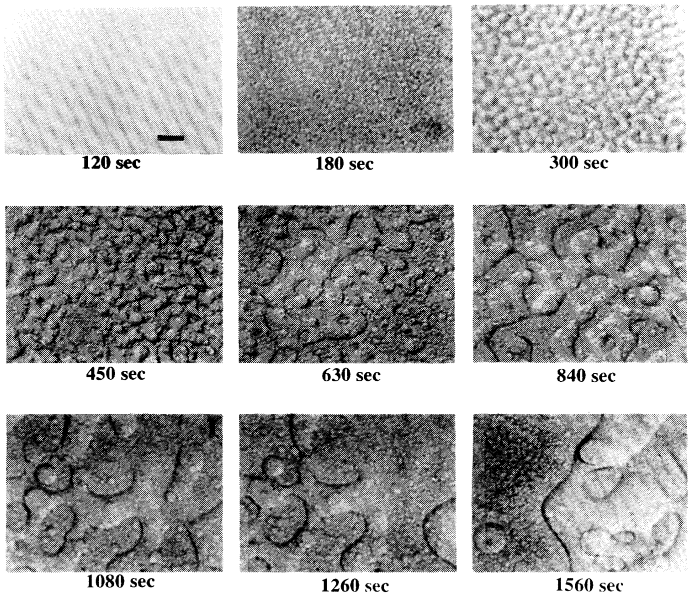

FIG. 4. A series of photomicrographs of the fast coarsening structure. At times greater than 400 sec the coexistence of two different length scales corresponding to interface and bulk growth is visible. The magnification in all the pictures is the same and the length of the bar in the first picture is 50 μm.

influence the growth law $q_m \sim t^{\beta}$ and exponents β between 0.3 and 2 were found. We performed experiments with our flat cell in a vertical and a horizontal position and observed the same large exponent of $\frac{3}{2}$. We can thus assume that the growth law is not influenced by gravity. Along similar lines we can exclude motion due to convection between the two quartz windows driven by a possible residual temperature gradient perpendicular to the windows. For a temperature gradient of 0.1 °C/cm, which is much bigger than we expect actual gradients to be, the calculated convection velocity is less than a micron per 100 sec, slow compared to the observed velocities, $dq_m^{-1}(t)/dt$, which range between 5 and 12 μm per 100 sec.

If there were a residual temperature gradient perpendicular to the glass windows, it would result in a gradient in surface tension and thus in thermocapillary motion of interfaces.[15] For a temperature gradient of 0.1 °C/cm, we calculate a velocity smaller than 0.1 μm per 100 sec, and can thus rule out thermocapillary force as an important component.

Length and time were rescaled by ξ and ξ^2/D_T for all quenches according to standard procedures[1,8,9,11] using the diffusion coefficient D_T and correlation length ξ obtained from linear stability analysis. We find that all the fast-mode data were taken between reduced times of 50 and 1000. In bulk samples, this time frame corresponds to late-stage coarsening,[4] where the domain walls between the coexisting phases are well established. At this point it is interesting to compare our data to those of Guenoun, Beysens, and Robert.[8] The data of the latter group are all at dimensionless times greater than 1000. Their method of direct visualization probably does not allow them to measure the small length scale of the coarsening domains at earlier times. It is thus our opinion that the reason that their exponents (-0.56 to -0.64) are different from ours (-1.5) is that we are in different time regimes.

The only plausible additional driving force leading to the fast-growth pattern that we can present now is a van der Waals force. An interface between two coexisting phases close to a wall experiences a long-range van der Waals force, which is proportional to the square of the difference in dielectric polarizability $\Delta\varepsilon$.[7] Since $\Delta\varepsilon$ is proportional to the difference in composition $\Delta\phi$, and for mean-field systems $\Delta\phi$ is proportional to the square root of the quench depth ΔT, we find that the van der Waals force should be proportional to ΔT. If an interface is at a distance from the wall which is not constant, the van der Waals force would lead to a pressure gradient and hence fluid flow parallel to the wall. Assuming that the fast mode is indeed driven by van der Waals forces, the experimental result

$$q_m^{-1} \sim l \sim t^{3/2}, \tag{2}$$

with l the characteristic length, can be rewritten as

$$\dot{l} \equiv \alpha l^{1/3} \text{ or } l \sim (\alpha t)^{3/2}, \tag{3}$$

where α is proportional to the van der Waals force. Equation (3) gives us a prediction for how the prefactor in $q_m = A t^{-3/2}$ should depend on quench depth. We expect $A \sim \alpha^{-3/2} \sim \Delta T^{-3/2}$. We find good agreement, lending support to the hypothesis that the fast growth is indeed driven by van der Waals forces.

In conclusion, we have carried out light-scattering experiments on polymer mixtures which phase separate in the vicinity of a quartz surface. Domains of characteristic length l parallel to the quartz surface coarsen according to the power law $l \sim t^{3/2}$. This is faster than the coarsening in bulk samples, where surface tension leads to the experimentally observed law that length grows linearly with time. Long-range van der Waals forces exerted by the quartz surface on the interfaces between the coexisting phases lead to wetting and act as an additional driving force. This is probably the physical cause of the observed fast growth. A theoretical treatment, based on the Navier-Stokes equations with the addition of van der Waals forces, is not available to date.

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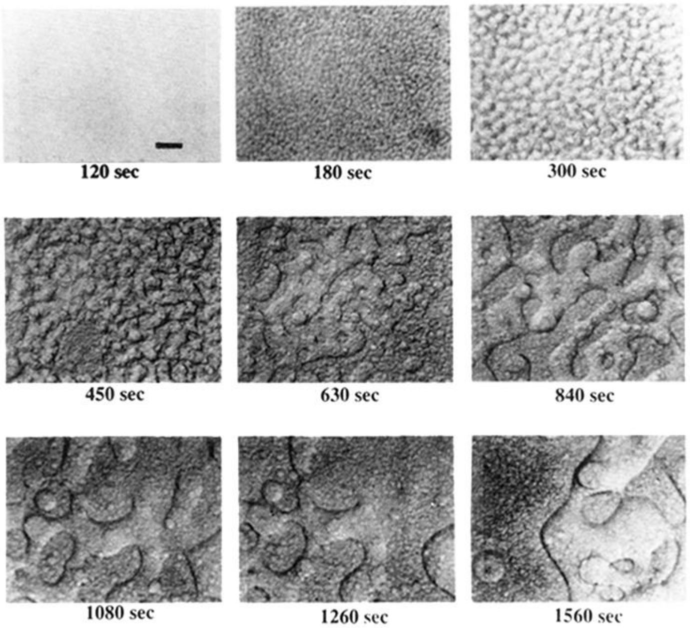

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