LETTERS TO THE EDITOR

The Letters to the Editor section is divided into four categories entitled Communications, Notes, Comments, and Errata. Communications are limited to three and one half journal pages, and Notes, Comments, and Errata are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 1995 issue.

COMMUNICATIONS

Bridging and looping in multiblock copolymer melts

M. W. Matsen[a)]
Department of Physics, Simon Fraser University, Burnaby, B.C., Canada V5A 1S6

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We apply both self-consistent-field theory (SCFT) and strong-segregation theory (SST) to the lamellar phase of a melt of linear multiblock copolymers. We present a new solution for the SST which now agrees with that obtained for the SCFT. Using both theories, we calculate the distribution of monomers from the center of blocks originating from a single interface, the lamellar spacing, and the fraction of blocks which bridge across lamellae. © *1995 American Institute of Physics.*

AB-block copolymer melts have attracted considerable interest due to their ability to self-assemble into ordered microstructures of various symmetries. They are particularly nice systems to study because the physics involved is straightforward. When A and B monomers are immiscible, they are driven to phase separate, but because A and B blocks are chemically joined macroscopic phase separation is prevented. Instead, the system forms a microstructure with an extensive amount of internal interface between the A- and B-rich regions. Although interfacial tension drives the system towards large domain sizes, this is countered by tension in the stretched copolymers. The actual structure the system forms is governed by the detailed balance between the tension in the A blocks and that in the B blocks. For the simple AB diblock melt, this composes the essential physics. However, as one goes beyond this architecture and considers multiblock copolymers such as triblocks, starblocks, and combs, another important ingredient enters the physics. Now one may have, for instance, an A block where each end is constrained to an interface by its connection to a B block. When the microstructure possesses distinct internal interfaces, one can then distinguish looped configurations where both ends of the block reside on the same interface from those where the block bridges from one interface to another (see Fig. 1). Evidence already exists that the presence of bridged configurations is important to the material properties of the melt.[1] As well, the resulting configurational entropy will effect phase boundaries.

Copolymer melts are well-suited for mean-field theory because fluctuation effects are small, particularly, for high molecular weights.[2] For polymers, this theory is referred to as the self-consistent field theory (SCFT),[3] and it reduces to the strong-segregation theory (SST)[4,5] when A and B monomers become well separated. The theory accounts for the mechanisms discussed above in the following way. The enthalpy of mixing A and B monomers is represented by an energy term, $k_BT\rho_0\chi\int d\mathbf{r}\ \phi_A\phi_B$, where $\phi_A(\mathbf{r})$ and $\phi_B(\mathbf{r})$ are dimensionless A- and B-monomer densities at $\mathbf{r}$, respectively, ρ_0 is the overall monomer density, and χ is the Flory-Huggins parameter. (Incompressibility of the melt requires that $\phi_A(\mathbf{r})+\phi_B(\mathbf{r})=1$.) To account for the degrees of freedom a polymer losses due to stretching, there is a penalty of $\frac{3}{2}k_BT(l/a)^2$ for stretching a monomer by a distance, l, where a is its statistical segment length. The SST then makes the assumption that there is no overlap between unlike monomers [i.e., $\phi_A(\mathbf{r})\phi_B(\mathbf{r})=0$ for all $\mathbf{r}$] and that the interfacial tension between A- and B-monomer regions is $k_BT\rho_0a(\chi/6)^{1/2}$. In addition, the SST assumes that monomers are stretched far beyond their statistical segment lengths preventing fluctuations about their lowest energy paths.

References 4 and 5 present an analytic solution of the SST for a lamella consisting of blocks with both ends constrained to an interface. This solution should match SCFT results for various multiblock copolymer melts in the limit of large segregation. However, this has not been the case. In Ref. 6, a lattice SCFT was used to evaluate the equilibrium number of bridges in the B-rich lamellae of an ABA triblock melt, but the results there did not behave as predicted by the SST solution. In another case,[3] the period of the lamellar phase was evaluated with SCFT for a linear copolymer of alternating A and B blocks. There the period was found to be significantly larger than the SST solution predicted.

In this Letter, we present a new solution to the SST, which agrees well with the SCFT results. This is demonstrated by comparing the two theories as applied to a melt of linear multiblocks. We find that a substantial fraction, ν_B, of the blocks exist in bridged configurations even for strong segregations. The expected power-law behavior

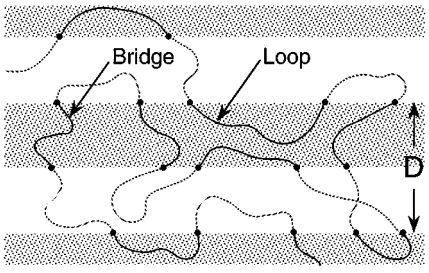

FIG. 1. Bridge and loop configurations of blocks from a copolymer in the lamellar phase.

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$\nu_B \sim (D^2/N)^{-1/3}$ does not occur until the lamellar spacing, D, becomes extremely large. At reasonable segregations, the fraction of bridges is $\nu_B \approx 0.4$ and they cause D to swell by a few percent over what would occur if all the blocks were cut at their midpoints producing a diblock melt. The previous solution predicts, instead, a slight contraction in the spacing.

The solution to the SST which we determine here is relevant to a number of copolymer architectures such as combs, triblocks, and linear multiblocks. We compare the two theories for the latter one, because it has already been examined with the SCFT.[3] In this architecture, the copolymer is formed from an alternating sequence of A and B blocks. We restrict ourselves to the symmetric case where both blocks have polymerizations of $N/2$, both monomers have statistical segment lengths, a, and the ordered structure that forms is the lamellar one.[3] Furthermore, we assume that the number of AB repeat units, M, is large so that the presence of end blocks can be ignored.

We first deal with the SST. Due to the symmetry, we need only consider a lamella of A blocks. The ends of these blocks will be constrained to the surfaces, $z=0$ and $z=1$, where we are measuring distances in terms of $D/2$, the width of the lamella. We now consider a block stretched from the $z=0$ interface so that its midpoint is at $z=y$. The probability of this occurring is defined to be $g(y)$, where $\int dy\ g(y)=1$. The distance, l, a monomer is stretched at position $z=x$ along that chain $(0 \leqslant x \leqslant y)$ defines the function, $E(x,y) \equiv Nl/D$.

The quantity $g(y)$ is instrumental in determining the fraction of blocks that bridge lamellae. Imagine an A block which starts at the $z=0$ interface. We would like to know the probability $p_L(y)$ that it will form a loop with its midpoint at $z=y$, and the probability $p_B(y)$ that it will form a bridge with its midpoint at $z=y$. In both cases, the probability that its midpoint will occur at $z=y$ is $g(y)$ by definition. From here the probability that it loops is proportional to $g(y)$ and the probability that it continues on forming a bridge is proportional to $g(1-y)$. It then follows that

$$p_L(y)=g^2(y)/[g(y)+g(1-y)], \tag{1}$$

$$p_B(y)=g(y)g(1-y)/[g(y)+g(1-y)]. \tag{2}$$

Using Eq. (2), the fraction of bridges is $\nu_B=\int dy\ p_B(y)$. We note that $g(y)+g(1-y)-4p_B(y) \geqslant 0$ for all y, which implies that $\nu_B \leqslant \frac{1}{2}$, a result obtained earlier in Ref. 6. We also point out that ν_B will approach this maximum value when $g(y) \approx g(1-y)$ [i.e., when $g(y)$ is nearly symmetric about $y=\frac{1}{2}$].

To obtain $g(y)$, it is necessary to minimize the free energy, F, of the melt with respect to $g(y)$, $E(x,y)$, and D subject to the constraints that the melt is incompressible and each block has a degree of polymerization $N/2$. To begin, we express the free energy in three parts; $f \equiv F/2Mk_BT = e+\gamma-s$ where

$$e=\tfrac{3}{2}\Delta^2 \int_0^1 dy \int_0^y dx\ g(y)E(x,y), \tag{3}$$

$$\gamma=\Delta^{-1}\sqrt{\chi N/6}, \tag{4}$$

$$s=-\int_0^1 dy\ [p_L \ln(p_L/\Delta)+p_B \ln(p_B/\Delta)],$$

$$=\int_0^1 dy\ g(y)\ln(\Delta[g(y)+g(1-y)]g^{-2}(y)), \tag{5}$$

and $\Delta \equiv D/a\sqrt{N}$. The first contribution, e, is the average elastic energy of stretching the monomers. The second, γ, comes from the interfacial tension between the A- and B-monomer regions. The last term results from the entropy associated with blocks choosing between bridged and looped configurations. (The factor of Δ inside the logarithms occurs because p_L and p_B are dimensionless quantities obtained by multiplying the actual probability densities by $D/2$.) The two constraints are expressed as

$$\Phi(x)=\int_x^1 dy\ g(y)E^{-1}(x,y) + \int_{1-x}^1 dy\ g(y)E^{-1}(1-x,y)=1, \tag{6}$$

$$\Lambda(y)=\int_0^y dx\ E^{-1}(x,y)=\tfrac{1}{2}. \tag{7}$$

The first one enforces local incompressibility over the range $x=0$ to $\frac{1}{2}$, which by symmetry is then enforced over the other half of the lamella. The second requires that each block has $N/2$ monomers. The combination of these two constraints ensures that $\int dy\ g(y)=1$.

Because the present calculation hinges on the entropy term in Eq. (5), we provide a more rigorous derivation. Following Ref. 7, $A(y)$ is defined as the partition function for half an A block stretched between $z=0$ and $z=y$. Its energy is $-k_BT\ln A(y)$. In terms of $A(y)$, $p_L(y)=DA^2(y)/Z$ and $p_B(y)=DA(y)A(1-y)/Z$, where $Z=D\int dy\ [A^2(y) + A(y)A(1-y)]$ is the partition function of an entire A block. The average energy of this A block in units of k_BT is

$$e+\gamma=-\int dy\ [p_L \ln A^2(y)+p_B \ln A(y)A(1-y)]. \tag{8}$$

Subtracting $f=-\ln Z$ from the above expression gives s in agreement with Eq. (5).

Now to minimize the free energy subject to the constraints, we define

$$\Omega=f+\int_0^{1/2} dx\ \phi(x)\Phi(x)+\int_0^1 dy\ \lambda(y)\Lambda(y), \tag{9}$$

where the functions $\phi(x)$ and $\lambda(y)$ are Lagrange multipliers. The function, $\phi(x)$, needs to be defined only for $0 \leqslant x \leqslant \frac{1}{2}$, but we extend its definition using the relation $\phi(x)=\phi(1-x)$ in order to simplify formulae that follow. Now setting the variation of Ω with respect to $E(x,y)$, $g(y)$, and Δ to zero yields

$$\frac{\mathscr{D}\Omega}{\mathscr{D}E}=\tfrac{3}{2}\Delta^2 g(y)-[g(y)\phi(x)+\lambda(y)]E^{-2}(x,y)=0, \tag{10}$$

$$\frac{\mathscr{D}\Omega}{\mathscr{D}g}=\int_0^y dx\ [\tfrac{3}{2}\Delta^2 E(x,y)+\phi(x)E^{-1}(x,y)] - \ln(\Delta[g(y)+g(1-y)]g^{-2}(y))+1=0, \tag{11}$$

$$\frac{\mathscr{D}\Omega}{\mathscr{D}\Delta}=(2e-\gamma-1)/\Delta=0. \tag{12}$$

Using Eq. (10), $E(x,y)$ can be expressed in terms of $\phi(x)$, $g(y)$, and $\lambda(y)$. Then for a given Δ, the functions $\phi(x)$, $g(y)$, and $\lambda(y)$ are determined by Eqs. (6), (7), and (11). Finally, $\chi N=6\Delta^2(2e-1)^2$ according to Eq. (12). We obtain our solution numerically.

A description of the SCFT as applied to a linear multiblock copolymer melt is presented in Ref. 3. However, this paper does not describe how to evaluate $g(y)$ and ν_B, and so we briefly do so now. We will need the mean field, $w_A(x)$, acting on A monomers, and the partition function, $q(x,t)$, for a segment of A block of polymerization tN with one end fixed at $z=x$ and an infinite sequence of full length B and A blocks attached to the other end. Reference 3 describes how to evaluate these quantities. From them, the distribution of junctions is proportional to $q(z,0)q(z,\frac{1}{2})$. Given this, we can calculate a normalized distribution of junctions at the $z=0$ interface which we define to be $P(z,0)$. Then we propagate this distribution along the A block using

$$\frac{\partial p}{\partial t}=\tfrac{1}{6}\Delta^{-2}\frac{\partial^2 p}{\partial z^2}-w_A(x)p, \tag{13}$$

where $p(z,t)\equiv P(z,t)/q(z,\frac{1}{2}-t)$. This equation is the analog to Eq. (22) in Ref. 6. The function $P(z,t)$ gives the monomer distribution of the tN'th monomer of an A block with its $t=0$ end located at the $z=0$ interface and thus

$$g(y)=P(y,\tfrac{1}{4}), \tag{14}$$

$$\nu_B=\int_{1/2}^{\infty} dz\ \ P(z,\tfrac{1}{2}). \tag{15}$$

It is equally valid to use the relationship $\nu_B=\int dy\ p_B(y)$ in conjunction with Eqs. (2) and (14) in place of Eq. (15). Both will give essentially the same result provided χN is large enough to prevent A blocks from bridging B-rich lamellae.

In Fig. 2, we compare the distributions $g(y)$ obtained from the two theories. The comparison is quite good especially for $y>0.7$. One notable difference is that $g(y)$ is peaked more towards the center of the lamella in the SST. In the SCFT, $g(y)$ extends slightly beyond the range $0\leqslant y\leqslant 1$ because the ends of a block are not confined to sharp interfaces, whereas in the SST, $g(y)$ is strictly 0 outside this interval. Nevertheless, $g(0)$ and $g(1)$ are both nonzero in the SST with a particularly large discontinuity at $y=0$. Interestingly, at $\chi N=300$ in the SCFT, $g(y)$ starts to produce a shoulder near $y=0$ resembling that discontinuity. Close

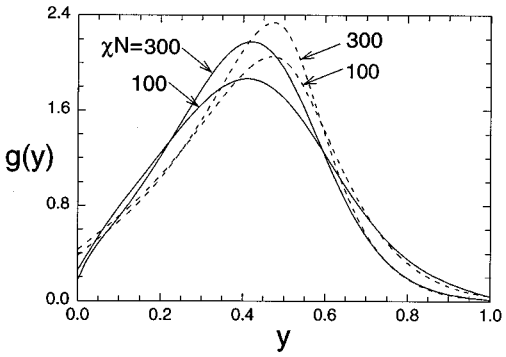

FIG. 2. Probability density of the midpoint for blocks originating from the $y=0$ interface when $\chi N=100$ and 300. Curves obtained from the SCFT and SST are shown with solid and dashed lines, respectively.

examination reveals similar behavior at the $y=1$ interface. Although we were unable to extend our calculations beyond $\chi N=300$ for the SCFT, we could easily do so for the SST. As predicted in Ref. 7 for $\chi N\to\infty$, $g(y)\to 4y/\sqrt{1-4y^2}$ for $y<\frac{1}{2}$ with a rapidly decaying tail for $y>\frac{1}{2}$. However, it is not until $\chi N\sim 10^6$ that the this asymptotic limit becomes accurate.

We next compare the lamellar spacing obtained from the two theories in Fig. 3. The results are remarkable. The SST theory produces reasonable values even down to $\chi N=30$ (the ODT occurs at 15.1 in the SCFT) and the two theories produce nearly indistinguishable spacings for $\chi N>200$. Using the SST and allowing χN to become extremely large (i.e., $\sim 10^6$), we see that the spacing starts to approach $\Delta=2(\chi N/6\pi^4)^{1/6}$, which is the expected limit[3] for a melt of diblocks with polymerization $N/2$. However, at segregations like $\chi N\approx 300$, the lamellar spacing is still about 2.5% in excess of this asymptotic behavior. In terms of the experiment in Ref. 8, this result implies that the lamellar spacing D_M of the $2M$ multiblock copolymer melt will contract to a value slightly larger than $D_1/2^{2/3}$ as $M\to\infty$.

The last quantity we examine here is the bridging fraction plotted in Fig. 3. The behavior agrees with that obtained previously for a triblock melt.[6] Again, the comparison between theories is good down to $\chi N=30$, but not to the same degree as it was for Δ. The explanation is simple; ν_B is

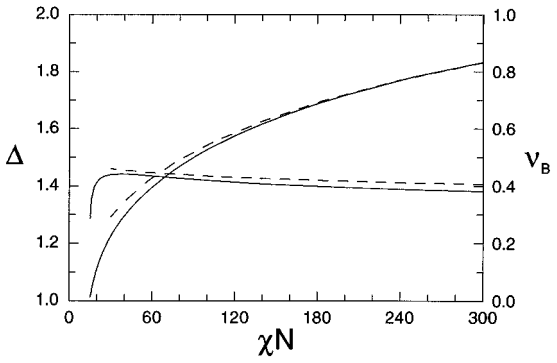

FIG. 3. Monotonically increasing curves show the lamellar spacing Δ, while the nearly horizontal ones show the bridging fraction ν_B. The solid curves are obtained with SCFT, and the dashed ones with SST.

much more sensitive to the functional form of $g(y)$ than is Δ. The fact that $g(y)$ peaks closer to the midplane, $y=\frac{1}{2}$, enhances the fraction of bridges in the SST. As χN approaches values of 10^6, we find that ν_B exhibits a power-law behavior, $\nu_B \approx 0.88(\chi N)^{-1/9}$, where the exponent has previously been anticipated.[4,7]

What we do differently than in Refs. 4 and 5 to obtain the present solution to the SST is simple. We allow $g(y)$ to be nonzero over the entire lamella and we account for the entropy of bridging and looping, Eq. (5), more accurately. At this point, there are a number of things worth future consideration such as the reexamination of works based on the earlier solution. We are presently exploring the analogous behavior in starblock melts so as to explain the dependence of phase boundaries on arm number.[9]

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[a]Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

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