

Early Stages of Nucleation and Growth in a Polymer Blend

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The early stages of nucleation and growth in a mixture of high polymers were studied by time-resolved neutron scattering. During the first 160 min, a slow clustering was evident, indicating a buildup of concentration fluctuations. The clusters formed at the end of this stage had the characteristics of “critical nuclei,” because phase separation proceeded rapidly after their formation. At this stage, the scattering profiles showed a peak at finite wave vectors (q_{\max}). The scaling exponents for the time dependence of the peak intensity and q_{\max} are inconsistent with current theories. [S0031-9007(96)01518-9]

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The formation of a new phase in a homogeneous mixture can occur either by spinodal decomposition or nucleation and growth [1]. Signatures of the early stage of spinodal decomposition are well established. Scattering experiments reveal the (nearly) instantaneous appearance of a halo which brightens and collapses as phase separation proceeds. Reasonable agreement between experiments and theory [2] is seen in many different materials such as metals, glasses, and polymers [3]. In contrast, signatures of the early stage of nucleation and growth are not well established. The classical approach, pioneered by Gibbs, is based on the growth of compact droplets (or nuclei) of the new phase which are greater than a certain “critical size.” Theoretical aspects of the evolution of such systems were studied by Langer and Schwartz [4] and others [3]. More recently, computer simulations have revealed the formation and growth of clusters with varying shape and compactness [5,6]. In one such study, the computed scattering profile during nucleation and growth contained a halo that was qualitatively similar to that obtained during spinodal decomposition [6]. Optical techniques have been used in experimental studies of nucleation and growth in mixtures of low molecular weight compounds [7], colloidal suspensions [8], and polymer mixtures [9]. However, the very early stages of the phase separation and the formation of the critical nuclei were not studied in either case [7–9]. In this paper we present time-resolved small angle neutron scattering (SANS) results obtained during the early stages of nucleation and growth in a polymer blend.

Model polyolefins—deuterium labeled polyethylbutylene (dPE), polymethylbutylene (hPM), and a polymethylbutylene-*block*-polyethylbutylene copolymer ($hPM-hPE$)—were synthesized and characterized by methods described in Ref. [10]. The numbers of repeat units per chain in the three components were determined to be: $N_{dPE} = 4260$, $N_{hPM} = 3350$, and $N_{hPM-hPE} = 3740$ (based on a 100 \AA^3 repeat unit), the average number of

deuterium atoms per repeat unit in dPE was 3.8, and the volume fraction of PM monomers in the $hPM-hPE$ block copolymer was 0.33. The radii of gyration (R_g) of the chains, estimated from literature values of statistical segment lengths [10], are nearly identical; $R_{g,dPE} = 15.9 \text{ nm}$, $R_{g,hPM} = 16.7 \text{ nm}$, and $R_{g,hPM-hPE} = 17.0 \text{ nm}$. Ternary blends containing dPE , hPM , and $hPM-hPE$ were prepared by dissolving the components in cyclohexane and then evaporating the solvent. We present data obtained from blends labeled B20 and B50, which contained 20 volume % and 50 volume % block copolymer, respectively. The ratio of homopolymer concentrations, ϕ_{dPE}/ϕ_{hPM} , was 0.33 in both blends (ϕ_i is the volume fraction of species i in the mixture, $i = dPE, hPM, \text{ or } hPM-hPE$).

Adding a block copolymer to a binary homopolymer blend results in a “compatibilization effect,” i.e., it lowers the demixing temperature [11]. The quench depth can thus be decreased at constant temperature by increasing the block copolymer concentration. Calculations based on the Flory-Huggins theory indicate that at $25 \text{ }^\circ\text{C}$, blend B20 is located in the unstable region of the phase diagram, while blend B50 at $25 \text{ }^\circ\text{C}$ is located in the metastable region of the phase diagram [12]. Since the molecular size (R_g) of the components and the relative concentration of PE and PM monomers are similar in both blends, we expect the time scale for molecular motion in the two blends to be the same. Any difference that we observe in the evolution of structure in these blends can be directly attributed to differences in “location” of the blend relative to the phase boundary. Experiments of this type are not possible in binary blends wherein such a change can be accomplished only by changing temperature or blend composition, which in turn changes the time scale for molecular motion.

In principle, the block copolymer could segregate to the interface between coexisting phases or form a separate, copolymer-rich phase. This, however, appears to be unlikely in the system studied here. For symmetric blends of two homopolymers A and B ($\phi_A = \phi_B$), and a symmetric

A-B diblock copolymer with $N_A = N_B \approx N_{A-B}$, Matsen and Schick [13] have shown that significant segregation of the block copolymer to the interface occurs when χN_{A-B} exceeds 7.3. For asymmetric systems like the one studied here, we expect the χN_i threshold to be larger, perhaps in the vicinity of 13 [14]. The value of χ between PM and PE chains at 25 °C is 1.08×10^{-3} [10], and therefore $\chi N_{PM-PE} = 4.0$ for blends B20 and B50. This is well below the threshold for interfacial segregation of the copolymer. Similarly, the formation of copolymer-rich phases occurs at χN_i values significantly greater than 4.0 [15].

The blends were encased in quartz cells, heated to 250 °C, which is well above the demixing temperature, and quenched rapidly (in 4 min) to 25 °C. The SANS profiles from these blends were then monitored as a function of time; instrumentation details are given in Ref. [10]. The scattering profiles reflect the distribution of *d*PPE chains in the mixtures; there is no neutron scattering contrast between *h*PM and *h*PM-*h*PE. The data obtained from B20 are shown in Fig. 1(a) where the scattering intensity *I* is plotted as a function of the scattering vector *q* [$q = 4\pi \sin(\theta/2)/\lambda$, θ is the scattering angle and λ is the wavelength of the incident neutrons]. The decomposition of B20 into two phases begins as soon as the blend is quenched and a scattering peak (halo), characteristic of spinodal decomposition is evident during the early stages. The data obtained from blend B50 at selected times are shown in Fig. 1(b). At times less than 160 min, the

scattering profiles are devoid of well-defined scattering peaks. There is, however, a gradual change in the SANS profile with time: The low *q* intensity increases and the gradient of *I* versus *q* increases. These observations indicate a clustering of the *d*PPE chains and the beginning of phase separation. However, the lack of a scattering peak during the first 160 min is a strong indication that the mechanism for phase separation in B50 is not spinodal decomposition.

We use the Guinier model to obtain the structural evolution of B50 from the measured scattering profiles [16]. In this model, the scattered intensity is given by: $I(q) = I_0 \exp(-q^2 R_g^2/3)$, where I_0 , the extrapolated intensity at $q = 0$, is proportional to the product of the scattering power and the average mass of the scatterers, and R_g is the average radius of gyration of the scatterers. The solid curves through the data in Fig. 1(b) represent Guinier fits through the data with I_0 and R_g as adjustable parameters.

The time dependence of R_g is shown in Fig. 2(a). The values of R_g obtained in the first 20 min range between 14 and 16 nm. These values are in very good agreement with R_g of the individual polymer chains in the mixture. This indicates that the scattering profiles from B50 at very early times ($t < 20$ min) are consistent with that expected from a homogeneous mixture well removed from a phase boundary. To confirm this, we fitted these data to the scattering function of polymer chains (the Debye function) and obtained R_g values that are similar to those reported in Fig. 2(a). For example, at $t = 5$ min, the Debye function

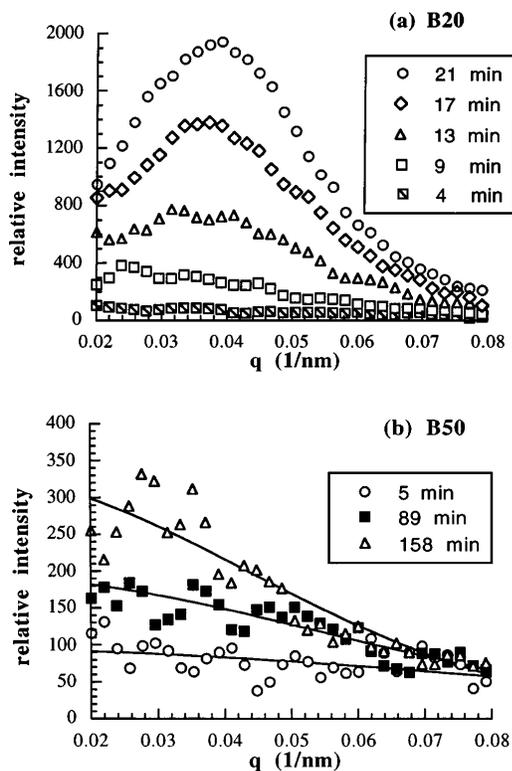


FIG. 1. Dependence of SANS profiles on time during the early stage. (a) B20, (b) B50. The solid lines in (b) represent fits to the Guinier model.

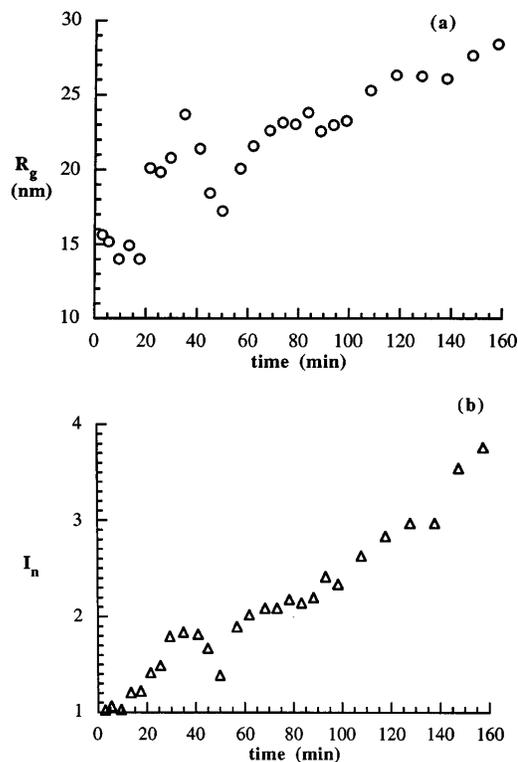


FIG. 2. (a) Time dependence of (a) radius of gyration of the clusters R_g and (b) normalized intensity as $q \rightarrow 0$, I_n , in B50, obtained using the Guinier model.

fit through the data gives $R_g = 14.7$ nm. The increase in R_g seen in Fig. 2(a) may be viewed as a gradual clustering of d PE chains.

In Fig. 2(b) we plot I_n , the normalized value of I_0 [$I_n(t) = I_0(t)/I_0(t \rightarrow 0)$], versus time. Since the scattering power of the clusters can only increase with time, and because we established that the scattering at early times ($t \rightarrow 0$) was due to individual chains, I_n represents an upper bound for the average number of chains per cluster, n ($n \leq I_n$). The early clustering processes in B50 are very slow; after 160 min the average cluster size is only 28 nm and it contains at most 4 d PE chains.

The topology of the clusters can be gauged from the dependence of size (R_g) on $I_n(t)$. In Fig. 3 we plot $R_g(t)$ versus $I_n(t)$. We find that the data at times less than 160 min are consistent with the scaling: $R_g \sim I_n^{0.54 \pm 0.07}$. If the clusters were compact spheres then the scaling exponent would be ≤ 0.33 . The fact that the observed exponent is significantly larger indicates that the clusters are not compact spheres (as suggested by classical theories). In the mean-field limit, the correlation length associated with concentration fluctuations (which is proportional to R_g) is proportional to the square root of susceptibility (which is proportional to I_n) [17]. The observed relationship between R_g and I_n is consistent with this scaling law. It is therefore appropriate to view the early clustering processes as a slow buildup of concentration fluctuations.

We now discuss the scattering data obtained from B20 and B50 at longer times. We refer to this as the intermediate stage. In Fig. 4(a) we show data obtained from B20, where we see typical behavior observed in blends undergoing spinodal decomposition; I_{\max} increases with t and q_{\max} decreases with t . This is a straightforward continuation of the early stage data shown in Fig. 1(a). In contrast, the intermediate stage data obtained for $t > 160$ min from B50 are dramatically different from the early stage data shown in Fig. 1(b). As shown in Fig. 4(b), a scattering maximum develops, and the intensity increases rapidly with time.

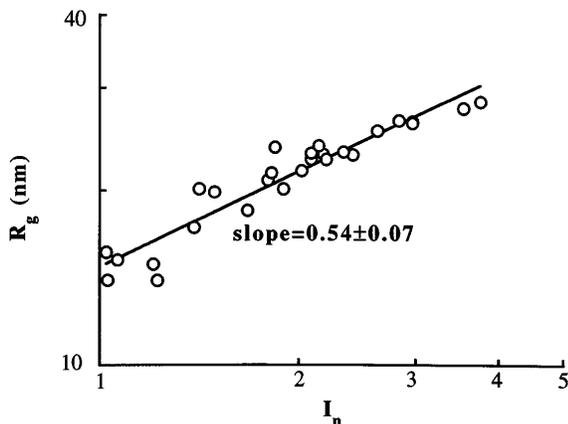


FIG. 3. A log-log plot of R_g at a given time versus I_n at that time. The solid line represents the best power law fit.

In Fig. 5(a) we compare the time dependence of the characteristic size of the phase separated structure L in B20 and B50. For monotonic scattering profiles $L = R_g$, and for scattering profiles with peaks $L = 1/q_{\max}$ (q_{\max} is the value of q at the peak). The values of L obtained from the early and intermediate stages in B50 are continuous through the early-to-intermediate stage transition, in spite of the fact that the methods for obtaining L in the two regimes are quite different. It is interesting to note the time dependence of L in B20 and B50 is similar [Fig. 5(a)]. However, dramatic differences are evident when one compares the time dependence of the peak intensity, I_{\max} . These data are shown in Fig. 5(b) (for monotonic scattering profiles, $I_{\max} = I_0$). The peak intensity from B20 increases rapidly in the early stage and slows down in the intermediate stage. This is typical of mixtures undergoing spinodal decomposition. The results obtained from B50 are diametrically opposite. The increase in scattering intensity is slow during the early stage and rapid during the intermediate stage. The data obtained in the early stage are reminiscent of the so-called "induction period" that is often reported in metastable systems. It is evident that the evolution of B50, in both early and intermediate stages, is consistent with well-established laws of spinodal decomposition. We are thus led to the conclusion that the mechanism of phase separation in B50 must be nucleation and growth.

To summarize, nucleation and growth in sample B50 occurs in two distinct stages: (1) In the early stage we

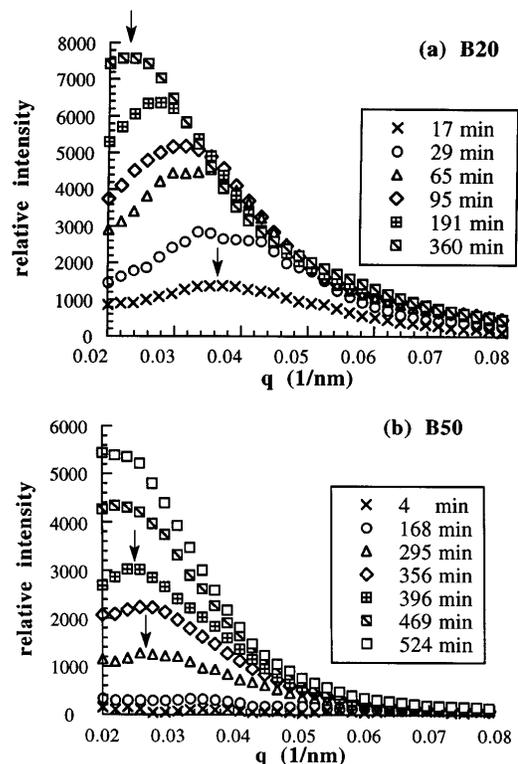


FIG. 4. Dependence of SANS profiles on time during the intermediate stage (a) B20, (b) B50.

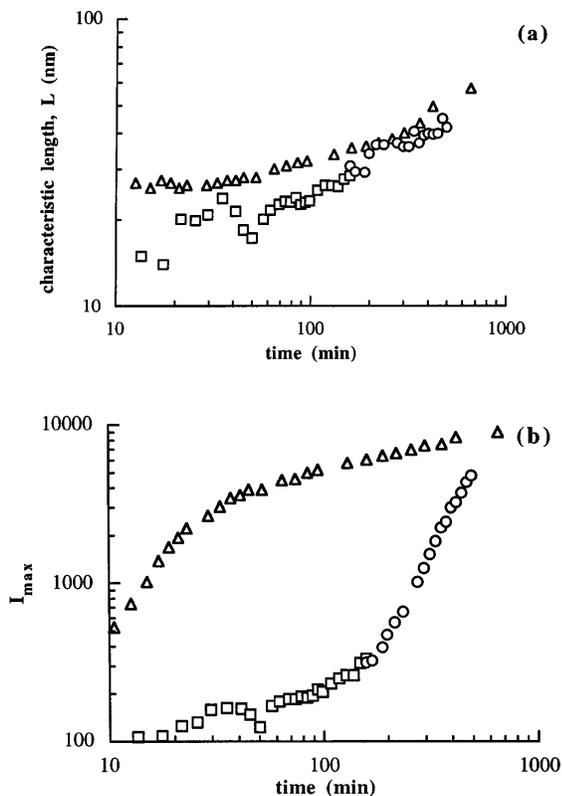


FIG. 5. (a) Time dependence of the (a) characteristic size of the phase L and (b) peak intensity I_{\max} . (triangles: B20; squares: B50-early stage; circles: B50-intermediate stage).

observe a gradual clustering of dPE chains. The clusters formed at the end of the early stage ($t = 160$ min) have the characteristics of “critical nuclei,” because the kinetics of phase separation increases dramatically after their formation. However, the nucleation process and the topology of the nuclei are in qualitative disagreement with classical theories [1]. The clustering during the early stage may be viewed as a buildup of concentration fluctuations, rather than the formation of compact spheres with well-defined interfaces. (2) In the intermediate stage, we find the emergence of a rapidly growing scattering peak. This may be due to the formation of a depletion zone around the growing clusters [9] or the formation of bicontinuous phases [3]. The coarsening of this structure, as revealed by the time dependence of q_{\max} and I_{\max} is surprising. The intermediate stage data from sample B50 were fitted by power laws ($q_{\max} \sim t^{-\alpha}$ and $I_{\max} \sim t^{\beta}$). We find that $\alpha = 0.30 \pm 0.07$ and $\beta = 2.54 \pm 0.09$. The value of β/α has been found to vary between 2 and 3 in a variety of systems [3–6,9]. If the composition of the coexisting phases remains unchanged and coarsening occurred only due to an increase in L , then the ratio β/α would be 3. Sur *et al.* [6] find that $\alpha/\beta = 2.6$ in their simulations, and Schatzel and Ackerson [9] find that β/α varies between 2 and 3 in crystallizing colloids. In contrast, the value of β/α in B50 is 8.47 ± 0.11 . The large α/β

value indicates that coarsening is accompanied by substantial changes in composition of the coexisting phases. This is probably related to the fact that the composition of the clusters formed at the end of the early stage is far from equilibrium. The early stages of nucleation and growth in B50 are thus not entirely in agreement with any of the available predictions [3–6].

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- [18] Certain equipment and instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply the materials are necessarily the best available for the purpose.