Anisotropy of lamellar block copolymer grains

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The Wulff construction and the theory of Milner and Morse [Phys. Rev. E **54**, 3793 (1996)] were used to calculate the shape of grains formed when a lamellar block copolymer phase is formed by a shallow quench into the ordered state. The calculations show that the grains are ellipsoids of revolution, with an aspect ratio $\rho = 2.37$. This value is in reasonable agreement with results of transmission electron microscopy and depolarized light scattering experiments, which indicate that the average value of ρ of grains formed during the early stages of the disorder-to-order transition is about 2.0.

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INTRODUCTION

Block copolymers self-assemble into a variety of equilibrium ordered phases such as lamellas and cylinders arranged on a hexagonal lattice [1–4]. While the equilibrium properties of these systems are well understood, many questions regarding the nonequilibrium processes that lead to the formation of ordered phases remain unanswered [5–16]. In the present paper we study the shape of weakly ordered grains formed during the early stages of the disorder-to-order transition.

The anisotropy of grains formed during the disorder-to-order transition of block copolymers was first noted in 1995. Hashimoto and Sakamoto studied electron micrographs of partially ordered lamellar block copolymer samples, and observed the presence of anisotropic lamellar grains embedded in a disordered matrix [8]. Newstein *et al.* found that the depolarized light scattering patterns obtained during the disorder-to-order transition of a block copolymer with cylindrical morphology exhibited fourfold symmetry [7]. This was interpreted as a signature of anisotropic grains. Subsequent experiments conducted by both groups on a variety of block copolymers confirmed the anisotropy of block copolymer grains [9–13,15,16]. It was recognized that these results are not entirely surprising because the anisotropy of grains of liquid crystalline materials is well established [17], and both lamellar and cylindrical phases of block copolymers have liquid crystalline symmetry. However, a quantitative understanding of the factors that control the observed shape of block copolymer grains does not exist. Grain anisotropy may be due to kinetic effects such as anisotropic growth rates along the liquid and crystal directions of the grain, or thermodynamic effects such as anisotropy of interfacial energy. In this paper we compute the shape of grains formed by block copolymers with lamellar order assuming that thermodynamic effects are dominant. The calculations are compared with experimental data reported in Ref. [18].

THEORY

The theoretical prediction of grain structure begins with an estimate of the energy penalty for forming an interface between an ordered lamellar phase and a disordered phase. We show such an interface in Fig. 1, where the lamellar normal points in the x direction and the lamellas lie parallel to the yz plane. The normal to the planar interface between the ordered and disordered phases is at an angle θ with respect to the x direction, as shown in Fig. 1. The interfacial energy, $\gamma(\theta)$, for such an interface, within the square gradient approximation [19,20], can be calculated from the results of Morse and Milner [5], who studied the lamellar phase of symmetric block copolymers within the Brazovskii approximation for the effect of concentration fluctuations [21]. From Eq. (A10) of Ref. [5], we obtain the following expression for block copolymer grains at the order-disorder transition temperature:

$$\gamma(\theta) = \gamma_0 (1 + \alpha \cos^2 \theta)^{1/2}. \tag{1}$$

For a symmetric diblock copolymer $\alpha = 4.65$ [5]. The prefactor in Eq. (1), γ_0, depends on a number of parameters as described in Ref. [5], but its value is not relevant for the present calculation. We thus see that the anisotropy (θ depen-

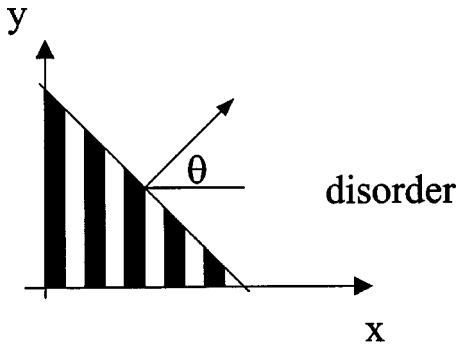

FIG. 1. Schematic view of an interface between ordered lamellas and the disordered phase and definition of the coordinate system.

dence) of the interfacial energy is independent of chain length, temperature, etc. It is evident from Eq. (1) that the interfacial energy is larger when the lamellar planes are in contact with the disordered phase ($\theta=0$) than the case when the edges of the lamellas are in contact with the disordered phase ($\theta=\pi/2$). This anisotropy will lead to grains that are elongated in the x direction. It is important to note that in the mean-field limit, the interfacial energy vanishes for the $\theta=\pi/2$ case [1]. This would lead to the formation of needle-shaped grains with an infinite aspect ratio. The fluctuation corrections that were included by Morse and Milner [5] are therefore crucial for obtaining ordered grains with a finite aspect ratio.

The Wulff construction [19] leads to a prediction of the shape of the lamellar grain that minimizes the total interfacial energy for a given grain volume. The coordinates (x,y) of the surface of a grain with lamellar normal along the x axis, in equilibrium with a disordered phase, are given by the equations

$$\frac{dx}{d\theta}=-(\sin\theta)\left[\gamma+\frac{d^2\gamma}{d\theta^2}\right] \tag{2}$$

and

$$\frac{dy}{d\theta}=(\cos\theta)\left[\gamma+\frac{d^2\gamma}{d\theta^2}\right], \tag{3}$$

where θ is the angle between the normal to the grain boundary and the x axis. Substituting Eq. (1) into Eqs. (2) and (3) with boundary conditions $x(\theta=\pi/2)=y(\theta=0)=0$ yields the contours of the grain surface $x(\theta)$ and $y(\theta)$:

$$x(\theta)=\frac{c(1+\alpha)\cos\theta}{\sqrt{1+\alpha\cos^2\theta}} \tag{4}$$

and

$$y(\theta)=\frac{c\sin\theta}{\sqrt{1+\alpha\cos^2\theta}}, \tag{5}$$

where the parameter c is a multiplying factor fixed by the volume of the grain.

It is straightforward to show that the grain boundary described by Eqs. (4) and (5) is an ellipse defined by

$$\frac{x^2}{1+\alpha}+y^2=c^2. \tag{6}$$

The grain shape is obtained by rotating the ellipse defined by Eq. (6) about the x axis, and this is shown in Fig. 2. The predicted aspect ratio ρ, the ratio of the major axis to the minor axis, of lamellar grains formed by symmetric block copolymers is thus $\sqrt{1+\alpha}$, i.e. 2.37.

COMPARISON BETWEEN THEORY AND EXPERIMENTS

The experiments in Ref. [18] were conducted on a polystyrene-polyisoprene diblock copolymer, SI(6-6). The weight-averaged molecular weights of both polystyrene and polyisoprene blocks were determined to be 6 kg/mol (polydispersity index=1.06). The order-disorder transition temperature of SI(6-6) was determined by the birefringence method and found to be 74 ± 1 °C. The periodic repeat distance of the lamellar phase, determined by small angle x-ray scattering, was 14 ± 1 nm. The ordered grains formed after quenching the sample from the disordered state to 72 °C (2 °C below the order-disorder transition temperature) were studied by depolarized light scattering and transmission electron microscopy (TEM). Two samples, S_{early} and S_{late}, which were tempered at 72 °C for 125 and 350 min, respectively, were analyzed.

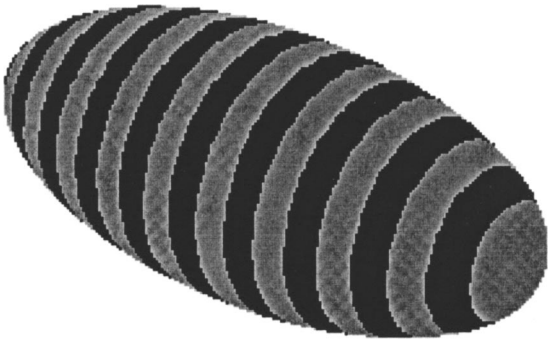

FIG. 2. Theoretically predicted grain shape for symmetric block copolymers, which is an ellipsoid of revolution with aspect ratio $\rho=2.37$.

In Figs. 3(a) and 3(b) we show typical TEM micrographs from S_{early} and S_{late} respectively, wherein ordered grains with long range order (lamellar stacks) are seen to coexist with a disordered fluid [22]. The disordered state is characterized by periodic concentration fluctuations without long range order. A wide variety of grain shapes can be seen in the two micrographs shown in Fig. 3. The micrographs were analyzed by the local Fourier transform method, as described in Ref. [18], to distinguish between the ordered grains and the disordered background. The results of this analysis on the micrographs in Figs. 3(a) and 3(b) are shown in Figs. 4(a) and 4(b), respectively. The black regions in Fig. 4 indicate the regions containing ordered grains. In Figs. 3(a) and 4(a) we see a large grain with an approximately elliptical cross section that is qualitatively similar to the cross section of the grain shown in Fig. 2. However, many other grains with complex nonellipisoidal shapes are also seen in the micrographs. We obtained ca. 60 such micrographs from S_{early} and S_{late}, and subjected them to the analysis described above. The ensemble-averaged properties of the grain structure, obtained from this analysis, are summarized in Table I. The TEM data indicated that the ordered grains occupied about 3% of the sample volume in S_{early} and about 7% of the sample volume in S_{late}. The average aspect ratio ρ was 2.0 for S_{early} and 1.5 for S_{late}. These results were in agreement with the average grain aspect ratio determined by depolarized light scattering (Table I, see Ref. [18] for more details). An advantage of depolarized light scattering is the direct relationship between ensemble-averaged properties of the grains and the raw data.

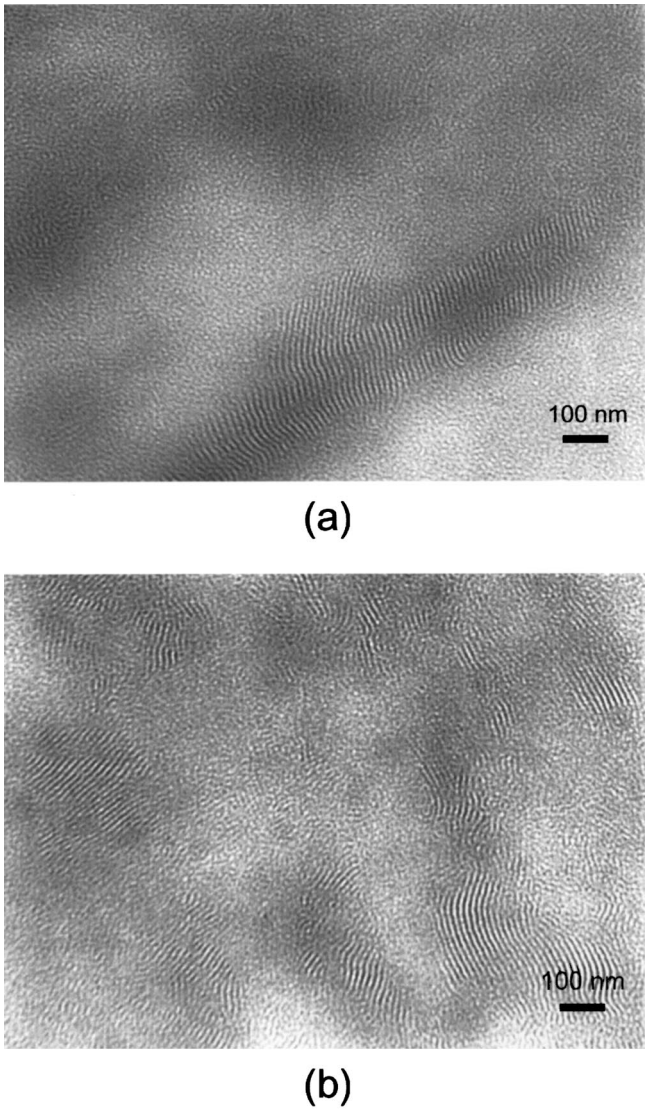

FIG. 3. Typical transmission electron micrographs obtained from (a) S_{early} and (b) S_{late} showing the presence of ordered grains surrounded by a disordered fluid.

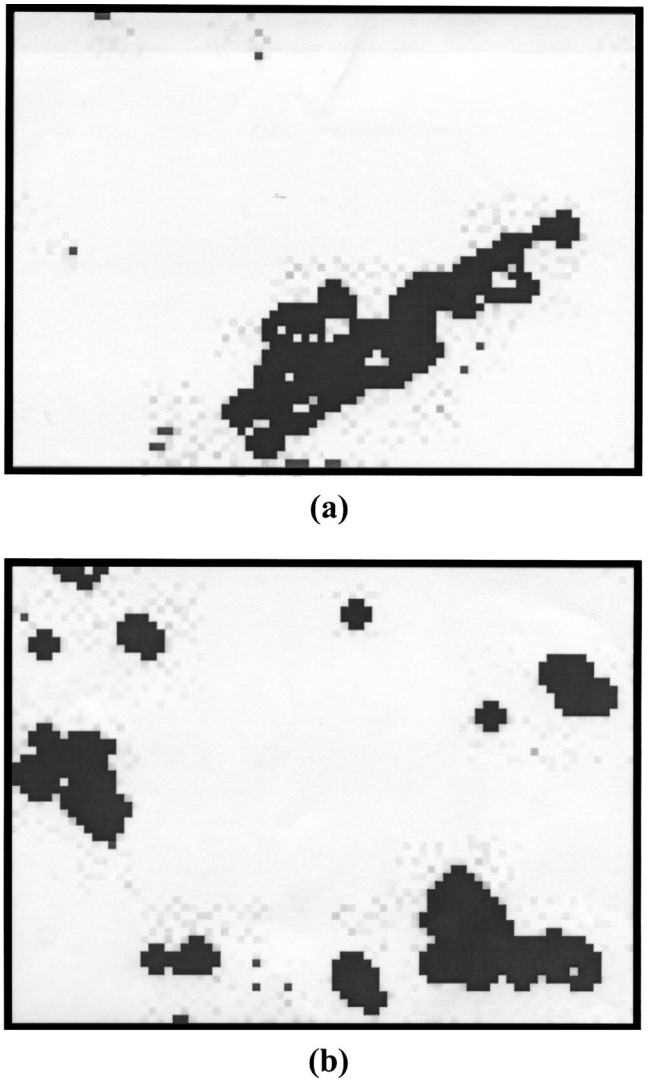

FIG. 4. Results of the Fourier transform analysis of the micrographs in Fig. 3 (Figs. 4(a) and 4(b) correspond to Figs. 3(a) and 3(b), respectively). The ordered regions are denoted by black squares; the disordered regions are denoted by white squares; and the regions where the distinction between order and disorder could not be made are denoted by gray squares. Scale is identical to Fig. 3.

The values of ρ obtained from S_{early} by both electron microscopy and light scattering are in reasonable agreement with the theoretical prediction of 2.37. It is important to note that our theory applies to the early stages of grain growth wherein their growth is not affected by the presence of neighboring grains. At later stages, grain growth is affected by the presence of neighboring grains, and this leads to a reduction in grain shape anisotropy [12]. The slight difference in grain anisotropy between S_{early} and S_{late} may be due to this effect.

If our data were in perfect agreement with the proposed model, then all of the cross sections of the grains would be ellipses of various sizes with aspect ratios of 2.37 or less (depending on the angle between the plane of the micrograph and the lamellas). The wide variety of grain cross sections seen in Figs. 3 and 4 indicates that the complexity of grain structure in our block copolymer is not entirely captured by the proposed theory. Understanding the origin of this complexity requires a more refined analysis wherein penalties for deviations (or fluctuations) from the optimal grain shape are computed. In the presence of such deviations, it is reasonable to expect the equilibrium calculation to give the average grain anisotropy.

TABLE I. Experimentally determined grain anisotropy in SI(6-6) taken from Ref. [18].

Sample	Grain volume fraction	Grain aspect ratio, ρ	
		Electron microscopy	Light scattering
S_{early}	0.03	2.0	1.9
S_{late}	0.07	1.5	1.6

CONCLUSION

The Wulff construction was used to predict the shape of grains formed by symmetric block copolymers during the disorder-to-order transition. The grains are predicted to be ellipsoidal with an aspect ratio $\rho = 2.37$, irrespective of chain length, Flory-Huggins interaction parameter, temperature, and pressure. The theory applies to noninteracting (dilute) grains grown at equilibrium (i.e., at an infinitesimal quench depth). The prediction is in good agreement with the average value of ρ determined in SI(6-6) melts, during the early stage of order formation at a quench depth of 2 °C. This agreement suggests that the anisotropy of lamellar block copolymer grains, grown in the vicinity of the order-disorder transition, is due to the anisotropy of interfacial energy between the ordered and disordered phases. This work lends support to previously developed models for analyzing depolarized light scattering profiles from block copolymers [9–13] wherein the shape and correlation functions of ordered grains were assumed to be ellipsoidal.

ACKNOWLEDGMENTS

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[1] L. Leibler, Macromolecules **13**, 1602 (1980).
[2] G. H. Fredrickson and E. Helfand, J. Chem. Phys. **87**, 697 (1987).
[3] M. W. Matsen and F. S. Bates, Macromolecules **29**, 1091 (1996).
[4] I. W. Hamley, *Physics of Block Copolymers* (Oxford University Press, Oxford, 1996).
[5] S. T. Milner and D. C. Morse, Phys. Rev. E **54**, 3793 (1996).
[6] P. C. Hohenberg and J. B. Swift, Phys. Rev. E **52**, 1828 (1995).
[7] M. C. Newstein, B. A. Garetz, H. J. Dai, and N. P. Balsara, Macromolecules **28**, 4587 (1995).
[8] T. Hashimoto and N. Sakamoto, Macromolecules **28**, 4779 (1995).
[9] H. J. Dai, N. P. Balsara, B. A. Garetz, and M. C. Newstein, Phys. Rev. Lett. **77**, 3677 (1996).
[10] N. P. Balsara *et al.*, Macromolecules **31**, 5309 (1998).
[11] N. P. Balsara, B. A. Garetz, M. C. Newstein, B. J. Bauer, and T. J. Prosa, Macromolecules **31**, 7668 (1998).
[12] M. C. Newstein, B. A. Garetz, N. P. Balsara, M. Y. Chang, and H. J. Dai, Macromolecules **31**, 64 (1998).
[13] W. G. Kim *et al.*, Chem. Phys. **114**, 10 196 (2001).
[14] D. A. Hadjuk *et al.*, J. Chem. Phys. **108**, 326 (1998).
[15] N. Sakamoto and T. Hashimoto, Macromolecules **31**, 3185 (1998).
[16] N. Sakamoto and T. Hashimoto, Macromolecules **31**, 8493 (1998).
[17] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Oxford University Press, Oxford, 1993).
[18] M. Y. Chang *et al.*, Macromolecules **35**, 4437 (2002).
[19] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, 1995).
[20] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[21] S. A. Brazovskii, Zh. Eksp. Teor. Fiz. **68**, 175 (1975) [Sov. Phys. JETP **41**, 85 (1975)].
[22] For clarity of presentation, only subsections of the micrographs (about $\frac{1}{3}$) are shown in Figs. 3(a) and 3(b). (Individual lamellas cannot be easily seen if the entire micrographs are shown on a page.)