Scaling Behavior of Block Copolymers in Spontaneous Growth of Lamellar Domains

Y. Shiwa, T. Taneike, and Y. Yokojima

Division of Natural Sciences, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

(Received 3 June 1996)

The kinetics of microphase-separated lamellar domains is studied in numerical simulations of the cell-dynamical-system model of block copolymers in two dimensions. At early stages the correlation length ξ is found to grow with time as a power law, $\xi \propto t^{1/2}$, and is understood theoretically. The later-stage behavior, where both lamellar period and the correlation length are observed to grow in the same way, as $\xi \sim t^{\phi}$ with $\phi \approx \frac{1}{5}$, suggests that the lamella-forming block copolymers and Rayleigh-Bénard convective systems belong to the same universality class. [S0031-9007(96)01700-0]

PACS numbers: 64.60.Cn, 61.41.+e, 64.75.+g

When a system is transferred from a homogeneous phase into an ordered phase where the initial state is thermodynamically unstable, a network of small domains of ordered phase develops spontaneously and the length scale associated with these domains grows with time. In systems (such as a binary mixture) where this domain coarsening proceeds to form *macroscopic* domains, it is now reasonably well established that the domain growth can be described in terms of dynamic scaling [1]. In this Letter we broaden the discussion to systems in which coarsening cannot proceed to a macroscopic scale but instead *microdomains* are formed.

We investigate the microphase separation of block copolymers (BCP) [2] with equal length subchains, so that the ordered state is given by a periodic lamellar structure. The existence of the spatial period $2\pi/q_0$ of the ordered structure renders the study of microphase separation kinetics quite intriguing in comparison with the case of macrophase separation for which $q_0 = 0$. To describe the kinetics of the system, a phenomenological model was introduced in terms of a cell dynamical system (CDS), and the corresponding partial differential equation was proposed [3]:

$$\tau_0 \frac{\partial \psi}{\partial t} = \epsilon\psi - (\nabla^2 + k_m^2)^2\psi + \tilde{g}\nabla^2\psi^3. \qquad (1)$$

Here $\psi(\mathbf{r}, t)$ is the order parameter field, which is the local monomer concentration deviation; τ_0, ϵ, k_m and $\tilde{g}$ are phenomenological parameters. Equation (1) has since been much used to test scaling hypothesis of the final equilibrium pattern (e.g., the lamellar thickness and the equilibrium structure factor) [4]. However, little attention has yet been paid to the study of domain coarsening in BCP. In this Letter we study the growth of domains of lamellas in numerical simulations of a CDS model corresponding to Eq. (1). For the order parameter $\psi(n, t)$ in the nth cell at time t, the CDS model reads

$$\psi(n, t+1) = \psi(n, t) - B\psi(n, t) - [J(n, t)]_1 . \qquad (2)$$

Here $J(n, t) \equiv f(\psi(n, t)) + D[\psi(n, t)]_1 - \psi(n, t)$ is the effective chemical potential, where $[X]_1 = \langle\langle X \rangle\rangle - X$, the operator $\langle\langle X \rangle\rangle$ being the isotropic spatial average of the quantity X; on the square lattice it is defined by $\langle\langle X \rangle\rangle = \frac{1}{6}\sum X$ (nearest neighbor cells) + $\frac{1}{12}\sum X$ (next-nearest neighbor cells). The injective map f models the local cell dynamics, and is chosen to be $f(\psi) = A\tanh(\psi)$. The parameter A controls the quench depth. The D is a positive constant proportional to the diffusion constant, and the positive constant B ensures the formation of lamellas.

The linear stability analysis of Eq. (2) shows that the homogeneous phase becomes unstable for $A \geq A_c$ where $A_c \equiv 1 + 2\sqrt{BD}$. The wave number k_m of the linearly most unstable mode (to be referred to as k_m mode hereafter) is given via the equation $2J_0(k_m) + J_0(\sqrt{2}k_m) = 3[1 + (1 - A)/2D]$, where J_0 is the Bessel function of the first kind. One also finds from the linear analysis that the wave number k_e, which minimizes the free energy (potential functional), is obtained as the solution of $2J_0(k_e) + J_0(\sqrt{2}k_e) = 3(1 - \sqrt{B/D})$ [5].

We have simulated Eq. (2) on two-dimensional square lattices of size 256×256 with periodic boundary conditions. The initial condition consisted of uniformly distributed random fluctuations of amplitude 0.05, and five samples were studied. The parameters used are $B = 0.005$ and $D = 0.5$, so that the critical value of A is $A_c = 1.1$, and $k_e = 0.56$. In the computation reported here, the data were hardened using the transformation $\psi(n, t) \rightarrow \mathrm{sgn}\psi(n, t)$ to remove any effect due to the finiteness of the ratio of the thickness of domain walls and the domain size; in this way we can make contact with the KYG calculation (see below) in which the order parameter field saturates exponentially fast away from the walls.

We first studied early stages of ordering kinetics. Taking advantage of the slower time scales owing to the critical slowing down, we have chosen $A = 1.12$ so that we are able to probe mostly the early and intermediate stages. We computed the scattering function $S(\mathbf{k}, t)$ defined as $S(\mathbf{k}, t) = \langle\psi(\mathbf{k}, t)\psi^*(\mathbf{k}, t)\rangle$ with $\psi(\mathbf{k}, t)$ being the Fourier transform of the order parameter. Time evolution of the circularly (in $\mathbf{k}$ space) averaged scattering function, $S(k, t)$, is shown in Fig. 1 (inset). Narrowing of the scattering profile and increase of the peak intensity

 0031-9007/96/77(21)/4378(4)$10.00

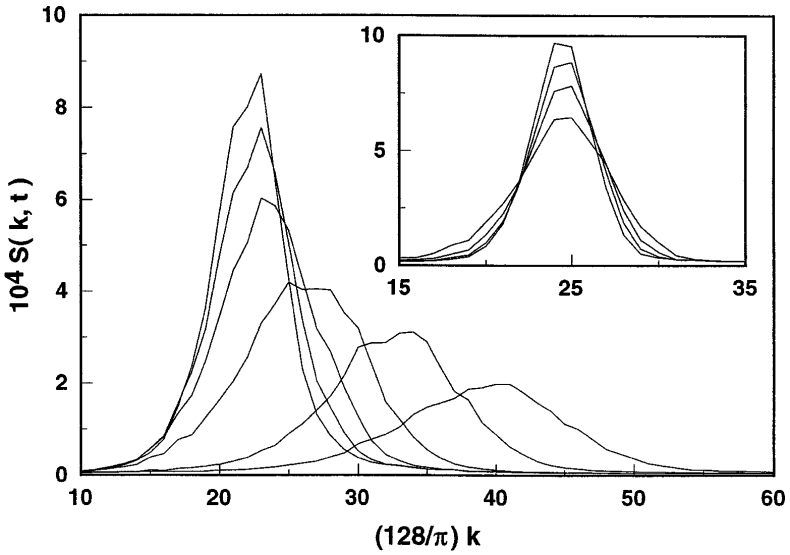

FIG. 1. Time evolution of the circularly averaged scattering function $S(k,t)$ for hardened data with $A = 1.3$ as a function of the wave number k; the times are, from lowest to uppermost, 100, 300, 900, 2000, 4000, and 10 000. The k is defined only for discrete multiples of $2\pi/256$, and the discrete values of $S(k,t)$ are connected by the straight lines. The scale of the vertical axis is in arbitrary units. In the inset, the early time behavior of $S(k,t)$ for $A = 1.12$ is shown in the same manner for times 800 to 2000 at intervals of 400 time steps.

are observed to occur at the position $k = k_m (= 0.61)$ for dimensionless times $t \lesssim 1900$. The time dependence of the peak height (S_M) and the full width at half maximum (Δk) of the scattering function is summarized in Fig. 2, obeying the power law as $S_M \propto t^{\alpha}$ and $\Delta k \propto t^{-\beta}$ with the exponent $\alpha \approx 0.47$ and $\beta \approx 0.50$ approximately. Clearly the time interval represented by Fig. 2 is not the so-called linear regime, which appears at much earlier stages and where the growth is exponential. We are unable to explain why the growth of $S(k,t)$at k_m persists far beyond the regime where the linearized theory is valid. We infer, however, that the nonlinear interaction of the unstable modes with $k \approx k_m$ is surely playing an important role here. This can be corroborated by the following observation.

Elder and Grant [6] proposed that a singular perturbation technique [7] (to be referred to as KYG), developed originally to study the nonconserved ordering kinetics, might be generalized to a broader class of other ordering dynamics problems. In fact, the extended KYG approach has been applied to the Rayleigh-Bénard convection to successfully explain the growth of roll patterns at an intermediate time domain [8]. When applied to Eq. (1), the extended KYG method formally expands the solution

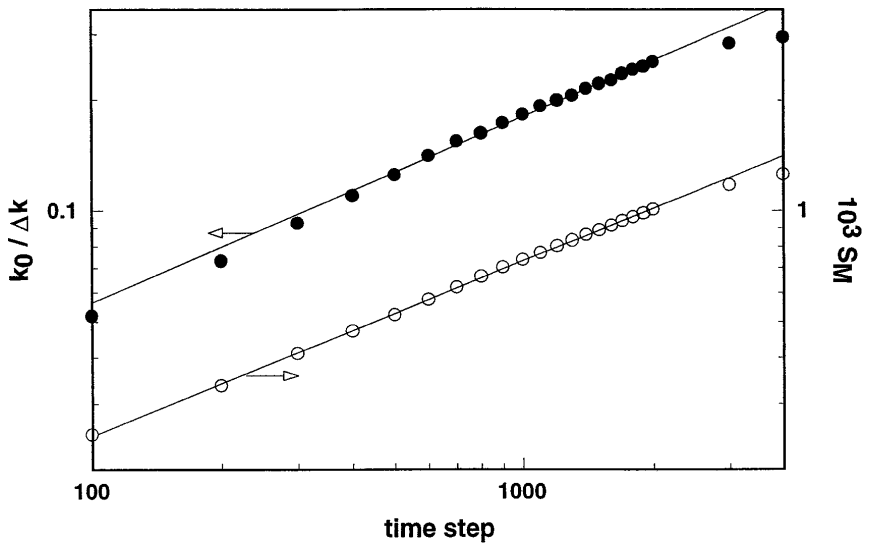

FIG. 2. Time evolution of the peak intensity (S_M) and the full width at half maximum (Δk) of the scattering function for $A = 1.12$. The wave number k is scaled with $k_0 = \pi/128$, and S_M is in arbitrary units. The straight line is the best fit to the data.

of Eq. (1) in terms of the solution (ψ^0) to its linearized part. Each term in the expansion (representing nonlinear interactions of fluctuations) is then approximated by replacing $\psi^0(\mathbf{k}, t)$ by its value of k_m mode. The resulting infinite series can then be resummed. We have calculated the equal-time correlation function $g(\mathbf{r} - \mathbf{r}', t) \equiv \langle \psi(\mathbf{r}, t)\psi(\mathbf{r}', t)\rangle$ in the manner of KYG to find that the circularly averaged [and normalized as $g(0, t) = 1$] correlation function is given by

$$g(r, t) = (2/\pi) \arcsin\{J_0(k_m r) \exp[-r^2/4l^2(t)]\}, \quad (3)$$

where $l(t) = 2k_m\sqrt{2t/\tau_0}$. To test if the extended KYG form (3) is indeed true in our case, we have used data from the CDS simulation. The characteristic length scale $l(t)$ was extracted from fitting Eq. (3) to the data. Very good agreement with the theory could be seen over the time domain considered, one example being shown in Fig. 3(a). In Fig. 3(b) we plot $l(t)$ thus obtained as a function of t; variation of l with time is consistent with $l \propto t^{1/2}$. It should be emphasized also that the result (3) implies the scattering function $S(k, t)$ has the scaling form $S(k, t) = l(t)h[(k - k_m)l(t)]$ apart from the dependence upon k_m itself; $h(x)$ is a scaling function. The results of Fig. 2 are indeed consistent with this scaling.

We next turn to the question of what are the scaling properties, if they exist, characterizing the late-stage coarsening process. To investigate this question we have taken the choice $A = 1.3$ in our simulation, since with $A = 1.12$ ("shallow" quenches) the late stages cannot be reached in practice because of the slower time scale and the larger length scale (hence the finite-size effect). Time evolution of the scattering function is shown in Fig. 1. It is seen that there is a shift in the position (k_p) where $S(k, t)$ has its maximum, the shift occurring from $k_m (= 0.99)$ to k_e with increasing time. Time dependence of the peak position is given in Fig. 4(a). Looking more closely into the scattering profiles during the time period $400 \lesssim t \lesssim 2000$, we found that as time went on the secondary peak developed at a smaller wave number, increasing its intensity gradually until it took over the original peak and shifted to k_e for $t \gtrsim 2000$. Because of this double-peaked nature of scattering profiles, the peak intensity and width changed nonmonotonically with time in this transient regime. After the peak had shifted to the position k_e, representing the equilibrium lamellar thickness, narrowing of the scattering profile and an increase of peak intensity occurred gradually as in other coarsening processes of phase separation. Figure 4(b) shows the time dependence of the peak intensity and width at the late stages. Figures 4(a) and 4(b) imply the characteristic length scale (ξ) obeying the power law $\xi \sim t^{\phi}$ with $\phi \approx \frac{1}{5}$ over the transient period of time and at late times. This scaling behavior is not understood theoretically at present. However we note a $t^{1/5}$ scaling of the length scale (as seen earlier by Elder *et al.* [9] in the simulation of the Swift-Hohenberg model [10]) has been found by Cross and Meiron [11] in the numerical simulations of equations that model Rayleigh-Bénard (RB) convections.

We expect that both features observed, namely, a law $\xi \propto t^{1/2}$ at early times and $\xi \sim t^{1/5}$ at later times, are not specific to BCP but occur in RB systems as well. Interestingly, a $t^{1/2}$ scaling at earlier times seems to have been observed in the simulations cited above. To address this expectation we close this Letter with the following observation. Equation (1) can be recast into the form

$$\tau_0 \frac{\partial \psi}{\partial t} = \nabla^2 \frac{\delta \mathcal{H}}{\delta \psi}, \quad (4)$$

where $\mathcal{H}$ is the Hamiltonian derived by Ohta and Kawasaki [5] in which there is a Coulomb-type long-range repulsive interaction; for the weakly segregated systems this Hamiltonian reduces to that derived by Leibler [12]. We then follow Fredrickson and Binder [13] to argue that since the operator ∇^2 in Eq. (4) reflects a

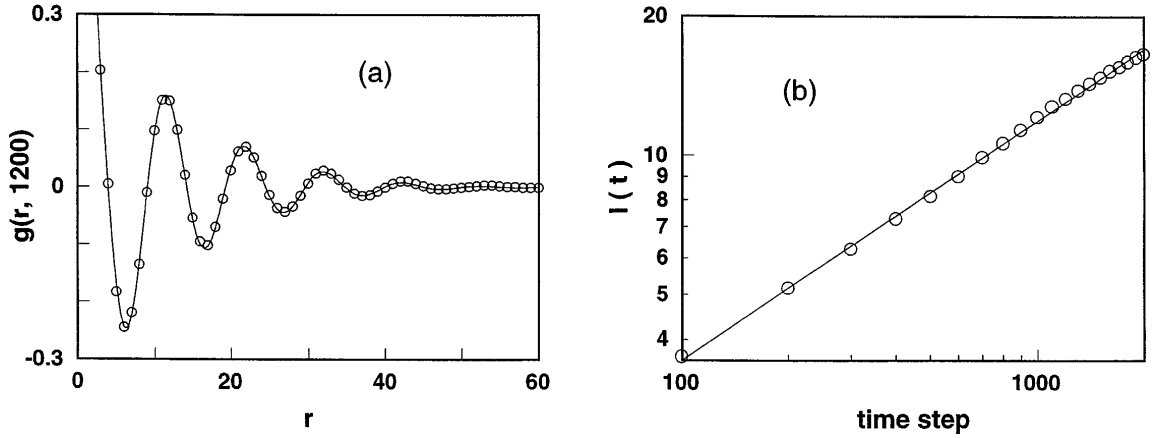

FIG. 3. (a) Test of the extended KYG approach. Data of the circularly averaged correlation function $g(r, t)$ at $t = 1200$ for $A = 1.12$ is shown by open circles, and the solid curve is the best fit to the data based on Eq. (3). (b) Time evolution of the characteristic length scale (l) of the correlation function. The line has the slope 0.52 corresponding to the best fit.

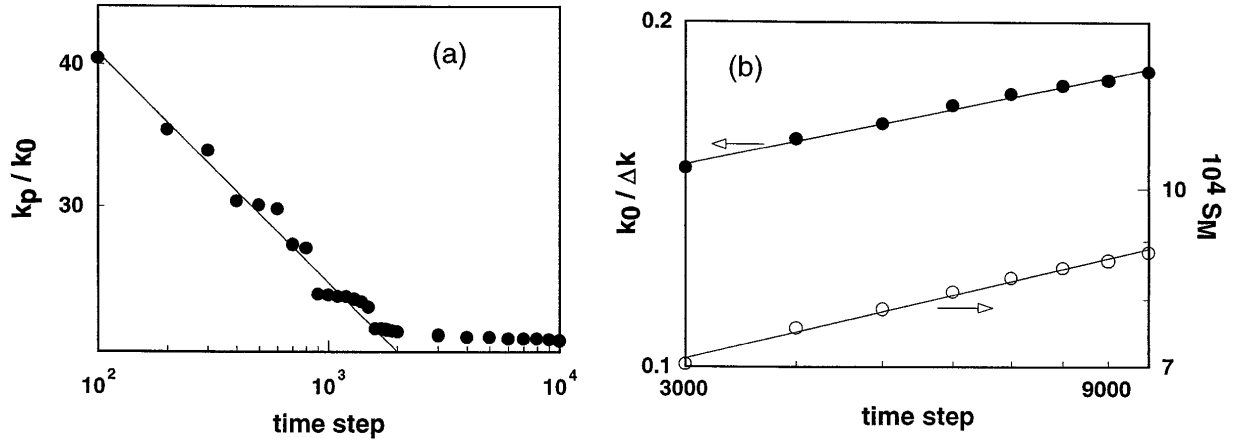

FIG. 4. Double-logarithmic plot of the (a) peak position k_p and (b) peak intensity S_M, and full width at half maximum Δk of the scattering function in the later stage for $A = 1.3$. The wave number is scaled with $k_0 = \pi/128$, and S_M is in arbitrary units. The straight line is the best fit to the data yielding the slope -0.20, 0.16, and 0.18 for k_p, $1/\Delta k$, and S_M, respectively.

global conservation of the order parameter, it plays no role in the late stages of microphase coarsening in which we may restrict ourselves to the wave number region where $k \sim k_e$. Hence ∇^2 may be replaced by $-k_e^2$, and $\mathcal{H}$ is taken to be of the so-called weak-segregation form. Then the resulting equation takes the form of a time-dependent Ginzburg-Landau equation for the RB convection (i.e., the Swift-Hohenberg model). We therefore hypothesize that BCP and RB convections belong to the same universality class with regard to the ordering dynamics.

In this connection it is worth adding that we have obtained similar results by analyzing the data without hardening, too, excepting one difference: the extended KYG prediction (3) exhibits a not so striking agreement with data as in Fig. 3(a). We have discussed, in this Letter, the results for the weak-segregation regime where the ratio k_e/k_m is of order unity [14]. However, the result that unhardened data yield the same growth exponents as the hardened data (at both early and later stages) would imply that the same power law growth occurs also in the strong-segregation regime.

[1] For recent reviews, see A. J. Bray, Adv. Phys. **43**, 357 (1994).
[2] For recent development, see K. Binder, Adv. Polym. Sci. **112**, 181 (1994).
[3] Y. Oono and Y. Shiwa, Mod. Phys. Lett. B **1**, 49 (1987).
[4] Y. Oono and M. Bahiana, Phys. Rev. Lett. **61**, 1109 (1988); F. Liu and N. Goldenfeld, Phys. Rev. A **39**, 4805 (1989); A. Chakrabarti, R. Toral, and J. D. Gunton, Phys. Rev. Lett. **63**, 2661 (1989); M. Bahiana and Y. Oono, Phys. Rev. A **41**, 6763 (1990); A. Chakrabarti, R. Toral, and J. D. Gunton, *ibid.* **44**, 6503 (1991); A. Chakrabarti and J. D. Gunton, Phys. Rev. E **47**, R792 (1993); see also S. C. Glotzer, E. A. DiMarzio, and M. Muthukumar, Phys. Rev. Lett. **74**, 2034 (1995); S. C. Glotzer, D. Stauffer, and N. Jan, *ibid.* **72**, 4109 (1994) for related work on phase separation in chemically reactive mixtures, for which the same equation as for block copolymers is employed.
[5] In the long-wavelength limit ($k_e \ll 1$) this equation yields $k_e = (9B/D)^{1/4}$, which is consistent with the well-known result of T. Ohta and K. Kawasaki, Macromolecules **19**, 2621 (1986).
[6] K. R. Elder and M. Grant, J. Phys. A **23**, L803 (1990).
[7] K. Kawasaki, M. C. Yalabik, and J. D. Gunton, Phys. Rev. A **17**, 455 (1978).
[8] Y. Shiwa, H. Matsunaga, M. Yoshikawa, and H. Yoshitomi, Phys. Rev. E **49**, 2082 (1994).
[9] K. R. Elder, J. Viñals, and M. Grant, Phys. Rev. Lett. **68**, 3024 (1992); Phys. Rev. A **46**, 7618 (1992).
[10] J. Swift and P. C. Hohenberg, Phys. Rev. A **15**, 319 (1977); J. Swift and P. C. Hohenberg, *ibid.* **46**, 4773 (1992).
[11] M. C. Cross and D. I. Meiron, Phys. Rev. Lett. **75**, 2152 (1995).
[12] L. Leibler, Macromolecules **13**, 1602 (1980).
[13] G. H. Fredrickson and K. Binder, J. Chem. Phys. **91**, 7265 (1989); G. H. Fredrickson, J. Rheol. **38**, 1045 (1994).
[14] Examining the cross sections of patterns for the period of the investigated time steps, we see that the copolymers for $A = 1.12$ are definitely of weak segregation. For $A = 1.3$ the interface is still with the same order of magnitude as the domain size, indicating that the system is in the weak-segregation regime.