Grain Growth and Defect Annihilation in Block Copolymers

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The time dependence of the size, shape, and concentration of ordered grains in a quenched block copolymer melt was studied by depolarized light scattering. Block copolymers are ideal systems for kinetic studies because the single scattering limit applies during all stages of grain growth. In the early stage, where the grains grow by consuming the disordered phase, grains have an elongated shape with an average aspect ratio of about 4. In the late stage, where the grains grow by defect annihilation, the grain growth occurs only along the minor axes. [S0031-9007(96)01425-1]

Equilibrium properties of periodic, ordered phases formed by amphiphilic molecules such as surfactants, phospholipids, and block copolymers have been studied extensively [1]. However, relatively little is known about the kinetics of order formation [2]. When these materials are subjected to a quiescent quench from the disordered state to the ordered state, the coherently ordered regions, which we refer to as "grains," are expected to form with random orientation. In the early stages, depicted in Fig. 1(a), these grains will grow at the expense of the disordered phase. This will continue until the grains occupy the entire sample volume. In this state, coherent order is disrupted by topological defects which can be either point, line, or wall imperfections, or continuous changes in local microstructure orientation [1]. Subsequent grain growth, depicted in Fig. 1(b), must occur by motion and annihilation of these defects. The quantities of fundamental interest are the size, shape, and concentration of the coherently ordered regions. In this paper we present the first measurements of the time evolution of these quantities in a block copolymer melt, using depolarized light scattering [3]. In previous experiments, small angle x-ray scattering was used to study the kinetics of ordering in block copolymers [4,5]. While clear signatures of the development of the ordered phase were evident in these experiments, grain characteristics could not be determined [6].

Defect dynamics and annihilation in ordered phases formed by symmetry-breaking phase transitions are subjects of considerable interest [7–9]. It has been proposed that defect dynamics in materials such as liquid crystals and superfluid ^{4}He is analogous to that involved in cosmology [8,9]. Yurke and co-workers have studied defect annihilation in nematic liquid crystals [10] where the local order was described by a single correlation length. In contrast, we find that two length scales are needed to describe the local correlations in the block copolymer sample studied here.

A polystyrene-polyisoprene diblock copolymer was synthesized by anionic polymerization under high vacuum. The weight average molecular weights of the polystyrene and polyisoprene blocks were determined to be 4 and 13 kg/mol, respectively, the polydispersity index of the copolymer = 1.07, and we refer to this polymer as SI(4-13). The equilibrium properties of this sample were obtained from high resolution x-ray scattering experiments [11]. The block copolymer forms an ordered phase consisting of hexagonally packed polystrene cylinders embedded in a polyisoprene matrix. The intercylinder spacing is 157 Å, and the cylinder radius is 40 Å. The sample exhibits an order to disorder transition when heated above 59 ± 1 °C.

A 0.5 cm thick SI(4-13) sample, confined between optical flats, was quenched quickly (in 5 min) from the disordered state (70 °C) to the ordered state at 56 °C. The sample was in the rubbery state at all times (the glass transition temperature of the polystyrene block, measured by differential scanning calorimetry, was 51 °C). The characteristics of the ordered grains were monitored as a function of time by depolarized light scattering. The apparatus used is shown schematically in Fig. 2(a). A 100 mW solid-state laser with wavelength $\lambda = 0.532$ μm was used as the source. The scattering profile ws projected on a screen and recorded by a charge coupled device camera. Coordinates in the scattering plane are determined by two angles, θ and μ [see Fig. 2(a)]. The radii of the SI(4-13) cylinders are much smaller than the wavelength of light and are not probed directly. However, the ordered grains behave the same as optically uniaxial crystals with the optic axis oriented along the cylinders, and these structures are responsible for depolarized light scattering [12]. The sample remained essentially transparent during all stages of grain growth due to the weak optical anisotropy of the grains. The difference in refractive indices parallel and perpendicular to the optic axis is estimated to be 10^{-4} [11]. Multiple scattering was therefore negligible.

In Fig. 2(b) we show typical two-dimensional scattering data, obtained at $t = 500$ min. Time zero is defined as the time at which the quench was initiated. It is evident that the scattering profiles depend on both θ and μ. For a given θ, the scattering profile exhibits fourfold symmetry with maximum intensity in $\mu = \pi/4 + n\pi/2$ directions,
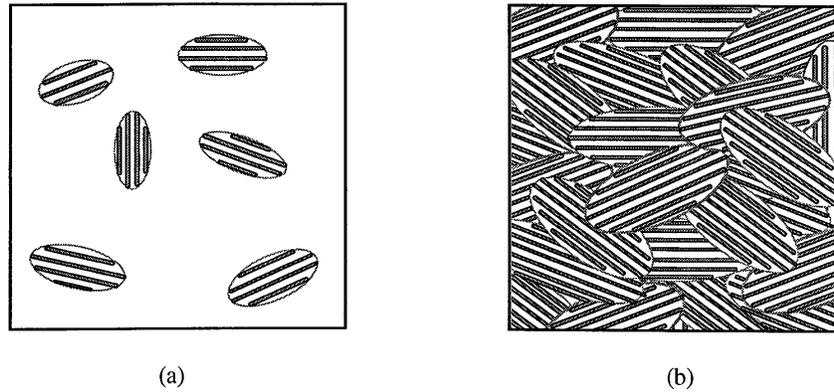
FIG. 1.   A schematic representation of the two regimes of order formation in block copolymers.   (a) Grain growth occurs at the expense of the disordered phase.   (b) Grain growth occurs due to defect annihilation.

and minimum intensity in the $\mu = n\pi/2$ directions (n is an integer).   The methodology for analyzing such scattering patterns was pioneered by Stein and co-workers [13].   The lack of azimuthal symmetry in the scattering profile indicates that the correlations within a grain cannot be described by a single parameter.   The simplest grain model consistent with the symmetry of the scattering profile is one in which the correlations within a grain are described by two length scales, L, along the optic axis, and W, perpendicular to that axis.   In our model, $C(\mathbf{r}', \mathbf{r}'')$, the probability that two locations in the sample defined by vectors $\mathbf{r}'$ and $\mathbf{r}''$ lie in the same grain, is given by

$$C(\mathbf{r}', \mathbf{r}'') = \exp\left[-\frac{[\mathbf{g} \cdot (\mathbf{r}' - \mathbf{r}'')]^2}{L^2}\right]$$
$$\times \exp\left[-\frac{[\mathbf{l} \cdot (\mathbf{r}' - \mathbf{r}'')]^2 + [\mathbf{m} \cdot (\mathbf{r}' - \mathbf{r}'')]^2}{W^2}\right], \quad (1)$$

where $\mathbf{g}$ is a unit vector in the direction of the optic axis, and $\{\mathbf{g}, \mathbf{l}, \mathbf{m}\}$ constitute an orthogonal set of unit vectors.   The depolarized light scattering intensity in the
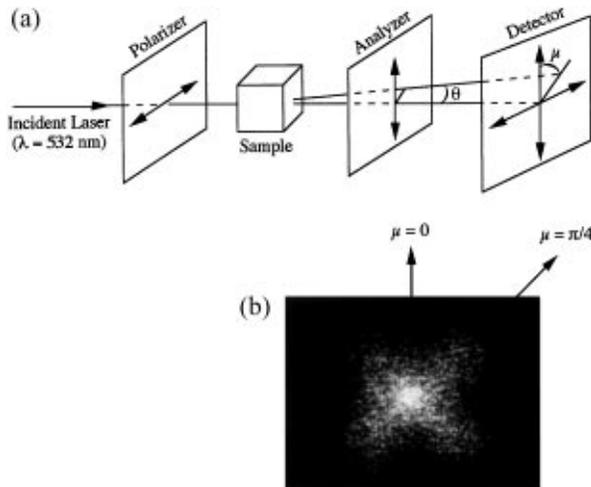

FIG. 2.   (a) A schematic of the experimental apparatus used to measure the depolarized scattering intensity profiles.   (b) Typical two-dimensional data, obtained at $t = 500$ min.

single scattering limit, $I(\theta, \mu)$, from a randomly oriented collection of grains described by Eq. (1) can be computed using the Born approximation [3,13]:

$$I(\theta, \mu) = K\phi W^2 L\{C(\theta) + D(\theta)\cos(4\mu)\}. \quad (2)$$

K is an optical constant, ϕ is the volume fraction occupied by grains, and functions $C(\theta)$ and $D(\theta)$ are given by

$$C(\theta) = \exp\left[-\frac{q^2 W^2}{4}\right]\int_0^\pi d\alpha \sin^5 \alpha \, \exp[-\beta(\alpha)]I_0[\beta(\alpha)],$$
$$(3)$$
$$D(\theta) = -\exp\left[-\frac{q^2 W^2}{4}\right]\int_0^\pi d\alpha \sin^5 \alpha \, \exp[-\beta(\alpha)]I_1[\beta(\alpha)],$$

where $q = 4\pi \sin(\theta/2)/\lambda$, $\beta(\alpha) = (q^2 W^2/8)[L^2/W^2 - 1]\sin^2 \alpha$, and I_m is the modified Bessel function of order m.

In Fig. 3, we plot the scattering intensity versus q along the $\mu = 0$ and $\mu = \pi/4$ directions for the data obtained at $t = 500$ min [same data are shown in Fig. 2(b)].   Each data set represents averages over the four degenerate directions.   For reference, we also show the scattering profile measured prior to the quench, which is presumably due to instrumental imperfections and small depolarized contributions from the disordered state.   The grain dimensions were obtained by fitting the experimental data (after subtracting the disordered state signal) to Eqs. (2) and (3).   The curves in Fig. 3 represent the best theoretical fits through the data with L and W as adjustable parameters—see [14] for details.   It is evident that the theory captures the essential features of the experimental data.   Quantitative agreement between theory and experiment requires exact expressions for the correlations at all length scales and in all directions.   We note that even in simple, disordered systems, with a single correlation length, different functional forms of the correlation function are required to fit the low q and the high q data [15].   Much less is known about locally anisotropic, partially ordered materials [2].   Given these uncertainties, the agreement between theory and experiment is reasonable.
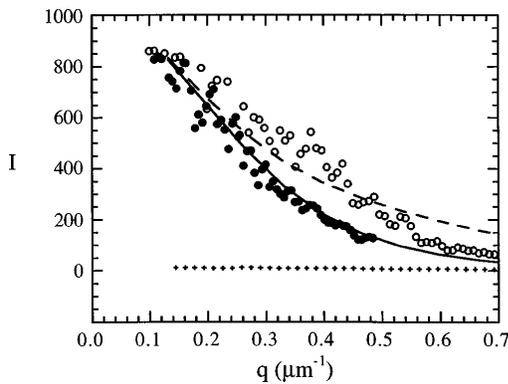
FIG. 3. Depolarized scattering intensity data, *I*, versus *q* along $\mu = 0$ (filled circles) and $\mu = \pi/4$ (unfilled circles) directions, obtained at $t = 500$ min [same data is shown in Fig. 2(b)]. The curves are the theoretical scattering profiles along the $\mu = 0$ (solid line) and $\mu = \pi/4$ (dashed line) directions with $L = 9.82$ μm and $W = 2.52$ μm. The crosses represent data obtained in the disordered state (70 °C) which were independent of μ.

In Fig. 4 we show the time dependence of *L, W,* and *L/W*. At times less than 300 min the depolarized scattering signal was comparable to that obtained in the disordered state. Therefore, structural changes occurring
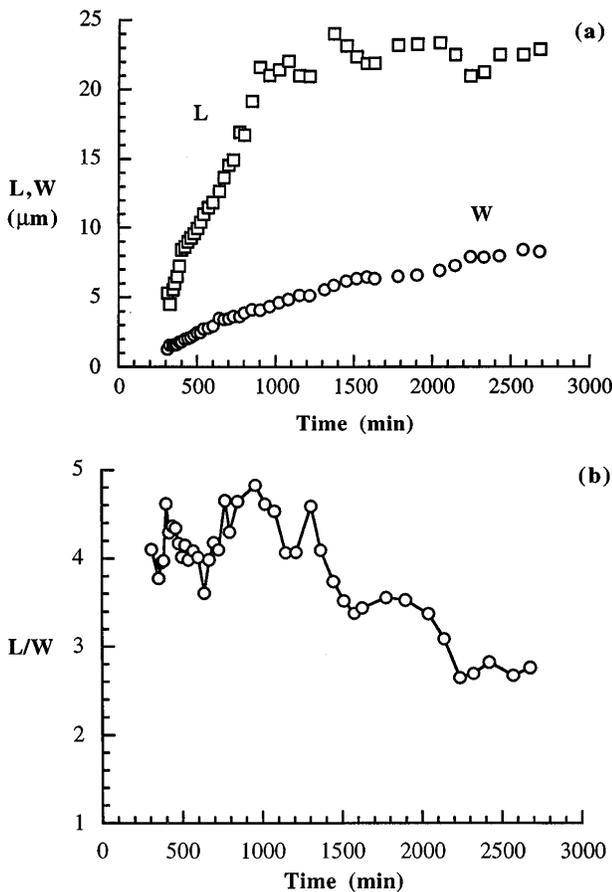

FIG. 4. The time dependence of (a) *L* (squares) and *W* (circles), and (b) *L/W*.

during this period could not be measured. The scattering profiles obtained at later times were similar to those shown in Fig. 3, and *L* and *W* values at different times were estimated by the procedure described in the previous paragraph. We find that, for $300 < t < 1000$ min, both *L* and *W* increase with time. However, there is no systematic change in the ratio *L/W* during this time, which fluctuates around a mean value of 4.2. This is shown in Fig. 4(b). In this time window, we thus observe the growth of elongated grains whose average aspect ratio is conserved. A possible explanation for the anisotropic grain shape is that the interfacial tension between the sides of the cylinders and the disordered phase is less than that between the ends of the cylinders and the disordered phase. A qualitative change in the grain growth characteristic occurs at $t \approx 1000$ min. Beyond this point, we find that *L* does not change significantly and appears to reach a plateau of about 22 μm, while *W* continues to increase with time.

To understand the changes occurring at $t \approx 1000$ min, it is necessary to compare the time dependence of the volume fraction of grains, ϕ, and grain volume *V* ($V = W^2 L$). According to Eq. (2), the ratio $I(0)/V$ is proportional to ϕ. $I(0)$ is the intensity as $q \to 0$. At long times we expect the entire sample to be occupied by grains, i.e., $\phi(t \to \infty) = 1$. The proportionality constant between ϕ and $I(0)/V$ was estimated by assuming that $\phi = 1$ for the data obtained at $t > 2000$ min; $I(0)/V$ was nearly constant in this time window. It is difficult to imagine a mechanism by which ϕ in a one component system would asymptotically approach a value that was different from unity. In Fig. 5, we show the time dependence of *V* and ϕ. Note that these two quantities are essentially independent of each other. *V* is obtained from the angular distribution of the scattered light and is not affected by the absolute intensity [14], while ϕ is directly proportional to the absolute intensity. It is evident from Fig. 5 that for $t < 1000$ min, the slopes of ϕ and *V*
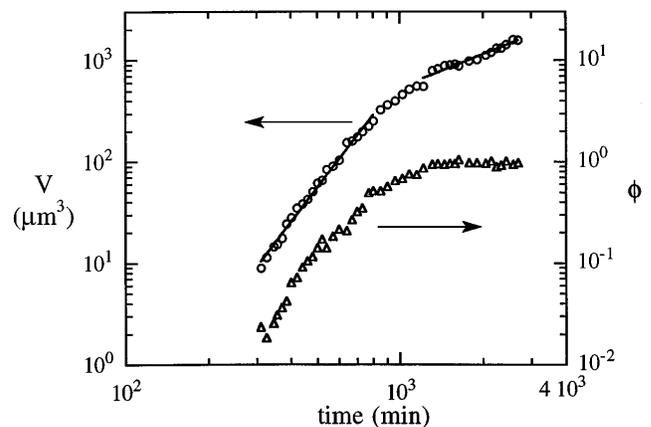

FIG. 5. The time dependence of grain volume, *V* (circles), and volume fraction occupied by grains, ϕ (triangles). The lines represent power law fits through the early- and late-stage *V(t)* data.

with respect to time are nearly identical. The increase in grain volume fraction with time is thus due entirely to the growth of existing grains and not to the formation of new grains. This is a characteristic of heterogeneous nucleation and growth. Grain growth after $t \approx 1000$ min requires annihilation of defects because the entire sample is occupied by grains. The onset of the plateau in L, seen in Fig. 4(a), occurs at the same time. Defect annihilation in this sample thus occurs preferentially along the minor axes (l and $\mathbf{m}$) of the grains.

Our conclusion that the mechanism for order formation in SI(4-13) is nucleation and growth is in agreement with the theory of Fredrickson and Helfand [16], which includes fluctuation corrections to the mean-field theory [17]. The (uncorrected) mean-field prediction is that order formation in SI(4-13) should occur by spinodal decomposition [17]. We are not aware of any theories of grain growth that are directly applicable to the kinetic data that we have obtained. Fredrickson and Binder have conducted a theoretical study of nucleation and growth of spherical grains of a lamellar block copolymer phase [18]. They found unusually small nucleation barriers and critically slowed growth kinetics. Since the ordering process involves molecular motion, a simple estimate for the rate of grain growth is given by R_g/τ, where R_g is the radius of gyration of the SI(4-13) molecule (4.6 nm [11]), and τ is the longest relaxation time [1 sec, based on rheological measurements on disordered SI(4-13)]. This gives a rate of 0.3 μm/min which is much larger than measured values of dL/dt and dW/dt during the early stage: 2×10^{-2} and 5×10^{-3} μm/min, respectively. This is typical of systems with critically slowed growth kinetics.

The time dependence of the average grain size during the late stages of ordering is expected to obey a power law: $V \sim t^\beta$ [19]. Yurke and co-workers found that $\beta = 1.0$ in nematic liquid crystals [10]. If we fit the time dependence of V obtained from SI(4-13) (which is a columnar liquid crystal [1]) to power laws, then we obtain $\beta = 3.45 \pm 0.14$ in the early stage ($t < 800$ min), and $\beta = 1.20 \pm 0.13$ in the late stage ($t > 1200$ min). While the similarity in the late stage results obtained in block copolymers and in nematic liquid crystals is encouraging, clearly, more work is required to establish the general principles of defect annihilation in these systems. Block copolymers are good models for such studies because the single scattering limit applies even in the late stages.

To summarize, we have identified two stages of order formation in SI(4-13): an early stage where grain growth occurs at the expense of the disordered phase, and a late stage where grain growth occurs by defect annihilation. In the early stage we find that, on average, grains are elongated, with an aspect ratio $L/W \approx 4$. In the late stage we find that L/W decreases with time. This appears to be the most efficient path for reducing defect density in systems in which the local order is characterized by two length scales.

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