

Slow dynamics of segregation in hydrogen-bonded polymer blends

E. K. Hobbie,* G. Merkle, B. J. Bauer, and C. C. Han

National Institute of Standards and Technology, Gaithersburg, Maryland 20899

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Time-resolved small-angle neutron scattering has been used to study the dynamics of phase separation in hydrogen-bonded polymer blends under a variety of shallow-quench conditions. Above a well defined cutoff wave vector q_c^* , the structure factor $S(q, t)$ is described by an exponential or a stretched exponential decay. The early-stage growth rate $R(q)$ appears to change sign *precipitously* at the cutoff, however, which is not consistent with a linear theory. Below the cutoff, $S(q, t)$ exhibits nonlinear growth with a characteristic time scale $t_m(q)$, and scales as $q^{-D}f(t/t_m)$ with a scaling exponent D that is often different from the universal value $d=3$.

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Spinodal decomposition (SD) remains a problem of fundamental importance in statistical physics. Despite extensive experimental and theoretical work [1], a detailed understanding of this inherently nonlinear phenomenon is still lacking [2]. Nonetheless, a variety of systems, such as small-molecule binary liquid mixtures [3], metallic alloys [4], and binary polymer mixtures, or blends [5–7], display strikingly similar behavior, suggesting an underlying common mechanism in the nonequilibrium critical dynamics. In the case of polymer blends, most light scattering studies indicate that the early-stage growth is reasonably well characterized by the linear theory of Cahn, Hilliard, and Cook [8], while the later stages exhibit universal scaling of the structure factor [5–7]. A clear picture of intermediate-stage growth, which marks the onset of nonlinear behavior, has not yet emerged [5–7].

In a recent paper [9], we presented small-angle neutron scattering (SANS) studies of a polymer blend made miscible by a dilute, random distribution of hydrogen bonds between two otherwise incompatible components. These measurements suggest that long-wavelength order-parameter fluctuations, the analogy of the so-called *critical opalescence*, are suppressed in the miscible phase [9]. The reason for this is unclear, although it may be attributed to macroscopic inhomogeneities in the interaction between unlike chains, the strong nature of the hydrogen bonding, or the nearby glass transition, all of which could conceivably create barriers to extended coherent fluctuations in composition just below T_c . In addition, preliminary dynamic measurements with time-resolved SANS suggest fractal-scaling behavior [9]. In the present paper, the growth kinetics of these blends are studied in detail under a variety of shallow quench conditions.

The blends studied were binary mixtures of deuterium-labeled modified polystyrene [PSD(OH)] and poly(butyl methacrylate) (PBMA) with a degree of polymerization $N_A \sim 150$ and $N_B \sim 300$, respectively ($R_{gA} \approx 3.5$ and $R_{gB} \approx 4.5$ nm). The PSD was modified by

the introduction of a dilute distribution (an average of 1 every 125 segments) of an OH containing comonomer at random segments along the chains. A low- T “miscible” phase forms via hydrogen bonding between this comonomer and a PBMA repeat unit [10]. The components were identical or almost identical (within reasonable polydispersity) to those considered previously [9]. SANS measurements were carried out at the Cold Neutron Research Facility of the National Institute of Standards and Technology. In all cases, the intensity was weak enough to eliminate multiple scattering.

Light scattering studies of SD in hydrogen-bonded PS-PBMA blends [11] suggest Cahn-Hilliard early-stage growth and a self-similar mechanism for late-stage coarsening similar to that proposed by Siggia [12]. For shallow quenches a second, stationary peak appears, suggesting an alternate growth mechanism such as stress relaxation or late-stage pinning due to long-wavelength inhomogeneities [11]. Equilibrium SANS shows an absence of long-wavelength fluctuations below a cutoff wave vector q_c in the low- T phase [9], where a second length scale emerges in $S(q)$. Over the q range probed (0.05 – 0.60 nm $^{-1}$), $S(q)$ changes very little between the glass transition (T_g) and the apparent spinodal (T_s). For the molecular weights used, the “critical” composition ϕ_c at which the Ψ^3 term in a Landau expansion of the free energy of mixing vanishes [13] is $\sim 60\%$ PSD(OH).

We show data here from two different jumps; 60% PSD(OH) jumped from 92°C to 107°C (“critical” composition, jump A, Fig. 2), and 40% PSD(OH) jumped from 95°C to 105°C (“off-critical” composition, jump B, Fig. 3). Others were of similar appearance, differing only in the values of the exponents found [14]. As shown in Fig. 1, the annealed low- q structure in A is less “coarse” than that in B, with $q_{cA} \sim 0.13$ and $q_{cB} \sim 0.20$ nm $^{-1}$. The correlation lengths describing the data above q_c are $\xi_A \sim 10$ and $\xi_B \sim 8$ nm. There is a well-defined *dynamic* cutoff wave vector q_c^* that separates growth ($q < q_c^*$) from decay ($q > q_c^*$) in the $t \rightarrow 0$ limit, with $q_{cA}^* = 0.13 \pm 0.01$ nm $^{-1}$ and $q_{cB}^* = 0.16 \pm 0.01$ nm $^{-1}$. The initial increase in intensity for $q < q_c^*$ suggests the growth of clusters spanning 1–10 chain dimensions. This occurs at the expense of smaller structures, as reflected by the decrease in intensity for $q > q_c^*$. As the clusters coalesce

*Present address: Department of Physics and Astronomy, University of Wisconsin, River Falls, WI 54022.

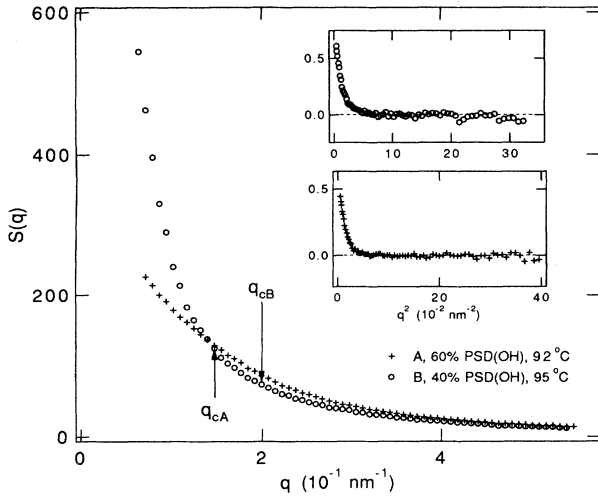


FIG. 1. Equilibrium structure in the initial "miscible" state for jumps A and B. Low- q Zimm plots of $1/S(q)$ vs q^2 show deviations from linear behavior below q_c , suggesting a second length scale R_0 . This is shown quantitatively in the insets, where the fractional deviation from Ornstein-Zernike (Lorentzian) behavior is plotted vs q^2 .

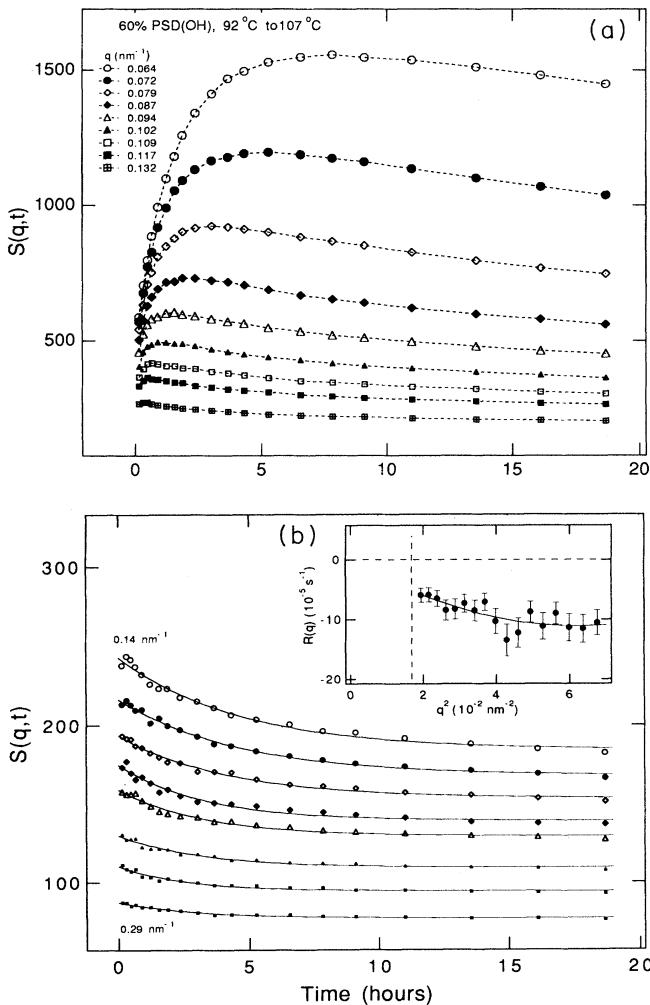


FIG. 2. The scattering intensity vs time in the vicinity of the cutoff for the 60% PSD(OH) sample. The inset shows the q dependence of the growth rate $R(q)$.

into larger droplets, the intensity exhibits a maximum at a characteristic time $t_m(q)$. In this way, the structure coarsens toward the final equilibrium distribution. As the clusters grow, a well defined length scale $R(t) \sim 1/q_m(t)$ will emerge that reflects the average size. For all of the jumps considered, q_m is below the q range probed in this study.

Above q_c^* , $S(q,t)$ decays exponentially in accordance with the linear theory of Cook [8]. This is shown in Figs. 2 and 3 (lower panel), where the lines are fits with

$$S(q,t) = S_\infty(q) + [S_0(q) - S_\infty(q)]e^{R(q)t}. \quad (1)$$

The growth rate $R(q)$ is negative for $q > q_c^*$. We also fit the data with a "stretched" exponential [$|Rt| \rightarrow |Rt|^\nu$ in Eq. (1)], with $\nu = 0.77$ and $\nu = 0.94$ for the two jumps, respectively. Although this gave a significantly smaller χ^2 value, in most cases the change in $R(q)$ was not significant. For $q < q_c^*$, the fact that there is initial growth would seem to imply that $R(q)$ must be positive. The position and intensity of the maximum follow the

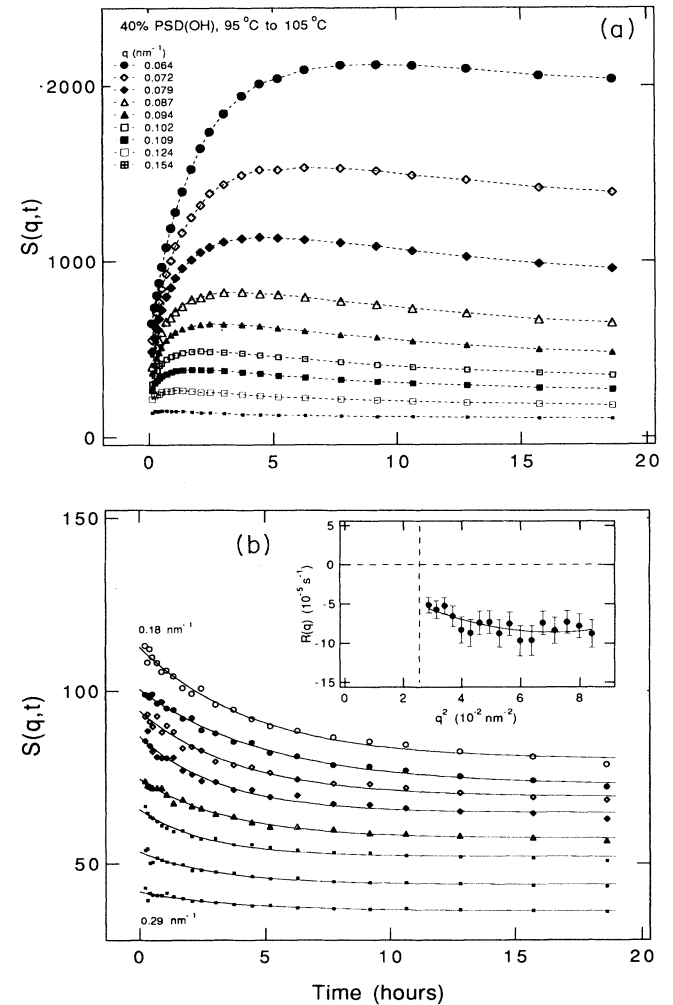


FIG. 3. The scattering density vs time in the vicinity of the cutoff for the 40% PSD(OH) sample. The inset shows the q dependence of the growth rate $R(q)$.

power laws $q \sim t_m^{-\alpha}$ and $S_m \sim q^{-D} \sim t_m^\beta$, with $\beta = D\alpha$ (Fig. 4). In general, we find $0.20 \leq \alpha \leq 0.40$ and $1.8 \leq D \leq 3$ [15]. Both exponents appear to depend on the annealing temperature as well as the depth of the jump. For deep quenches, the maximum quickly moves behind the beam stop and there is limited information. For extremely shallow jumps, $S(q, t)$ versus t does not exhibit a maximum, but shows a slowly tapering increase, perhaps indicative nucleation.

Because there appears to be no linear early-stage growth for $q < q_c^*$, we cannot determine $R(q) > 0$. Recent numerical simulations carried out by Gross, Klein, and Ludwig [16] suggest that the interval of linear growth decreases with increasing q , although these simulations did not address the behavior for $q > q_c^*$. Our data are consistent with this, as the growth just below the cutoff exhibits a maximum almost immediately. The insets of Figs. 2 and 3 show the linear growth rate $R(q)$ above q_c^* . The vertical dashed line shows q_c^* and the horizontal dashed line shows $R(q) = 0$. Although there is considerable scatter due to the weakness of the signal, the data present a perplexing question. To have early-stage growth for $q < q_c^*$, $R(q)$ must change sign precipitously at the cutoff, which is inconsistent with a linear theory. Like the unusual static behavior below T_s in the low- T phase, this may indicate the presence of energy barriers. It seems quite plausible that both q_c and q_c^* reflect the distribution of hydrogen bonds in the initial annealed state.

The presence of such barriers, along with the fact that T_s is not far above T_g , may explain the ultraslow dynamics and extreme hysteresis observed in these materials [14]. In light of Ref. [16], however, it is also possible that Eq. (1) is simply inappropriate, and the mechanism for $q > q_c^*$ is the same as that on the late-time tail for $q < q_c^*$.

Figure 5 shows $q^D S(q, t)$ versus $t/t_m(q)$. The inset is a log-log plot with error bars arising from the uncertainty in $t_m(q)$. Similar scaling was observed in all cases. The usual late-time scaling expression is $S(q, t) \sim q_m^{-d} F(q/q_m)$, where $q_m(t) \sim t^{-\alpha}$ locates the peak in $S(q, t)$ versus q , and d is the dimensionality [1]. The Furukawa function $F(x) = x^2 / (\gamma/2 + x^{2+\gamma})$ is peaked at $q = q_m(t)$, with $\gamma = d + 1$ in the "cluster" (shallow-quench) region [17]. It is not difficult to transform this expression to one with time as the scaled variable, or $S(q, t) \sim q^{-d} f(t/t_m(q))$, where the universal function

$$f(x) = x^{(2+d)\alpha} [x^{(2+\gamma)\alpha} + (\gamma - d)/(2 + d)] \quad (2)$$

exhibits a maximum at $t = t_m(q) \sim q^{-1/\alpha}$ for $q > q_m$, with $f \sim x^{-\alpha}$ for large x ($t \rightarrow \infty$). Here the decay is quite slow for large x , and Eq. (2) is inadequate over the q range in question. This is related to the fact that $S(q, t)$ approaches a nonzero "virtual" or "pinned" value as $t \rightarrow \infty$ for the shallow quenches under consideration. The lines shown are fits with a generalized form of Eq. (2), $f(x) = x^m [x^n + n/m - 1]$, with $m = 0.71$ and $n = 0.86$ for A, and $m = 0.62$ and $n = 0.82$ for B.

The scaling extends over a significant window of time, and a more detailed consideration seems warranted. From a linear model of early-stage SD, Klein [18] has

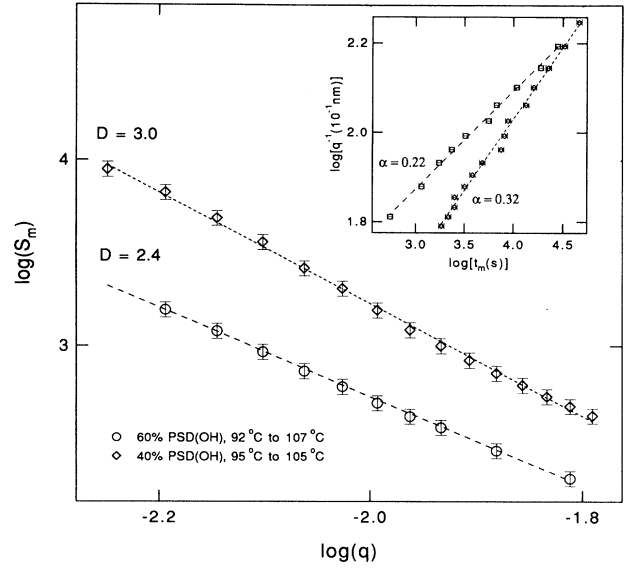


FIG. 4. A log-log (base 10) plot of the maximum intensity vs q and (inset) a log-log plot of q vs t_m for the two quench experiments.

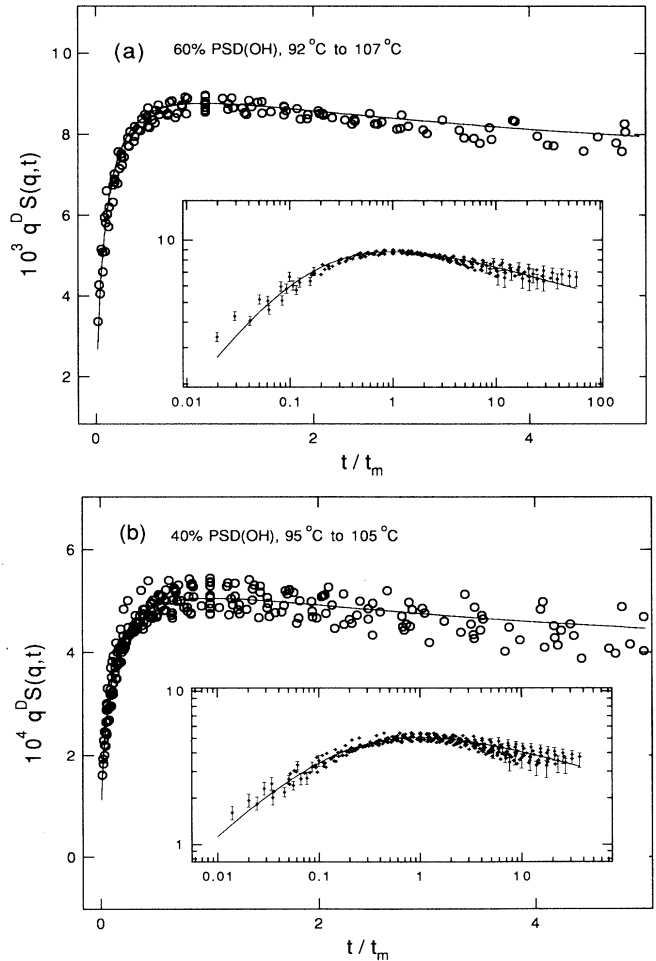


FIG. 5. The scaled structure factor $q^{-D} S(q, t)$ vs t/t_m for the two quench experiments. The lines are fits with a generalized form of the Furukawa expression [Eq. (2)].

proposed a fractal dimension $D=2$ for $d=3$. Although we often find $D \sim 2.5$ in the vicinity of ϕ_c , our data rule out the possibility of a universal value for D . The presence of a *single* characteristic length scale $R(t) \sim 1/q_m$ in the pair-correlation function $g(r,t) = \langle \delta\phi(\mathbf{r},t)\delta\phi(0,t) \rangle$ leads to the dynamic-scaling hypothesis of Binder and Stauffer [19]. If $g(r,t) = g(r/R(t))$, then $S(q,t) \sim q_m^{-d} F(qR)$ follows from the fact that $S(q,t)$ and $g(r,t)$ are related by a Fourier transform. If the domains are compact, g should remain finite for $r \rightarrow 0$ [20]. It is likely that the clusters are not always compact over the length scales in question, in which case a *second* length scale should emerge for $r \rightarrow 0$, or $g(r,t) = (r/\xi_0)^{-2} g_0(r/R)$ (Ref. [21]), and which would then imply $S(q,t) \sim q^{-D} F(qR)$, where $D = d - s$.

In the above scenario, $R_0 \sim 1/q_c^*$ would reflect the structure present in the annealed state. Following a shallow

jump to higher T , a modulated pattern would begin to emerge as structures larger than $1/q_c^*$ grew at the expense of smaller ones, eventually being stabilized by the competing interactions. In the weak-segregation limit, this modulation would be diffuse, which would be apparent in the scattering for $q > q_m$. The exponent s would reflect the compactness of the constituent blocks, the second length scale ξ_0 being related to the monomer size. The potential for controlling domain morphology on a molecular level creates a strong incentive for a deeper understanding. In addition, the unique dynamics reported here in the vicinity of q_c^* should give some insight into the nonlinear nature of SD. A rigorous theory of strongly interacting polymer blends is clearly lacking.

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