## **Block-Copolymer Ordering with a Spatiotemporally Heterogeneous Mobility**

August W. Bosse, Jack F. Douglas, Brian C. Berry, Ronald L. Jones, and Alamgir Karim

Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8541, USA (Received 7 June 2007; revised manuscript received 7 August 2007; published 20 November 2007)

Motivated by recent zone annealing measurements on stripe-forming block-copolymer films [B. C. Berry *et al.*, Nano Lett. **7**, 2789 (2007)], we study block-copolymer ordering with a spatiotemporally heterogeneous mobility. Specifically, we implement a time- and space-dependent mobility field in the relaxation of a diblock copolymer self-consistent field theory. The model includes a gradient in the local mobility *and* intrinsic nanoscale mobility variations characteristic of glass phenomenology. The simulations demonstrate that a spatiotemporally heterogeneous mobility can have a significant influence on microdomain ordering in block-copolymer systems, and that nanoscale dynamic heterogeneities associated with glass formation can impact the structure of the ordered block-copolymer microphase.

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There is considerable scientific and technological interest in using microphase-separated block-copolymer (BCP) films as lithographic masks in the fabrication of nextgeneration nanostructured devices (e.g., see Refs. [1,2]). However, if BCP thin films are to evolve into a commercially viable nanofabrication material, one must have significant control over microdomain ordering.

Recently, there have been efforts in using time- and space-dependent thermal fields to improve order in BCP materials—a process termed zone refinement or zone annealing. This approach was pioneered by Hashimoto and co-workers in bulk BCPs [3-5]. In addition, Angelescu et al. [6] and Berry et al. [7] have shown that zone annealing can also be a powerful tool for controlling order in BCP films. Perhaps the most unexpected aspect of this new work is the finding by Berry et al. that significantly enhanced microdomain ordering can be obtained for glassy BCP films zone annealed over a temperature range well below the microphase separation transition (MST) temperature  $T_{\rm MST}$  of the BCP melt. This observation suggests that dynamics-in particular, glassy dynamics-and the physics of glass formation may have a significant impact on BCP microdomain ordering.

The observation of Berry et al. prompted our investigation of how time-dependent thermal gradients could influence BCP ordering under conditions where the temperature is always below  $T_{MST}$  and where the physics of glass formation is prevalent. Previous computational studies of directional ordering in BCPs have focused on temperature gradients that heat the system to temperatures above  $T_{MST}$ [8,9]. However, these studies do not directly apply to the ordering of block copolymers under conditions where T < $T_{\rm MST}$ . Specifically, we need to address physical aspects of glass formation that are relevant to BCP ordering for T < $T_{\rm MST}$ . Accordingly, we explore the influence of a time- and space-dependent mobility field associated with an applied time- and space-dependent thermal field. We also incorporate local mobility heterogeneities intended to model the intrinsic dynamic heterogeneities of glass-forming polymer liquids (see Ref. [10], and references therein). Previous work has indicated that this kind of heterogeneity can influence the degree of polycrystalline growth during crystallization [11], and we anticipate a similar effect for BCP ordering.

We base our modeling and simulation on a standard polymer self-consistent field theory (SCFT) where an applied thermal gradient is modeled as a mobility gradient in the SCFT relaxation. The virtue of this technique, in comparison to Ginzburg-Landau, phase-field, and other simulation methods of BCP ordering, is that we can introduce dynamic heterogeneities in the mobility at a physically relevant scale. In this Letter, we show that gradients in the mobility field have a significant effect on the ordering process of the BCP, and that mobility heterogeneities associated with glass formation can indeed dramatically impact the structure of the resulting ordered BCP microphase.

The polymer thin film is modeled using a standard 2D SCFT for an incompressible melt of monodisperse AB diblock copolymers in a volume V, each with an index of polymerization N (all spatial variables are specified in units of  $R_g$  [9], the unperturbed radius of gyration of a diblock copolymer). The fraction of the A block along the copolymer is denoted f. Individual diblocks are modeled as a Gaussian thread (i.e., a continuous bead-spring), and local A-segment-B-segment interactions are parametrized by a Flory  $\chi$  parameter [9]. The segment-segment interactions are decoupled to yield a formally equivalent field theory in terms of two "chemical potential" fields  $W_+$  and  $W_{-}$  that are conjugate to the local total density and the local composition, respectively [9]. The average local volume fractions of A segments,  $\phi_A$ , and B segments,  $\phi_B$ , are calculated as functional derivatives of the canonical partition function with respect to  $W_{\pm}$ . The mean-field phase behavior of this model is fully determined by the values of f and the product  $\chi N$  [9].

We use a saddle point approximation to calculate the mean-field values of  $W_{\pm}$ . This approximation is carried out

by minimizing the Hamiltonian  $\mathcal{H}[W_+, W_-]$  with respect to  $W_{\pm}$ ,  $\delta \mathcal{H}/\delta W_{\pm} = 0$ . Specifically, we introduce a time variable *t* and then relax the fields in the direction of the thermodynamic forces,

$$\frac{\partial}{\partial t}W_{-}(\mathbf{x},t) = -\Lambda \frac{\delta \mathcal{H}[W_{+},W_{-}]}{\delta W_{-}(\mathbf{x},t)},$$
(1)

and

$$\frac{\partial}{\partial t}W_{+}(\mathbf{x},t) = \lambda \frac{\delta \mathcal{H}[W_{+},W_{-}]}{\delta W_{+}(\mathbf{x},t)},$$
(2)

where  $\Lambda$ ,  $\lambda > 0$  are mobility and relaxation parameters, respectively. The saddle point equations are satisfied when Eqs. (1) and (2) are stationary.

The complete numerical SCFT framework involves an iterative scheme for finding the saddle point configurations of  $W_{\pm}$ . Details of the basic model and the SCFT outlined here can be found in Ref. [9].

In order to examine specific mobility related effects, we consider a linear-gradient form for the temperature  $T(\mathbf{x}, t)$  that connects a maximum temperature  $T_{\text{max}}$  and a minimum temperature  $T_{\text{min}}$  [see Fig. 1(a)].  $T(\mathbf{x}, t)$  is assumed to be uniform in the y direction, and the thermal gradient defined by  $T(\mathbf{x}, t)$  moves across the sample in the x direction with a constant speed  $v_x$ . As mentioned above, we assume that  $T_{\text{min}} < T_{\text{max}} < T_{\text{MST}}$ .

The Flory  $\chi$  parameter exhibits an inverse dependence on temperature  $\chi \sim 1/T$ , so we could *model* a thermal gradient as a phenomenological  $\chi$  gradient; however, we are interested in systems at temperatures well below  $T_{\text{MST}}$ , or equivalently  $\chi N$  well above the MST value, where variations in  $\chi$  are relatively unimportant. Accordingly, we expect a  $\chi$  gradient to have little or no effect on ordering in SCFT simulations above the MST value of  $\chi N$ , and our test simulations confirmed this expectation.

However, when BCP systems are heated above their glass transition temperature, they experience a significant increase in mobility. Evidently, for  $T_{\rm min} < T_g < T_{\rm max} < T_{\rm MST}$ , where  $T_g$  is the BCP melt glass transition temperature [12], a thermal gradient must induce a mobility gradient. We consider whether this time-dependent mobility gradient results in coarsening toward a highly ordered state.

The coarse-grained, field-theoretic nature of SCFT simulations makes it computationally unreasonable to examine the molecular-scale phenomena responsible for glass formation in BCP materials. However, it is generally appreciated that the glass transition involves an increase in the structural relaxation time  $\tau$  of a polymeric glassforming liquid by *many* orders of magnitude (  $\geq 10^{10}$  s) over a relatively small temperature range. If we suppose that the time-dependent thermal gradient induces a timedependent mobility gradient, where  $\Lambda \sim 1/\tau$ , and that the specific molecular details of the glass transition are largely unimportant, then we are reasonably justified in modeling the mobility gradient in terms of a time- and spacedependent mobility field in SCFT. That is, we implement a spatiotemporally heterogeneous mobility field  $\Lambda(\mathbf{x}, \mathbf{x}', t, \mathbf{v}, \dots; [T, \nabla T, \dots])$  in the relaxation given by Eq. (1). Effectively, all of the details of the molecular glass transition are absorbed into  $\Lambda$ . Furthermore, we note that the glass transition in a polymer system involves multiple characteristic temperatures, including  $T_c$ , the "mode coupling" crossover temperature separating the high- and lowtemperature regimes of glass formation (including the onset of significant changes in fluid properties such as dynamic heterogeneities), and  $T_g$ , the approximate tem-



FIG. 1 (color online). (a) The assumed temperature profile  $T(\mathbf{x}, t)$ . The parameter  $\delta$  corresponds to the width of the spatial region defined by  $T_g < T < T_c$ . (b) Mobility field profile  $\log_{10}[\Lambda(\mathbf{x}, t)]$  with  $\Lambda_{\max} = 10^2$ ,  $\Lambda_{\min} = 10^{-8}$ , and  $\Lambda_h(\mathbf{x}) = 10^{n(\mathbf{x})}$ , where  $n(\mathbf{x})$  is randomly selected from a uniform distribution defined on the interval [-5, 1], for all  $\mathbf{x}$ —these values of  $\Lambda_{\max}$ ,  $\Lambda_{\min}$ , and  $\Lambda_h(\mathbf{x})$  are used throughout this Letter. The volume of a single lattice site is selected to be  $d\mathbf{x} = 0.5^2$ . Assuming  $R_g \approx 10$  nm, we have  $d\mathbf{x} \approx (5 \text{ nm})^2$ , so that the size of the dynamic heterogeneities modeling by  $\Lambda_h(\mathbf{x})$  are consistent with previous work [10]. (c) Partial 2D plot of  $\log_{10}[\Lambda(\mathbf{x}, t)]$  with  $\Lambda_{\max}$ ,  $\Lambda_{\min}$ , and  $\Lambda_h(\mathbf{x})$  specified above. The central speckled area is the region of significant mobility heterogeneities. The light- and dark-colored areas are the regions of fast and slow relaxation, respectively. The arrow indicates the positive x direction.

perature at which the structural relaxation time becomes exceptionally long [13]. Figure 1(a) shows a simple schematic of the thermal gradient relative to the characteristic temperatures  $T_g$  and  $T_c$ .

We assume that  $\tau$  for  $T > T_c$  is much smaller than  $\tau$  for  $T < T_g$ . In the intermediate range,  $T_g < T < T_c$ ,  $\tau$  has been shown to obey the Vogel-Fulcher-Tammann-Hesse equation [13]. Furthermore, intrinsic "dynamic heterogeneities" (i.e., intrinsic "fluctuations" in  $\tau$ ) have a significant effect on the polymer fluid dynamics near and below  $T_c$  [10]. In this Letter, we focus on modeling essential aspects of these intrinsic dynamic heterogeneities instead of focusing on the precise functional form of the structural relaxation time. Specifically, for temperatures in the glass formation range,  $T_g < T < T_c$ , we assume that the local structural relaxation time  $\tau(\mathbf{x})$  is characterized by significant heterogeneities covering many orders of magnitude and having a length scale of order 1 to 5 nm (see [10], and references therein).

The dynamic heterogeneities enter our model though the mobility field  $\Lambda \sim 1/\tau$  mentioned above. The spatial width of the region containing significant mobility heterogeneities [ $\delta$  from Fig. 1(a)] is determined by the slope of the temperature gradient  $\Delta T/\Delta x = (T_g - T_c)/\delta$ , for  $T_g < T < T_c$ , as seen in Fig. 1(a). We assume that  $\Lambda$  depends on

only position and time so that

$$\Lambda(\mathbf{x}, t) = \begin{cases} \Lambda_{\max}, & x \le \mu(t) - \delta/2\\ \Lambda_h(\mathbf{x}), & |x - \mu(t)| < \delta/2\\ \Lambda_{\min}, & \mu(t) + \delta/2 \le x, \end{cases}$$
(3)

where  $\mu(t)$  is the time-dependent spatial center-point of the gradient [see Fig. 1(a)]. Our model of the local mobility heterogeneities  $\Lambda_h(\mathbf{x})$  is selected to have *random* values extending over many orders of magnitude, and  $\Lambda_{\min} \ll \min[\Lambda_h(\mathbf{x})] \ll \max[\Lambda_h(\mathbf{x})] \ll \Lambda_{\max}$ . Consistent with the above specification of the thermal gradient,  $\mu(t) = v_x t + \mu_0$ , where  $\mu_0$  is the initial value of  $\mu(t)$ .

Within this model, the thermal gradient effectively "smooths out" the mobility heterogeneities above  $T_c$ , resulting in a region of uniform, fast relaxation. For illustrative purposes, we plot in Fig. 1(b) a profile view of  $\log_{10}[\Lambda(\mathbf{x}, t)]$  at a time t when  $\mu(t)$  is at the midpoint of the simulation space, and in Fig. 1(c) we show a 2D realization of  $\log_{10}[\Lambda(\mathbf{x}, t)]$ . This pair of images allows for easy visualization of  $\Lambda(\mathbf{x}, t)$  and the assumed form of the mobility heterogeneities in our model.

In Fig. 2, we provide a series of SCFT mobility field and composition snapshots for a lamellar-forming *AB* diblock copolymer melt. System and simulation details are pre-

Case A	Case B	Case C	Case D	Case E	Case F
" $v_x = \infty$ "	$v_x = 0.384$	$v_x = 0.384$	$v_x = 0.0384$	$v_x = 0.0384$	" $v_x < \infty$ "
" $\delta < \infty$ "	$\delta = 128$	$\delta = 16$	$\delta = 16$	$\delta = 128$	" $\delta = \infty$ "
t = 200	t = 500	t = 300	t = 3000	t = 5000	t = 200
Λ	Λ	Λ	Λ	Λ	$\Lambda$
$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$
t = 10000	t = 10000	t = 10000	t = 16000	t = 16000	t = 16000
$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$	$\phi_A$
$x \longrightarrow$	$x \longrightarrow$	$x \longrightarrow$	$x \longrightarrow$	$x \longrightarrow$	$x \longrightarrow$

FIG. 2 (color online). Partial 2D SCFT mobility field and composition snapshots of a  $V = 128^2 AB$  diblock melt with f =0.5 and  $\chi N = 15$  simulated on a periodic  $256^2$  square lattice. Time is in units of  $W_{-}$ -update time steps with  $\Delta t = 1$ . The system is subjected to the timedependent mobility gradient specified in Fig. 1. The first row of images illustrates the mobility field  $\Lambda$  at an early time, and the second row of images illustrates the corresponding composition of the melt  $\phi_A$ . The third row of images illustrates the composition of the melt  $\phi_A$  after the mobility gradient passed and the system was allowed to further relax. All relevant system parameters are specified in the figure. Case A represents a fully relaxed simulation with a uniform mobility field  $\Lambda(\mathbf{x}) = 10^2$ . Cases B to E represent a series of simulations with various gradient velocities  $v_x$  and gradient widths  $\delta$ . For case F, the system is subjected to a mobility field characterized by significant heterogeneities  $\Lambda_{h}(\mathbf{x})$ , as specified in Fig. 1. For all frames, we plot 25% of the total simulation space, and the arrows indicate the positive x direction.

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sented in the figure. Motivated by the zone annealing experiments previously mentioned [7], we began all simulations from an "as-cast," nearly homogeneous state. The data in Fig. 2 are arranged into six cases.

Case A shows a relaxed SCFT snapshot with a constant mobility (formally equivalent to  $v_x = \infty$  and finite  $\delta$ , as indicated in the figure). The defect structures in case A are characteristic of those found in experimental studies of quenched lamellar BCP systems [9]. We note that BCP systems also exhibit glassy behavior on a morphological scale (in addition to the molecular scale modeled with the mobility field) in the sense that they tend to get stuck in metastable configurations due to the complexity of the free-energy landscape [14]. Accordingly, defective configurations like the one found in case A are typical of BCP systems, and further relaxation will yield minimal additional defect annihilation.

Case F illustrates the ordering effects of a *static* mobility field characterized by significant heterogeneities  $\Lambda_h(\mathbf{x})$ , as specified in Fig. 1 (formally equivalent to finite  $v_x$  and  $\delta = \infty$ , as indicated in the figure). Clearly, relaxation occurs slowly and nonuniformly.

Cases B to E in Fig. 2 illustrate the ordering effects of a time-dependent mobility gradient as defined by Eq. (3) and specified in Fig. 1. For the fast and narrow gradient illustrated in case C, the long axes of the lamellae are observed to align parallel to the mobility gradient front, and for the slow and narrow gradient illustrated in case D, the long axes of the lamellae are observed to align perpendicular to the front. The alignment crossover velocity was in the neighborhood of  $v_x = 0.150$ . This crossover behavior has been observed in previous simulations of BCPs subjected to a directional quench [8]. We believe that the mechanism for the orientation crossover is the same as discussed in Ref. [8]. Specifically, the transition from case C to D represents a transition to a quasistatic situation where the mobility gradient is essentially stationary on the time scale of phase separation, and thus the preferred orientation minimizes the A-B interfacial free energy at the microphase-homogeneous phase interface. It is worth noting that Berry et al. observed a preferential alignment direction similar to case D in their zone annealing experiments [7]; however, the thermal gradients and spatiotemporal scales of the real system were significantly different than those presented in this Letter, which suggests that additional or other mechanisms could be responsible for the preferential alignment observed in the experiments.

Cases B and E in Fig. 2 illustrate the effects for both large and small gradient velocities, respectively, for large  $\delta$ . The wide region of mobility heterogeneities defined by  $\delta$  significantly affects the resulting order. Specifically, we see that the local mobility heterogeneities "nucleate" de-

fects as the thermal gradient passes over them, resulting in a polycrystalline morphology. The observation that dynamic heterogeneities can yield polycrystalline morphologies has been previously suggested in simulations of crystal growth [11], and the results presented here indicate that this mechanism extends to ordering in BCP films.

In summary, we have examined ordering phenomena in BCP systems subjected to a spatiotemporally heterogeneous mobility field using a simple extension to standard polymer SCFT. The simulations presented here provide strong evidence that a time-dependent mobility gradient can be successfully implemented as a means to control microdomain ordering in BCP systems. Furthermore, the simulations suggest that nanoscale dynamical phenomena, such as intrinsic dynamic heterogeneities associated with glass formation, can *dramatically* affect the ordering process and the resulting order of the BCP microphase.

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