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On the Theory of Linear Multiblock Copolymers

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ABSTRACT: We apply the functional integral theory of copolymer/homopolymer blends of Hong and Noolandi to linear, multiblock copolymers, treating molecules consisting of N blocks, with N ranging from 2 to the large N limit. Our main result incorporates unequal block degrees of polymerization, Kuhn statistical lengths and monomer volumes, and even or odd numbers of blocks. We find that the microphase-separation transition is governed primarily by the degree of polymerization per block and the overall composition, with corrections for small numbers of blocks ($N \lesssim 20$). The results are consistent with the generalization of Leibler's random-phase approximation to this architecture by Benoit and Hadziioannou.

1. Introduction

The modern theory of block copolymers has its roots in the early work of Helfand and coworkers,[1–4] who developed a self-consistent mean-field theory for the free energy of homopolymer blends and block copolymers. By assuming strong segregation of species into domains with narrow interfacial regions, Helfand and Wasserman were able to make detailed predictions for the lamellar, cylindrical, and spherical microphases of copolymer systems.[3,4]

In 1980, Leibler[5] generalized the random-phase approximation (RPA) of de Gennes[6] to formulate a theory of diblock copolymers near the microphase-separation transition (MST). In this theory, the monomer density fluctuations were identified as the appropriate order parameter with which to construct a Landau-type theory of the MST. It was explicitly assumed that the individual chains remain essentially Gaussian in the weak segregation regime. Leibler showed that an unstable mode with a finite wavevector can develop, signaling the appearance of a microphase with a free energy less than that of the homogeneous phase. The spinodal for microphase separation is the point at which the (leading) second-order term in the free energy is zero. More recently, Fredrickson and Helfand examined the effects of concentration fluctuations, finding corrections to the mean-field result that are significant for finite molecular weight but that vanish in the infinite molecular weight limit.[7] In recent years, several workers have generalized these methods to include polydispersity,[8] triblock and star copolymers,[9] and multiblock copolymers.[10]

A functional integral approach was introduced by Hong and Noolandi,[11,12] which makes no a priori assumptions of weak or strong segregation limits, except implicitly through the use of mean-field theory. It is a self-consistent theory of blends in which the polymer density distributions, effective potentials, and free energy are calculated via the self-consistent solution of modified diffusion equations. This theory has been applied to copolymer/solvent blends,[11–13] copolymer/homopolymer mixtures,[12–14] and polydisperse systems.[15,16] For example, it has recently been used to calculate the lamellar thickness as a function of molecular weight for diblock copolymer/neutral solvent blends from the weak to the strong segregation regimes,[13] predicting different scaling relations in the two regimes. The predictions agree with recent measurements made on diblock copolymers.[17]

For systems in which the potential is weak, Hong and Noolandi introduced perturbative solutions to the diffusion equations and obtained expressions for the other quantities of interest, as systematic expansions in powers of the potentials.[12] As discussed by Tanaka et al.,[16] the method provides a natural way of including unequal Kuhn statistical lengths and monomer specific volumes. In this paper we apply this perturbative approach to linear multiblock copolymers comprised of N blocks connected in the sequence ABAB..., terminating with either an A or B block. Our focus is not on locating the MST per se; fluctuation effects, which we do not include, preclude this.[7] Rather, we focus on the dependence of the MST on the number of blocks, the total degree of polymerization, and the degree of polymerization of each block. For simplicity we assume that the first ordered phase to appear from the homogeneous phase is the lamellar phase and approximate the MST criterion as the one in which the second-order term in the free-energy expansion vanishes. For this reason we restrict our attention primarily to copolymers that have overall composition ratios of approximately $\bar{\phi}_A:\bar{\phi}_B \simeq 50:50$. We also assume monodisperse blocks, although polydispersity could be included as in refs 15 and 16.

Earlier, Benoit and Hadziioannou applied the RPA theory of Leibler to this system, for the case of equal monomer volumes and equal Kuhn lengths, focusing on even numbers of blocks (AB...AB).[10] Our results are consistent with theirs for these cases.

2. Underlying Theory

In this section we apply the formalism of Hong and Noolandi to multiblock copolymers, following closely the approach and notation of ref 12. We start with a functional integral expression for the partition function Z for $\tilde{N}$ identical copolymer chains

$$Z = \frac{z^{\tilde{N}}}{\tilde{N}!}\int\Big(\prod_{i=1}^{\tilde{N}}\mathrm{d}\mathbf{r}_i(\cdot)\;P[\mathbf{r}_i(\cdot)]\Big)e^{-\beta\hat{V}} \tag{1}$$

Here z is the contribution due to the kinetic energy of a molecule, $\beta = 1/k_BT$, $\hat{V}$ is the potential energy due to the so-called long-range interactions, and the integrals are over all space curves $\{\mathbf{r}_i(\cdot)\}$, which represent possible configurations of the macromolecules. We assume that each

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molecule consists of N alternating blocks ABAB... and that in the absence of the long-range interactions each block would be Gaussian. Thus, for each block, j, there is a weighting

$$P_j[\mathbf{r}(\cdot)] \propto \exp\left[-\frac{3}{2b_j^2}\int_0^{Z_j}\mathrm{d}\tau\, \dot{\mathbf{r}}(\tau)^2\right] \tag{2}$$

with Z_j and b_j the degree of polymerization and Kuhn statistical length for block j. Taking into account the connectedness of the blocks, for each molecule

$$P[\mathbf{r}(\cdot)] = (\prod_{j=1}^{N} P_j[\mathbf{r}_j(\cdot)])(\prod_{j=1}^{N-1}\delta[\mathbf{r}_j(Z_j) - \mathbf{r}_{j+1}(0)]) \tag{3}$$

The Dirac δ functions in this expression ensure that the end of block j is attached to the beginning of block $j + 1$.

For a given set of space curves $\{\mathbf{r}_i(\cdot)\}$, the number densities are given by

$$\begin{aligned}\hat{\rho}_\mathrm{A}(\mathbf{r}) &\equiv \hat{\rho}_\mathrm{A}(\mathbf{r};\{\mathbf{r}_i(\cdot)\}) \\ &= \sum_{i=1}^{\tilde{N}}\sum_{j=\mathrm{odd}}\int_0^{Z_j}\mathrm{d}\tau\, \delta[\mathbf{r}-\mathbf{r}_{ij}(\tau)]\end{aligned} \tag{4}$$

for the A blocks, and a corresponding expression for $\hat{\rho}_\mathrm{B}(\mathbf{r})$. Here $\mathbf{r}_{ij}(\tau)$ is the section of space curve i that represents block j of that molecule.

We assume that the interaction energy can be written in terms of effective two-body interactions $W_{\kappa\kappa'}(\mathbf{r}-\mathbf{r}')$. Defining $\hat{W} = \beta\hat{V}$ and using $k_\mathrm{B}T$ as the unit of energy, then

$$\hat{W} = \frac{1}{2}\sum_{\kappa,\kappa'=\mathrm{A}}^{\mathrm{B}}\int \mathrm{d}^3r\, \mathrm{d}^3r'\, \hat{\rho}_\kappa(\mathbf{r})\, W_{\kappa\kappa'}(\mathbf{r}-\mathbf{r}')\, \hat{\rho}_{\kappa'}(\mathbf{r}') \tag{5}$$

It is convenient to make two changes of variable by first introducing two Dirac δ functions and writing

$$e^{-\hat{W}} = \int \prod_{\kappa=\mathrm{A}}^{\mathrm{B}} \mathrm{d}\rho_\kappa(\cdot)\, \delta[\rho_\kappa(\cdot) - \hat{\rho}_\kappa(\cdot)] e^{-W} \tag{6}$$

with W given by eq 5 but for general functions $\rho_\mathrm{A}(\mathbf{r})$ and $\rho_\mathrm{B}(\mathbf{r})$ and then by representing them using Fourier integrals

$$\delta[\rho_\kappa(\cdot) - \hat{\rho}_\kappa(\cdot)] = \mathcal{N}\int \mathrm{d}\omega_\kappa(\cdot) \times \exp\{\int \mathrm{d}^3r\, \omega_\kappa(\mathbf{r})[\rho_\kappa(\mathbf{r}) - \hat{\rho}_\kappa(\mathbf{r})]\} \tag{7}$$

where $\mathcal{N}$ is a normalization constant, the limits on the integrals are $\pm i\infty$, and there are two fields $\omega_\mathrm{A}(\mathbf{r})$ and $\omega_\mathrm{B}(\mathbf{r})$. Substituting these into eq 1, the partition function can be written

$$Z = \frac{z^{\tilde{N}}}{\tilde{N}!}\mathcal{N}[\prod_{\kappa=\mathrm{A}}^{\mathrm{B}} \mathrm{d}\rho_\kappa(\cdot)\, \mathrm{d}\omega_\kappa(\cdot)]\mathcal{Q}_\mathrm{C}^{\tilde{N}} \times \exp\{\sum_{\kappa=\mathrm{A}}^{\mathrm{B}}\int \mathrm{d}^3r\, \rho_\kappa(\mathbf{r})\, \omega_\kappa(\mathbf{r}) - W\} \tag{8}$$

The quantity $\mathcal{Q}_\mathrm{C}$ can be expressed in terms of N propagators $Q_j(\mathbf{r},\tau|\mathbf{r}')$:

$$\mathcal{Q}_\mathrm{C} = \int \mathrm{d}^3r_0\, \mathrm{d}^3r_1 ... \mathrm{d}^3r_N\, Q_1(\mathbf{r}_1,1|\mathbf{r}_0)Q_2(\mathbf{r}_2,1|\mathbf{r}_1)... Q_N(\mathbf{r}_N,1|\mathbf{r}_{N-1}) \tag{9}$$

which satisfy

$$\left[-\frac{b_j^2}{6}\nabla^2 + \omega_{\kappa_j}(\mathbf{r})\right]Q_j(\mathbf{r},\tau|\mathbf{r}') = -\frac{1}{Z_j}\frac{\partial}{\partial\tau}Q_j(\mathbf{r},\tau|\mathbf{r}') \tag{10}$$

and

$$Q_j(\mathbf{r},0|\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}') \tag{11}$$

Here, κ_j = A or B and is the chemical species of block j.

Using Stirling's approximation, the partition function can be written

$$Z = \mathcal{N}\int [\prod_{\kappa=\mathrm{A}}^{\mathrm{B}} \mathrm{d}\rho_\kappa(\cdot)\, \mathrm{d}\omega_\kappa(\cdot)] e^{-F(\{\rho_\kappa(\cdot)\},\{\omega_\kappa(\cdot)\})} \tag{12}$$

where the free-energy functional F is given by

$$F(\{\rho_\kappa(\cdot)\},\{\omega_\kappa(\cdot)\}) = W(\{\rho_\kappa(\cdot)\}) + \tilde{N}\left[\ln\left(\frac{\tilde{N}}{z\mathcal{Q}_\mathrm{C}}\right) - 1\right] - \sum_{\kappa=\mathrm{A}}^{\mathrm{B}}\int \mathrm{d}^3r\, \rho_\kappa(\mathbf{r})\, \omega_\kappa(\mathbf{r}) \tag{13}$$

The thermal average density distributions can be expressed as

$$\langle\hat{\rho}_\kappa(\mathbf{r})\rangle = \frac{1}{Z}\mathcal{N}\int [\prod_{\kappa'=\mathrm{A}}^{\mathrm{B}} \mathrm{d}\rho_{\kappa'}(\cdot)\, \mathrm{d}\omega_{\kappa'}(\cdot)]\, \hat{\rho}_\kappa(\mathbf{r})\, e^{-F(\{\rho_{\kappa'}(\cdot)\},\{\omega_{\kappa'}(\cdot)\})} \tag{14}$$

which is equivalent to

$$\langle\hat{\rho}_\kappa(\mathbf{r})\rangle = -\frac{1}{Z}\mathcal{N}\int [\prod_{\kappa'=\mathrm{A}}^{\mathrm{B}} \mathrm{d}\rho_{\kappa'}(\cdot)\, \mathrm{d}\omega_{\kappa'}(\cdot)]\frac{\tilde{N}}{\mathcal{Q}_\mathrm{C}} \times \frac{\delta\mathcal{Q}_\mathrm{C}}{\delta\omega_\kappa(\mathbf{r})} e^{-F(\{\rho_{\kappa'}(\cdot)\},\{\omega_{\kappa'}(\cdot)\})} \tag{15}$$

Equations 9–15 in principle provide a very detailed description of the system. For example, there is no mean-field approximation to this point. In order to make some progress toward solving these equations, however, we need to make further approximations. In this paper we are interested in the weak segregation regime and consider variations in the $\rho_\kappa(\mathbf{r})$ about the overall average densities, $\bar{\rho}_\kappa = N_\kappa/V$. The free-energy functional can be written as

$$F = F_\mathrm{h} + \Delta F \tag{16}$$

where F_h is the free energy of a homogeneous system, and

$$\begin{aligned}F_\mathrm{h} &= F(\{\bar{\rho}_\kappa\}) \\ &= W(\{\bar{\rho}_\kappa\}) + \tilde{N}\left[\ln\left(\frac{\tilde{N}}{zV}\right) - 1\right]\end{aligned} \tag{17}$$

and ΔF is the free energy associated with fluctuations in the potentials and densities. It is convenient to express this in terms of Fourier transforms:

$$\frac{\Delta F}{\rho_{0r}} = \chi\int\frac{\mathrm{d}^3k}{(2\pi)^3}\tilde{\psi}_\mathrm{A}(\mathbf{k})\, \tilde{\psi}_\mathrm{B}(-\mathbf{k}) - \sum_{\kappa=\mathrm{A}}^{\mathrm{B}}\int\frac{\mathrm{d}^3k}{(2\pi)^3}\tilde{\psi}_\kappa(\mathbf{k})\, \tilde{\omega}_\kappa(-\mathbf{k}) - \frac{1}{r_\mathrm{c}}\ln\left(\frac{\mathcal{Q}_\mathrm{C}}{V}\right) \tag{18}$$

Here $\tilde{\psi}_\kappa(\mathbf{k})$ is the Fourier transform of $\psi_\kappa(\mathbf{r})$, which is defined as

$$\psi_\kappa(\mathbf{r}) = \phi_\kappa(\mathbf{r}) - \bar{\phi}_\kappa \tag{19}$$

with $\phi_\kappa(\mathbf{r}) = \rho_\kappa(\mathbf{r})/\rho_{0\kappa}$, r_c is given by

$$r_\mathrm{c} = \rho_{0r}\sum_{j=1}^{N} Z_j/\rho_{0j} \tag{20}$$

and χ is the Flory interaction parameter describing net

A–B interactions. It is defined using $\rho_{0\mathrm{r}}$ as the reference density and is related to the potentials $W_{\kappa\kappa'}$ as described in ref 12.

In terms of the Fourier transform, eq 9 becomes

$$\mathcal{Q}_{\mathrm{C}} = \int \frac{\mathrm{d}^3k_1}{(2\pi)^3} \cdots \frac{\mathrm{d}^3k_{N-1}}{(2\pi)^3} \tilde{Q}_1(0,1|\mathbf{k}_1)\, \tilde{Q}_2(\mathbf{k}_1,1|\mathbf{k}_2) \ldots \tilde{Q}_{N-1}(\mathbf{k}_{N-2},1|\mathbf{k}_{N-1})\, \tilde{Q}_N(\mathbf{k}_{N-1},1|0) \quad (21)$$

In order to evaluate eqs 18 and 21, we need to solve the diffusion equation, eq 10. One method of approach is numerical solutions of the diffusion equations.[11,13] In this paper we use the perturbative solutions introduced by Hong and Noolandi.[12] To second order, the solution for a given $\tilde{\omega}$ is

$$\tilde{Q}_j(\mathbf{k},\tau|\mathbf{k}_0) = (2\pi)^3\delta(\mathbf{k}-\mathbf{k}_0)\, G_j^{(0)}(-\mathbf{k};\tau) - r_j G_j^{(1)}(-\mathbf{k},-\mathbf{k}_0;\tau)\, \omega_{\kappa_j}(\mathbf{k}-\mathbf{k}_0) + \frac{r_j^2}{2} \int \frac{\mathrm{d}^3k}{(2\pi)^3} G_j^{(2)}(-\mathbf{k},-\mathbf{k}-\mathbf{k}_1,-\mathbf{k}_0;\tau)\, \omega_{\kappa_j}(-\mathbf{k}_1) \times \omega_{\kappa_j}(\mathbf{k}+\mathbf{k}_1-\mathbf{k}_0) + \ldots \quad (22)$$

where the $G_j^{(n)}$ are given in ref 12. Substituting this solution into eq 21 leads to an expansion for $\mathcal{Q}_{\mathrm{C}}$ in powers of the potentials. As in earlier work,[12,16] the first term is simply the total volume V, and the term linear in the potentials is made to be zero by choosing the spatial average of the potentials to be zero. To second order in the potentials, therefore

$$\mathcal{Q}_{\mathrm{C}} = V + \mathcal{Q}_{\mathrm{C}}^{(2)} \quad (23)$$

where for these linear multiblock polymers $\mathcal{Q}_{\mathrm{C}}^{(2)}$ can be written

$$\mathcal{Q}_{\mathrm{C}}^{(2)} = \lim_{\substack{\mathbf{k}_0\to 0\\ \mathbf{k}_N\to 0}} \int \frac{\mathrm{d}^3k_1 \ldots \mathrm{d}^3k_{N-1}}{(2\pi)^{3(N-1)}} \times \{\sum_{i=1}^{N} Q_i^{(2)}(\mathbf{k}_{i-1},1|\mathbf{k}_i) \prod_{j\neq i}^{N} Q_j^{(0)}(\mathbf{k}_{j-1},1|\mathbf{k}_j) + \sum_{i=1}^{N}\sum_{j\neq i}^{N} Q_i^{(1)}(\mathbf{k}_{i-1},1|\mathbf{k}_i)\, Q_j^{(1)}(\mathbf{k}_{j-1}|\mathbf{k}_j) \prod_{l\neq i,j}^{N} Q_l^{(0)}(\mathbf{k}_{l-1},1|\mathbf{k}_l\} \equiv \mathcal{Q}_{\mathrm{C}}^{(2,1)} + \mathcal{Q}_{\mathrm{C}}^{(2,2)} \quad (24)$$

The $\mathcal{Q}_i^{(n)}$ are the successive terms in the solutions to the diffusion equation given in eq 22. Substituting eq 22 into eq 24 and using the fact that each $Q_j^{(0)}$ contains a δ-function, this reduces to

$$\mathcal{Q}_{\mathrm{C}}^{(2,1)} = \sum_{i=1}^{N} \frac{r_i^2}{2} \int \frac{\mathrm{d}^3k}{(2\pi)^3} G_i^{(2)}(0,-\mathbf{k},0;1)\, \tilde{\omega}_{\kappa_i}(-\mathbf{k})\, \tilde{\omega}_{\kappa_i}(\mathbf{k})$$

$$\mathcal{Q}_{\mathrm{C}}^{(2,2)} = \sum_{i=1}^{N}\sum_{j=1}^{N} r_i r_j \int \frac{\mathrm{d}^3k}{(2\pi)^3} G_i^{(1)}(0,-\mathbf{k};1) \times [\prod_{l=i+1}^{j-1}{}' G_l^{(0)}(-\mathbf{k};1)] G_j^{(1)}(-\mathbf{k},0;1) \tilde{\omega}_{\kappa_i}(-\mathbf{k})\, \tilde{\omega}_{\kappa_j}(-\mathbf{k}) \quad (25)$$

where the prime on the product in the second expression means that i and j are to be exchanged in the upper and lower limits when $i > j$. These two contributions represent couplings within and between different blocks, respectively.

Only a few $G_{\mathrm{i}}^{(n)}$'s are needed, which are

$$G_i^{(0)}(\mathbf{k};1) = e^{-x_i} \equiv g_i^{(0)}(k)$$

$$G_i^{(1)}(\mathbf{k},0;1) = \frac{1-e^{-x_i}}{x_i} \equiv g_i^{(1)}(k)$$

$$G_i^{(2)}(0,-\mathbf{k},0;1) = 2\left(\frac{x_i - 1 + e^{-x_i}}{x_i^2}\right) \equiv g_i^{(2)}(k,-k) \quad (26)$$

where $x_i = Z_i b_i^2 k^2/6$.

Using the convention that all repeated indices imply summation and integration over wavevectors, we can combine eqs 24–26 to express $\mathcal{Q}_{\mathrm{C}}^{(2)}$ as

$$\mathcal{Q}_{\mathrm{C}}^{(2)} = \frac{1}{2} r_{\mathrm{c}}^2 g_{ij}^{(\mathrm{c})} \tilde{\omega}_{\kappa_i} \tilde{\omega}_{\kappa_j} \quad (27)$$

where

$$g_{ij}^{(\mathrm{c})}(\mathbf{k}_i,\mathbf{k}_j) = (2\pi)^3 f_i^2 \delta(\mathbf{k}_i+\mathbf{k}_j)\, g_i^{(2)}(\mathbf{k}_i,-\mathbf{k}_i) \quad (28)$$

for $i = j$ and

$$g_{ij}^{(\mathrm{c})}(\mathbf{k}_i,\mathbf{k}_j) = f_i f_j \delta(\mathbf{k}_i+\mathbf{k}_j)\, g_i^{(1)}(\mathbf{k}_i)[\prod_{l=i+1}^{j-1}{}' g_l^{(0)}(\mathbf{k}_l)] g_j^{(1)}(\mathbf{k}_j) \quad (29)$$

for $i \neq j$, and

$$f_i = (\rho_{0\mathrm{r}} Z_i)/(\rho_{0i} r_{\mathrm{C}}) \quad (30)$$

Carrying out the summations of eq 27 remains. Recalling that all odd-numbered blocks are A blocks and that the others are the B blocks, we have

$$\tilde{\omega}_{\kappa_1} = \tilde{\omega}_{\kappa_3} = \ldots = \tilde{\omega}_{\mathrm{A}}$$

$$\tilde{\omega}_{\kappa_2} = \tilde{\omega}_{\kappa_4} = \ldots = \tilde{\omega}_{\mathrm{B}} \quad (31)$$

Using this, the summations of eq 27 can be simplified to

$$\mathcal{Q}_{\mathrm{C}}^{(2)} = \frac{1}{r_{\mathrm{c}}^2} \sum_{\alpha=\mathrm{A}}^{\mathrm{B}} g_{\alpha\beta} \tilde{\omega}_\alpha \tilde{\omega}_\beta \quad (32)$$

where there are four $g_{\alpha\beta}$, which are given by

$$g_{\mathrm{AA}} = \sum_{i=\mathrm{odd}} \sum_{j=\mathrm{odd}} g_{ij}^{(\mathrm{c})} \quad (33)$$

etc. The evaluation of these sums is described in the appendix.

This expression for $\mathcal{Q}_{\mathrm{C}}^{(2)}$ is next substituted into eq 18 for the free energy. The resulting expression is then minimized with respect to the $\tilde{\omega}_{\mathrm{A}}$ and ω_{B}, which gives a second-order expression for the free energy associated with small fluctuations in the local volume fractions:

$$\Delta f_2 = \frac{1}{2V}\left(\chi + \frac{1}{r_{\mathrm{c}}}[g]_{\alpha\beta}^{-1}\right)\tilde{\psi}_\alpha \tilde{\psi}_\beta \quad (34)$$

For the cases of all equal reference densities and Kuhn statistical lengths, this is equivalent to the result derived by Benoit and Hadziioannou.[10] From it one can calculate the small-angle X-ray scattering (SAXS) from the homogeneous phase or the approximate MST criterion. In the remainder of this paper we focus on some aspects of the MST that were not explicitly discussed by Benoit and Hadziioannou, in particular, the dependence of the MST and the period of the microphase on the number of blocks and the total degree of polymerization and their relationship to the nature of the couplings between the blocks.

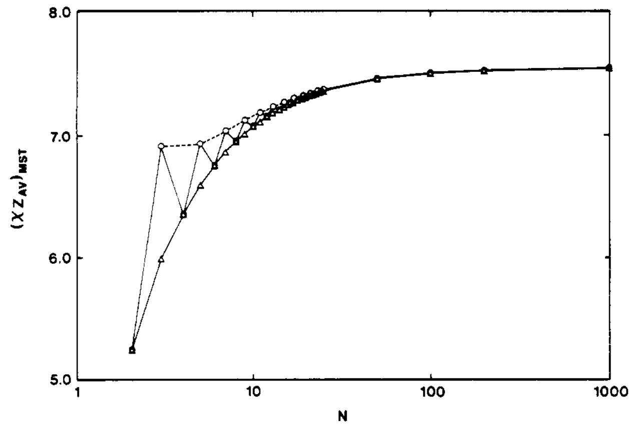

Figure 1. Microphase-separation transition criteria $(\chi Z_{av})_{MST}$ for linear, alternating, multiblock copolymers as a function of the number of blocks N, for two families of copolymers. For each family, $(\chi Z_{av})_{MST}$ is the predicted MST threshold. For a system with $\chi Z_{av} > (\chi Z_{av})_{MST}$, the microphase is indicated to be stable relative to a homogeneous phase (in this level of approximation). The circles correspond to copolymers with $Z_A b_A^2 = Z_B b_B^2$, and the triangles to copolymers with fixed overall composition $\bar{\phi}_A = \bar{\phi}_B = 0.5$. The dotted line connects systems with odd numbers of blocks, highlighting the even–odd effect.

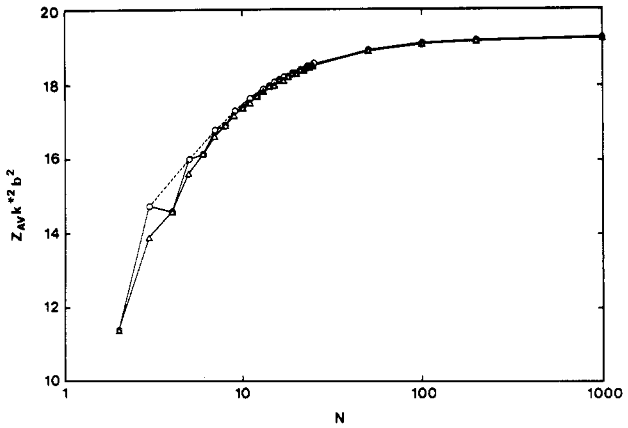

Figure 2. Dominant wavevector k^*, expressed as $Z_{av}(k^*)^2b^2$, at the MST for linear, multiblock copolymers as a function of the number of blocks N, for the two families of copolymers used in Figure 1. The even–odd effect for the first family of copolymers (circles), although still present, is not as pronounced as that in Figure 1.

3. Results and Discussion

We associate the MST with an instability of the homogeneous phase with finite wavenumber k^*. This can be stated as the condition

$$\lambda_-(k^*) = 0 \tag{35}$$

where

$$\lambda_- = \frac{[g]_{AA}^{-1} + [g]_{BB}^{-1} - 2[g]_{AB}^{-1}}{2r_c} - \chi \tag{36}$$

and the wavevector k^* is the value of k that minimizes λ_-. In this level of approximation, we identify the period of the resulting microphase as $d = 2\pi/k^*$. It is also the value of the scattered wavevector at which the SAXS peaks for scattering from the homogeneous phase (at least away from the MST). These identifications of the MST and the periodicity are of course only approximate: fluctuation effects are predicted to shift the MST,[7] in at least one experiment diblock copolymers are stretched by about 10% from their unperturbed Gaussian conformations near the order–disorder transition,[17] and even very near the MST, moving away from the transition toward the strong segregation regime induces further increases to d.[13]

We discuss numerical results for two families of molecules. In both cases we assume that all A blocks are identical, as are all B blocks. In the first family, the degrees of polymerization and the Kuhn lengths of the blocks satisfy $Z_A b_A^2 = Z_B b_B^2$, while in the second family the degrees of polymerization of the A and B blocks are varied in order to retain a constant A to B composition ratio of 50:50; i.e., $\bar{\phi}_A = \bar{\phi}_B = 0.5$. For even block numbers the two families are identical. In each case we vary the number of blocks, N. For all these numerical results we assume the monomer specific volumes to be equal, a restriction which can be removed in this formalism by using eq 34 for a particular system of interest. The numerical results are obtained by first minimizing λ_- to locate k^* and then solving $\lambda_-(k^*) = 0$.

Figure 1 illustrates the predicted dependence of the MST criterion on block number for the two families. A basic result is that for each family the criterion can be expressed in terms of the product χZ_{av}, where Z_{av} is the average degree of polymerization of each block (for the first family $Z_A = Z_B = Z_{av}$). The diblock case $N = 2$, of course, agrees with Leibler's original mean-field prediction, $\chi Z_{av} = 5.25$, i.e., $\chi(Z_A + Z_B) = 10.5$. The figure shows that as the number of blocks increases, the average block degree of polymerization must also increase, saturating at $\chi Z_{av} = 7.55$. There is some difference in detail between the two families. For the first ($Z_A b_A^2 = Z_B b_B^2$), there is an "even–odd" effect, with a larger value of Z_{av} required for odd N than for even N. This is due primarily to the changes in overall composition, i.e., $\bar{\phi}_A \neq \bar{\phi}_B$ for this family for odd N. It should also be noted that the result for the triblocks should be viewed with caution since, for this composition, $\bar{\phi}_A:\bar{\phi}_B = 2:1$, and the cylindrical phase may be stable relative to the layered phase. The second family does not show this even–odd effect, and the MST criterion rises monotonically from the diblock case to the large N limit.

The characteristic wavevector k^* is presented in Figure 2. It, like the MST, is controlled primarily by Z_{av}, rising from $Z_{av}(k^*)^2b^2 = 11.4$ for symmetric diblocks to $Z_{av}(k^*)^2b^2 = 19.3$ for the many-block limit. Again, the first family of copolymers shows an even–odd effect, but it is less pronounced than it was for the MST criterion.

These figures show that the MST and k^* depend primarily on Z_{av} and composition and that the weaker dependence on N is independent of Z_{av}, conclusions which are consistent with those of Benoit and Hadziioannou.[10] We can understand them by returning to our expressions for $Q_C^{(2,2)}$, eq 25. The coupling between two nonadjacent blocks i and j is proportional to

$$\prod_{l=i+1}^{j-1} g_l^{(0)}(\mathbf{k}) \tag{37}$$

which according to eq 26 consists of a product of $(j - i - 1)$ exponential terms of the form

$$e^{-x_{i+1}}e^{-x_{i+2}}...e^{-x_{j-1}} \tag{38}$$

where each $x_l = Z_l b_l^2 k^2/6$. The coupling between any two blocks thus diminishes exponentially with the number of intermediate blocks, whether or not all blocks have the same degree of polymerization, etc. On the other hand, since the dominant wavevector k^* is approximately $k^* \propto Z_{av}^{1/2}$, the corresponding value of x_l is approximately independent of Z_{av}, the coupling is approximately independent of Z_{av}, and the dependence of the MST criterion on N is essentially independent of Z_{av}.

We end this section with a brief comment on a commonly made approximation for triblocks. Consider the ABA triblock with block degrees of polymerization $(Z/4, Z/2, Z/4)$. For this case $\bar{\phi}_A = \bar{\phi}_B = 0.5$, $Z_{av} = Z/3$, and our analysis indicates that the MST should be at $\chi Z_{av} \simeq 6$ or $\chi Z \simeq 18$, and $(k^*)^2 \simeq 41.7/(Zb^2)$. If this triblock were approximated as a symmetric diblock with degrees of polymerization $(Z/4, Z/4)$, then the MST would be predicted to occur at $\chi Z/4 = 5.25$ or $\chi Z = 21$ and k^* would be given by $(k^*)^2 \simeq 45.6/(Zb^2)$. Thus this approximation for the triblock tends to underestimate both the tendency to microphase separate and the repeat distance.

4. Summary

We have applied the mean-field formalism developed by Hong and Noolandi to the case of linear ABA... multiblock copolymers, considering both A and B terminated polymers, and the number of blocks N varying from 2 to the large N limit. Two special cases were considered numerically; in both cases we chose $\rho_{0A} = \rho_{0B}$ and $b_A = b_B$. In the first case we chose N equal size blocks, whereas in the second case we chose all A blocks and all B blocks to be identical but with the block degrees of polymerization Z_A and Z_B chosen so that $\bar{\phi}_A = \bar{\phi}_B = 0.5$.

Approximating the MST criterion as the condition for the homogeneous phase to be unstable relative to the lamellar microphase, we found that this instability is controlled primarily by the average degree of polymerization per block, Z_{av}, by the overall composition $\bar{\phi}_A$ and $\bar{\phi}_B$, and to a lesser extent by the number of blocks N. The dependence on N is essentially independent of the individual block size. For both families of molecules, the MST criterion can be stated as $\chi Z_{av} = C$, where C increases by about 45% from 5.25 for symmetric diblocks to 7.55 for large N. This implies that for a given Z_{av} and composition, diblocks microphase separate more readily than triblocks, which in turn do so more readily than tetrablocks, etc., and that for a given total degree of polymerization Z, diblocks microphase separate *much* more readily than triblocks, etc. These results agree with those of Benoit and Hadziioannou, who presented results for copolymers with even N.[10]

The approach does not incorporate the fluctuation effects studied by Fredrickson and Helfand,[7] nor does it explain the apparent stretching of diblock copolymers by about 10% at temperatures just above the MST.[17] However, we do not expect that these effects would alter our main conclusion that the location of the MST is determined primarily by the average degree of polymerization per block and that this conclusion can be traced to the exponentially decreasing coupling between nonadjacent blocks in each chain.

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Appendix

In this appendix we begin by outlining the evaluation of g_{AA}, eq 33, for a system of copolymers that begin and end with the same block type, for the particular case in which all A blocks and all B blocks are identical. We then tabulate the $g_{\alpha\beta}$ for both even and odd numbers of blocks.

For this case of odd N, eq 33 can be divided into two terms

$$g_{AA} = \sum_{i=\mathrm{odd}}^{N} g_{ii}^{(c)} + \sum_{j\neq i}^{N} g_{ij}^{(c)} \tag{39}$$

where $g_{ii}^{(c)}$ and $g_{ij}^{(c)}$ are defined in eqs 28 and 29. For the case of all A blocks identical and all B blocks identical, the $g_i^{(n)}$ of eq 26 reduce to (n = 0, 1, or 2)

$$g_i^{(n)} = \begin{cases} g_A^{(n)} & \text{if } i \text{ odd} \\ g_B^{(n)} & \text{if } i \text{ even} \end{cases} \tag{40}$$

Substituting eq 40 into eq 39 we obtain

$$g_{AA}(\mathbf{k}_1,\mathbf{k}_2) = (2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_2)\, f_A^{\,2}\left[\left(\frac{N+1}{2}\right) g_A^{(2)}(\mathbf{k}_1,\mathbf{k}_2) + g_A^{(1)}(\mathbf{k}_1)\, S_{AA} g_A^{(1)}(-\mathbf{k}_1)\right] \tag{41}$$

where f_A and r_c are defined in eqs 20 and 30, and

$$S_{AA} = \sum_{i=\mathrm{odd}}^{N} \sum_{\substack{j\neq i\\ j=\mathrm{odd}}}^{N} {\prod_{l=i+1}^{j-1}}' g_l^{(0)}(\mathbf{k}_1) \tag{42}$$

where the prime on the product means that the upper and lower limits are to be reversed if $j < i$. The product appearing here can be written as

$${\prod_{l=i+1}^{j-1}}' g_l^{(0)}(\mathbf{k}_1) = [g_B^{(0)}(\mathbf{k}_1)]^{(j-i)/2}[g_A^{(0)}(\mathbf{k}_1)]^{(j-i-2)/2} \tag{43}$$

The summations of eq 41 thus reduce to a finite geometric series, which can be evaluated directly, yielding

$$S_{AA} = \frac{2g_B^{(0)}}{1-g_A^{(0)}g_B^{(0)}}\left[\frac{N+1}{2} - \frac{1-(g_A^{(0)}g_B^{(0)})^{(N+1)/2}}{1-g_A^{(0)}g_B^{(0)}}\right] \tag{44}$$

where the wavevector $\mathbf{k}_1$ is understood. Substituting this into eq 41 gives g_{AA} for this case.

The other $g_{\alpha\beta}$ of eq 33 are calculated similarily. The results can be expressed as

$$\begin{aligned} g_{AA} &= (2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_2)\, f_A^{\,2}[N_A g_A^{(2)}(\mathbf{k}_1,-\mathbf{k}_1) + g_A^{(1)}(\mathbf{k}_1)\, S_{AA} g_A^{(1)}(-\mathbf{k}_1)] \\ g_{AB} &= (2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_2)\, f_A f_B g_A^{(1)}(\mathbf{k}_1)\, S_{AB} g_B^{(1)}(-\mathbf{k}_1) \\ &= g_{BA} \\ g_{BB} &= (2\pi)^3\delta(\mathbf{k}_1+\mathbf{k}_2)\, f_B^{\,2}[N_B g_B^{(2)}(\mathbf{k}_1,-\mathbf{k}_1) + g_B^{(1)}(\mathbf{k}_1)\, S_{BB} g_B^{(1)}(-\mathbf{k}_1)] \end{aligned} \tag{45}$$

where N_A and N_B are the number of A and B blocks in the copolymer, respectively, and

$$\begin{aligned} S_{AA} &= \frac{2g_B^{(0)}}{1-g_A^{(0)}g_B^{(0)}}\left[N_A - \frac{1-(g_A^{(0)}g_B^{(0)})^{N_A}}{1-g_A^{(0)}g_B^{(0)}}\right] \\ S_{BB} &= \frac{2g_A^{(0)}}{1-g_A^{(0)}g_B^{(0)}}\left[N_B - \frac{1-(g_A^{(0)}g_B^{(0)})^{N_B}}{1-g_A^{(0)}g_B^{(0)}}\right] \end{aligned} \tag{46}$$

and

$$S_{AB} = \frac{2}{1-g_A^{(0)}g_B^{(0)}}\left[N_B - (g_A^{(0)}g_B^{(0)})\frac{1-(g_A^{(0)}g_B^{(0)})^{N_B}}{1-g_A^{(0)}g_B^{(0)}}\right] \tag{47}$$

for odd N and

$$S_{AB} = \frac{2}{1 - g_A^{(0)} g_B^{(0)}} \left[N_B - \left(\frac{1 + g_A^{(0)} g_B^{(0)}}{2} \right) \frac{1 - (g_A^{(0)} g_B^{(0)})^{N_B}}{1 - g_A^{(0)} g_B^{(0)}} \right] \tag{48}$$

for even N.

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