

Does coarsening begin during the initial stages of spinodal decomposition?

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The initial stages of spinodal decomposition were studied by subjecting a critical blend of model polyolefins to a pressure quench and monitoring the evolution by time-resolved small angle neutron scattering. Contrary to the predictions of the widely accepted Cahn–Hilliard–Cook theory, we demonstrate that coarsening of the phase-separated structure begins immediately after the quench and occurs throughout the initial stages of spinodal decomposition. © 2005 American Institute of Physics. [DOI: 10.1063/1.1905584]

INTRODUCTION

Our understanding of spinodal decomposition in critical binary mixtures^{1–12} rests on a landmark publication by Cahn.¹ In this paper, the linearized diffusion equation was solved to obtain the evolution of scattering intensity $I(q, t)$ during phase separation (q is the scattering vector and t is time). $I(q, t)$ was found to increase with time but only for scattering vectors less than a critical scattering vector q_c . This indicates the presence of a lower cutoff for the length scale of the emerging phase-separated structure. In addition $I(q, t)$ contains a time-independent peak at $q = q_m$, indicating that the emerging structure is periodic and characterized by a dominant length scale $L_m = 2\pi/q_m$. In the linearized theory, this length scale is independent of time. At later times the structure coarsens due to effects, such as interfacial tension and hydrodynamics, which are not included in the linearized theory.¹²

Many aspects of published experimental data obtained during the initial stages of phase separation^{6–11} are in quantitative agreement with the linearized theory.^{1–5} However, the important question of whether or not the periodic structure obtained during the initial stages of phase separation can emerge without coarsening has, to our knowledge, not been adequately addressed experimentally. In particular, we were unable to find any experimental data set wherein q_m obtained during the early stages of spinodal decomposition was independent of time (within experimental error). In this paper we present experimental data that provides a definitive answer to the question posed in the title of the paper.

EXPERIMENT

Our system is a binary blend composed of two nearly-monodisperse high-molecular-weight liquid homopolymers: partially deuterated polymethylbutylene (*d*PMB) and hydrogenous polyethylbutylene (*h*PEB), synthesized and char-

acterized using the methods described in Ref. 13. The numbers of repeat units per chain in the two components were determined to be $N_{dPMB} = 2806$ and $N_{hPEB} = 2535$ (at ambient T and P , and based on a 100 \AA^3 repeat unit which is the basis for all of the parameters reported here), the average number of deuterium atoms, for every five carbon atoms in *d*PMB, was 4.5. The radii of gyration (R_g) of both *d*PMB and *h*PEB chains are $14 \pm 1 \text{ nm}$.¹³ A blend with critical composition based on the Flory–Huggins theory,^{14–16} *d*PMB volume fraction $\phi = 0.493$, was studied by time-resolved small-angle neutron scattering (SANS). We report the azimuthally averaged absolute SANS intensity (after corrections for the background and empty cell scattering), I , as a function of q [$q = 4\pi \sin(\theta/2)/\lambda$, θ is the scattering angle and λ , the wavelength of the incident neutrons, was 1.2 nm]. Details regarding the instrument configurations and data reduction procedures are similar to our previous studies.¹⁷

RESULTS AND DISCUSSION

The equilibrium thermodynamic properties of blends of the *d*PMB and *h*PEB polymers used in this study have been thoroughly investigated.^{13,17} In Fig. 1 we show the phase behavior of our critical blend using a temperature–pressure (T – P) phase diagram. The curve shows the Flory–Huggins prediction for the variation of the critical temperature with pressure. SANS data obtained from blends above the critical curve were independent of time (after an initial relaxation process due to the finite time that is required for dense polymer samples to respond to changes in temperature and pressure¹⁸). The circles in Fig. 1 show the locations where $I(q=0)$ obtained in the one-phase region diverges, based on extrapolations of the measured $1/I(q=0)$ versus $1/T$ data at fixed pressure.¹⁹ The agreement between theory (curve) and experiment (circles) in Fig. 1 indicates a thorough understanding of the equilibrium properties of our blend. The blend was homogenized at the start of each experiment by heating to $115 \text{ }^\circ\text{C}$ and $P = 0.03 \text{ kbar}$. The blend was cooled under isobaric conditions to $67.5 \text{ }^\circ\text{C}$ and then subjected to an

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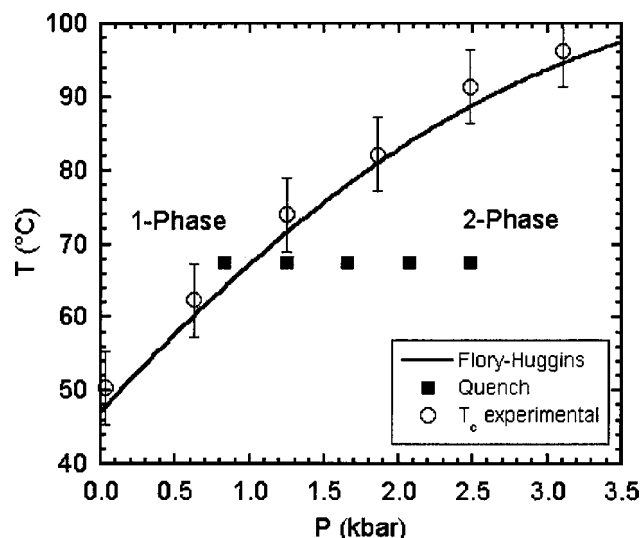


FIG. 1. T - P phase diagram of a critical $dPMB/hPEB$ blend calculated by the Flory-Huggins theory (curve). Circles: experimentally determined critical points. Squares: location of experimental quenches.

isothermal pressure quench to locations indicated by the filled squares in Fig. 1. The SANS profiles were monitored throughout the quenching process. In all cases, no evidence of phase separation was observed prior to the pressure quench ($t=0^-$). We thus define time zero ($t=0$) as the time at which the pressure quench was initiated.

Typical $I(q,t)$ data obtained during the initial stages of phase separation are shown in Fig. 2 where the symbols represent the data obtained at $P=1.24$ kbar and selected times. As expected, the data in Fig. 2 show the emergence of the spinodal peak. The well-established Cahn-Hilliard-Cook (CHC) theory^{2,3} provides a unified approach for interpreting $I(q,t)$ data obtained after quenching the sample in the vicinity of the critical point.

$$I(q,t) = I_T(q) + [I_0(q) - I_T(q)] \exp[2R(q)t], \quad (1)$$

where $I_0(q)$ is the initial scattering intensity function and $I_T(q)$ is the terminal scattering intensity function, obtained in

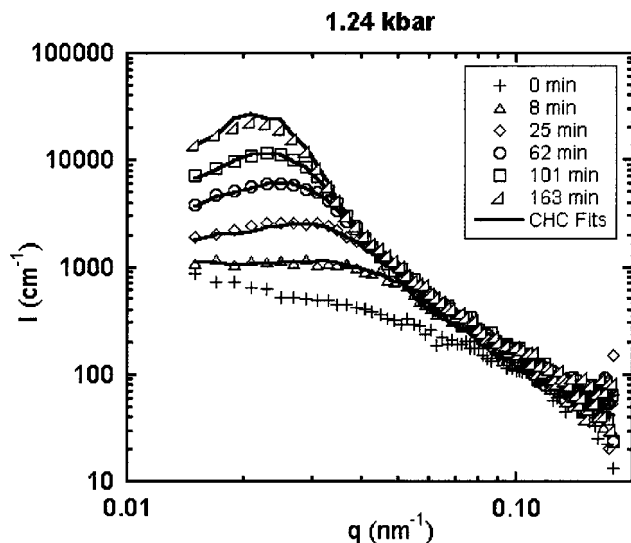


FIG. 2. SANS intensity vs q at selected times during the 1.24 kbar quench. The solid curves represent CHC fits.

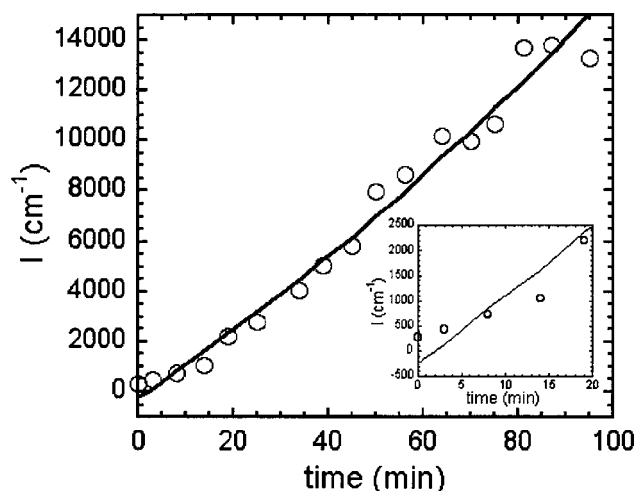


FIG. 3. SANS intensity vs time for $P=2.48$ kbar and $q=0.051$ nm⁻¹. The solid curve is the CHC fit through the data. Inset shows early time results for the same quench.

the limits $t \rightarrow 0$ and $t \rightarrow \infty$, respectively, and $R(q)$ is a kinetic parameter that is related to the growth [if $R(q)$ is positive] or decay [if $R(q)$ is negative] of $I_0(q)$ towards $I_T(q)$. The curves in Fig. 2 are examples of the CHC fits through the $P=1.24$ kbar data with $I_0(q)$, $I_T(q)$, and $R(q)$ as fitting parameters.²⁰ It is clear that the time dependence of $I(q,t)$ is well described by the CHC theory for all scattering vectors. Similar agreement was seen at other quench depths.

Data showing the time dependence of the SANS intensity at a particular scattering vector are shown in Fig. 3 for a quench to $P=2.48$ kbar and $q=0.051$ nm⁻¹. The curve in Fig. 3 shows the CHC fit through the data. There is a small but systematic deviation between the CHC fit and the early time data, seen more clearly in the inset of Fig. 3. However, it is clear from Figs. 2 and 3 that the CHC fits capture the essential features of the data. We thus focus on the qualitative behavior of the fitted parameters, $I_0(q)$, $I_T(q)$, and $R(q)$.

The $I_T(q)$, $R(q)$, and $I_0(q)$ data for different quench depths are presented in Figs. 4(a), 4(b), and 4(c), respectively. For the $P=0.83$ kbar quench, we obtain positive values for $I_0(q)$ and $I_T(q)$ and negative values for $R(q)$ at all accessible q values. This is the expected behavior for quenches within the one-phase region.¹⁸ More interesting behavior is seen for the other quenches located within the two-phase region (Fig. 1). In the inset of Fig. 4(a) we show the full range of $I_T(q)$ obtained at $P=1.24$ kbar. We find that $I_T(q)$ is a positive, monotonically decreasing function of q for large q , a negative, monotonically decreasing function of q for small q , and that these regimes are separated by a singularity (pole) in $I_T(q)$ at $q=0.028$ nm⁻¹. Similar singularities were obtained for all of the quenches within the two-phase region as shown in Fig. 4(a). This singularity in $I_T(q)$ is an unambiguous signature of q_c .^{2,3} In Fig. 4(b) we see the second unambiguous signature of q_c ; $R(q) \rightarrow 0$ at q_c , the scattering vector corresponding to the singularity in $I_T(q)$. For $q > q_c$, $R(q) < 0$ [$R(q)$ for all quenches except $P=2.48$ kbar have been truncated by the $R(q)$ axis scale²¹] whereas for $q < q_c$, $R(q)$ is a positive, peaked function that decays to zero both at $q=q_c$ and at $q=0$ (theoretically).

In Fig. 4(c) we show $I_0(q)$ versus q for all of the

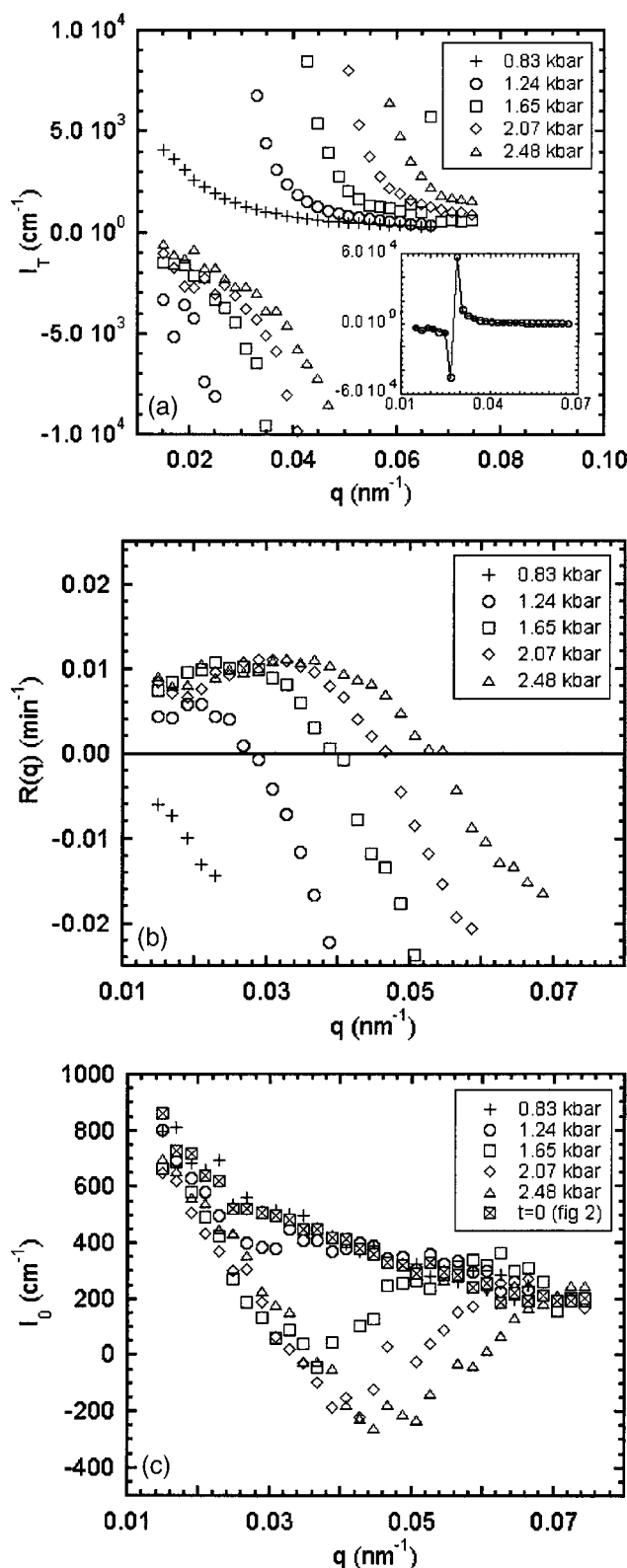


FIG. 4. CHC fitting parameters for all five quenches, the open symbols represent two-phase quenches. (a) $I_T(q)$ vs q . (b) $R(q)$ vs q . (c) $I_0(q)$ vs q , including $I(q, t=0)$ from Fig. 2 for reference. Inset in (a) shows the full range of $I_T(q)$ vs q for $P=1.24$ kbar.

quenches and include $I(q, t=0)$ from Fig. 2 for reference. Since all of the quenches start at $P=0.03$ kbar and $T=67.5$ °C, in theory, $I_0(q)$ must be within experimental error of $I(q, t=0)$. For the quench into the one-phase region ($P=0.83$ kbar), we find an excellent agreement between $I_0(q)$

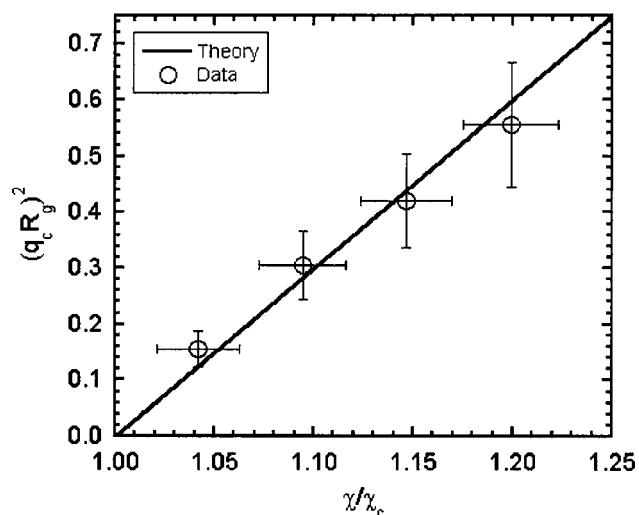


FIG. 5. Quench depth dependence of the normalized critical scattering vector, $q_c R_g$, shown as $[q_c R_g]^2$ vs $\chi(T, P)/\chi_c(P)$. The solid line represents the theoretical prediction of the CHC theory.

and $I(q, t=0)$. At larger quench depth, we see an excellent agreement between $I_0(q)$ and $I(q, t=0)$ in the low and high q limits. However, systematic departures between $I_0(q)$ and $I(q, t=0)$ are seen at intermediate q values. This is a reflection of the fact that the CHC theory is unable to accurately capture the full time dependence of the SANS profiles during the initial stages of spinodal decomposition (e.g., inset of Fig. 3). It is worth noting, however, that the deviation between $I_0(q)$ and $I(q, t=0)$ is relatively small, maximum ~ 600 cm^{-1} for $P=2.48$ kbar and $q=0.051$ nm^{-1} , the conditions depicted in Fig. 3. This is comparable in magnitude to the uncertainty in our estimate of $I_0(q)$, which we assume to be the standard deviation between the scattering data and the CHC fits, 500 cm^{-1} for the data set in Fig. 3.

According to the CHC theory, the variation of q_c with quench depth for a critical polymer blend, is given by

$$[q_c R_g]^2 = 3[\chi(T, P)/\chi_c(P) - 1], \quad (2)$$

where $\chi(T, P)$ is the value of the Flory–Huggins interaction parameter at the quench conditions and $\chi_c(P)$ is the value of the Flory–Huggins interaction parameter at the critical point for the quench pressure.²² In Fig. 5 we compare the experimentally determined quench depth dependence of q_c [based on $I_T(q)$ and $R(q)$ data given in Figs. 4(a) and 4(b), respectively] with theoretical predictions by plotting $[q_c R_g]^2$ versus $\chi(T, P)/\chi_c(P)$. The agreement between theory and experiment is excellent, especially when one considers the fact that this agreement is obtained without any adjustable parameters.

The agreement between the data and the CHC theory seen in Figs. 2, 3, and 5 leaves no doubt that the data presented here were acquired during the initial stages of spinodal decomposition. We are thus poised to answer the question posed in the title. The $I(q)$ data obtained in the vicinity of the spinodal peak (e.g., Fig. 2) were fit to a quadratic function of q and the locations of the peaks thus obtained, q_m , are shown in Fig. 6. The scattering profiles for $t < 14$ min did not contain peaks and are thus not represented in Fig. 6. We find that for all quenches in the two-phase

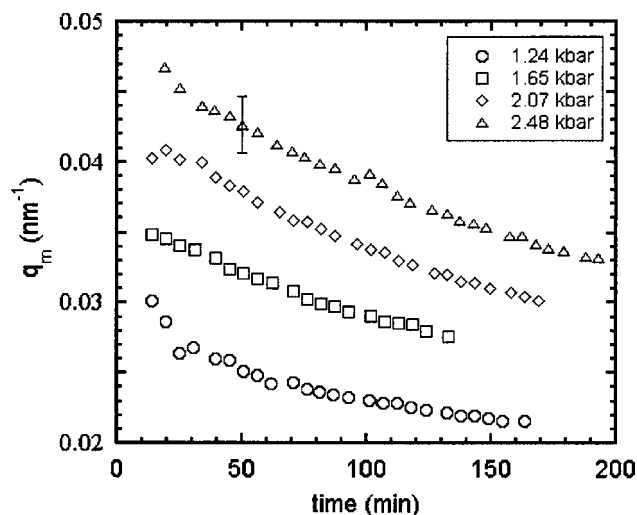


FIG. 6. SANS peak position q_m vs time for the quenches into the two-phase region. The typical uncertainty in q_m is shown.

region, q_m is a monotonically decreasing function of time throughout our experimental time window.^{23,24} The decrease in q_m is also evident when the raw SANS data are examined visually (e.g., Fig. 2). We expect departures between the CHC theory and experiment because the theory does not account for the time dependence of q_m . The lack of agreement between $I_0(q)$ and $I(q, t=0)$ [Fig. 3 (inset) and Fig. 4(c)], and the lack of a well-defined peak in $R(q)$ [Fig. 4(b)] are examples of such departures.²⁵ One expects a linearized theory to apply when changes in the dependent variable (scattering intensity in this case) are small. This may be the reason for the applicability of the CHC theory in the vicinity of q_c but not in the vicinity of q_m .

The answer to the question “Does coarsening begin during the initial stages of spinodal decomposition?” is thus “Yes.”

We are not aware of any experimental data set that is at odds with this conclusion. In most cases, e.g., Refs. 6, 7, and 9, the authors attribute their observation of decreasing q_m to their inability to access the initial stages of the phase separation. In Ref. 11 the authors argued that they had observed a regime where q_m was time independent. However, their data [Fig. 3(a) in Ref. 11] show an initial increase in q_m with time followed by a short “plateau,” and then a decrease in q_m . The authors concluded that the initial increase in q_m was due to an artifact of the quenching process (they used temperature quenches to initiate phase separation as opposed to the pressure quenches used here), and that smaller values of q_m were due to the finite time that their sample spent at lower quench depths during the thermal quench. We argue that the observed q_m versus t plateau is simply a crossover from the artifact-dominated regime to a spinodal decomposition-dominated regime where q_m is a monotonically decreasing function of time.

In summary, we studied the initial stage of phase separation in a critical blend of model polyolefins subjected to a pressure quench. We show that coarsening begins immediately after the quench and occurs throughout the initial stages of spinodal decomposition. Our data suggest the need for a revised nonlinear theory.

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- ¹⁹ $I(q=0)$ was obtained by fitting $1/I(q)$ versus q^2 to a line limited to $0.040 < q < 0.088 \text{ nm}^{-1}$, the low q regime for $\lambda=0.6 \text{ nm}$. See Ref. 17 for more details.
- ²⁰For each quench $I(q, t)$ was fit to the CHC equation for times $0 < t < t_{\text{final}}$, where $t_{\text{final}}=225, 93, 87, 76$, and 75 min , respectively, for $P=0.83, 1.24, 1.65, 2.07$, and 2.48 kbar . The fitting results are insensitive to the exact value of t_{final} .
- ²¹In Fig. 4(b) we have omitted the data for $R(q) < -0.025 \text{ min}^{-1}$ because we do not have adequate time resolution in this range.
- ²²Both $\chi(T, P)$ and $\chi_c(P)$ are linear functions of pressure. For $T=67.5^\circ\text{C}$, $\chi/\chi_c=0.127P(\text{kbar})+0.885$. See Ref. 17 for more details.
- ²³Multiple scattering becomes important for long times, especially at higher quench depth. However, as shown in Ref. 24, the value of q_m remains unaffected.
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- ²⁵In our discussion of $I_0(q)$, $I_T(q)$, and $R(q)$, we have restricted our attention to the qualitative features of these curves. In past analyses, e.g., Ref. 10, deviations in the measured $R(q)$ and that predicted by the CHC theory are attributed to the q dependence of the Onsager coefficient. We have shown that in the present system, substantial deviations between theory and experiment arise due to coarsening. Quantitative comparison between the measured $I_0(q)$, $I_T(q)$, and $R(q)$ and theory can only be made after theories that incorporate both coarsening and q -dependent Onsager coefficient are available.