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Published in:
Journal of Physical Chemistry B

DOI:
[10.1021/jp9113943](https://doi.org/10.1021/jp9113943)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2010

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Subbotin, A., Markov, V., & ten Brinke, G. (2010). Parallel versus Perpendicular Lamellar-within-Lamellar Self-Assembly of A-b-(B-b-A)(n)-b-C Ternary Multiblock Copolymer Melts. *Journal of Physical Chemistry B*, 114(16), 5250-5256. <https://doi.org/10.1021/jp9113943>

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Parallel versus Perpendicular Lamellar-within-Lamellar Self-Assembly of A-*b*-(B-*b*-A)_{*n*}-*b*-C Ternary Multiblock Copolymer Melts

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Received: December 1, 2009; Revised Manuscript Received: March 3, 2010

Different types of lamellar-within-lamellar structure formations in A-*b*-(B-*b*-A)_{*n*}-*b*-C terpolymer melts, with a volume fraction of components A, B, and C in the ratio of 1:1:2, are analyzed in the strong segregation limit using a simple theoretical approach. We consider the lamellar, parallel lamellar-within-lamellar, and perpendicular lamellar-within-lamellar self-assembled states. The influence of the copolymer chain length *N*, the value of the Flory–Huggins interaction parameters χ_{AB} , χ_{AC} , and χ_{BC} , and the number of blocks *n* in the AB multiblock chain on the phase behavior is discussed. We show that in the limiting case of *n* $\gg$ 1, the perpendicular lamellar-within-lamellar state becomes stable when the interaction parameters satisfy the relation $0 < \chi_{BC} < 0.22 \chi_{AC}$.

Introduction

In recent years, multiblock copolymers that self-assemble in the form of periodical hierarchical structures involving different length scales have become an attractive area both for experimental^{1–12} and theoretical^{13–21} investigations. The simplest hierarchical structures characterized by two length scales can best be described as a structure-within-structure morphology. One of the first observations of a system having two periods was concerned with comb-shaped supramolecules consisting of polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers and hydrogen-bonded pentadecylphenol (PDP) side chains attached to the P4VP blocks.^{1–3} Depending on the relative volume fraction of the polystyrene block, hierarchical structures such as lamellar-within-lamellar, lamellar-within-spheres, spheres-within-lamellar, and so forth were identified.

Undecablock copolymers PS-*b*-(PI-*b*-PS)4-*b*-PI-*b*-PS and P2VP-*b*-(PI-*b*-PS)4-*b*-PI-*b*-P2VP appeared to be the first examples of block copolymers with a linear architecture forming a double periodic parallel lamellar-within-lamellar structure.^{4,5} Here, P2VP, PI, and PS denote poly(2-vinylpyridine), polyisoprene, and polystyrene, respectively, components that are mutually strongly immiscible. Recently, Fleury and Bates demonstrated^{11,12} that a terpolymer A–B–A–B–A–C, consisting of poly(cyclohexylethylene) (A), poly(ethylene) (B), and poly(ethylene-*alt*-propylene) (C) blocks, self-assembled in the form of a perpendicular lamellar-within-lamellar structure when the copolymer chain length exceeded some critical value. The authors attributed this particular mutual arrangement of the layers to a relatively small value of the Flory–Huggins interaction parameter between the B and C blocks as compared to that between the A and C blocks.

Multiblock copolymers have been extensively studied theoretically in the framework of self-consistent field theory,^{13–16} the weak segregation Landau approach,^{17,18} as well as the strong segregation theory.^{19–21} In this paper, we focus on a theoretical

description of the lamellar structure formation in A-*b*-(B-*b*-A)_{*n*}-*b*-C ternary multiblock copolymers in the strong segregation regime.

Model and Simple Lamellar Structure

We assume that all blocks are Gaussian chains, the total A-*b*-(B-*b*-A)_{*n*}-*b*-C copolymer chain length is *N*, and the length of the C block *N*_C = *N*/2 equals the length of the total AB multiblock. The fraction of A and B segments is assumed to be equal; hence, the lengths of the A and B blocks are *N*_A = *N*/(4(*n* + 1)) and *N*_B = *N*/4*n*, respectively. The volume and the length of the statistical segments of all components are assumed to be equal and denoted as *v* and *a*. The interaction energies between the different species are described by the Flory–Huggins interaction parameters χ_{AB} , χ_{AC} , and χ_{BC} . They are assumed to be positive, in accordance with unfavorable interactions.

We first consider the transition from the disordered (D) phase to the ordered lamellar phase consisting of alternating layers of C blocks and AB multiblocks. The dominating contribution to the free energy of the disordered phase is due to interactions between different segments. Per copolymer chain, this energy is given by

$$F_I = \frac{\chi_{AB}N}{16} + \frac{\chi_{AC}N}{8} + \frac{\chi_{BC}N}{8} \quad (1)$$

For a fixed chain architecture and positive interaction parameters, an increase in the chain length *N* will result in incompatibility between the different blocks and the lamellar (L) structure formation. The most simple one is the lamellar structure with one periodicity length scale corresponding to phase separation between the C blocks and the AB multiblocks (Figure 1).

It is easy to see that this structure can appear only if $(\chi_{AB}/2) < \chi_{AC} + \chi_{BC}$. Indeed, complete separation between the AB and C components without taking the polymer connectivity into account gives an interaction energy per chain equal to $(1/2) \cdot (\chi_{AB}N/4) + (1/2) \cdot 0$, where the first term represents the interaction energy of A and B segments, which occupy half of

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Figure 1. Schematic representation of the simple lamellar structure consisting of C and AB layers.

the volume, and the second term represents the energy of C segments occupying the other half of the volume. Comparison of this energy with eq 1 gives the desired condition. The polymer connectivity of the segments leads to an additional contribution to the free energy due to conformational loss associated with the nonhomogeneous structure formation. In the strong segregation limit, where the thickness of the interfacial layer Δ between the C and AB domains is much smaller than the Gaussian size of the copolymer chain $R_0 = aN^{1/2}$, the stretching energy of the blocks and the interfacial energy should be taken into account (we will omit the translational energy of the chains). The interfacial energy can be derived from minimization of the free energy with respect to the profiles of the components. Let us denote the thickness of the C layer as H (it is equal to the thickness of the AB layer) and the concentration profile of C segments as $\phi_C(z)$. Assuming that the size of a AB diblock, which equals $a(N_A + N_B)^{1/2}$, is smaller than the thickness of the interfacial layer Δ (the concentration profiles of A and B segments are nearly equal, $\phi_A(z) = \phi_B(z) = (1 - \phi_C(z))/2$), the free energy per copolymer chain in the scope of the Alexander de Gennes approximation is given by

$$F_L = 2\frac{3H^2}{a^2N} + \frac{a^2\Sigma}{24\nu} \int_{-H}^H dz \frac{\phi_C^2}{\phi_C(1-\phi_C)} + \frac{\Sigma}{\nu} \int_{-H}^H dz \times \left(\chi_{AB} \frac{(1-\phi_C)^2}{4} + \frac{\chi_{AC} + \chi_{BC}}{2} \phi_C(1-\phi_C) \right) \quad (2)$$

Here, $2H\Sigma = N\nu$, with Σ as the interface surface per chain, and the period of the lamellar structure is $L = 4H$. The total energy (eq 2) includes the elastic energies of C and AB blocks, the gradient term due to the nonhomogeneous composition profiles of the components, and the interaction energy between A, B, and C segments. After minimization of this free energy with respect to $\phi_C(z)$ using the additional condition $(\Sigma/\nu) \int_{-H}^H dz \phi_C(z) = N/2$ (in eq 2, we can put $(1 - \phi_C)^2 = 1 - \phi_C - \phi_C(1 - \phi_C)$ and then use the method of ref 22), we arrive at $\phi_C(z) = (1/2)(1 + \tanh(z/\Delta))$, where $\Delta = R_0[1/(3(\chi_{AC}N + \chi_{BC}N - 0.5\chi_{AB}N))]^{1/2}$ is the interfacial thickness. With this, the free energy becomes

$$F_L \cong 2\frac{3H^2}{a^2N} + \frac{Na}{2H} \sqrt{\frac{\chi_{AC} + \chi_{BC} - 0.5\chi_{AB}}{12}} + \frac{\chi_{AB}N}{8} \quad (3)$$

Further minimization with respect to H gives

$$F_L \cong \frac{3}{2^{5/3}} (\chi_{AC}N + \chi_{BC}N - 0.5\chi_{AB}N)^{1/3} + \frac{\chi_{AB}N}{8} \quad (4)$$

Figure 2. Schematic representation of parallel lamellar-within-lamellar (a) and perpendicular lamellar-within-lamellar (b) structures.

For large values of N , the free energy (eq 4) increases linearly with N . The period of the lamellar structure equals

$$L = 4H \cong 0.916R_0(\chi_{AC}N + \chi_{BC}N - 0.5\chi_{AB}N)^{1/6} \quad (5)$$

The transition between the isotropic and lamellar phases occurs when the free energies (eqs 1 and 4) are equal. Hence, the lamellar phase becomes stable for

$$\chi_{AC}N + \chi_{BC}N - 0.5\chi_{AB}N > 20.8 \quad (6)$$

As an example, we consider the copolymer A-B-A-B-A-C consisting of poly(cyclohexylethylene) (A), poly(ethylene) (B) and poly(ethylene-*alt*-propylene) (C) blocks as investigated in the group of Bates.^{11,12} The Flory-Huggins interaction parameters (at 140 °C) satisfy $\chi_{AB} \cong 0.054$, $\chi_{AC} \cong 0.034$, and $\chi_{BC} \cong 0.0054$. The last ones were calculated using the fitting formulas proposed in ref 23. According to eq 6, the transition to the simple lamellar phase should occur at $N = N_c \cong 1680$. This value is indeed in the range of the molecular masses where the lamellar phase was observed experimentally.

Perpendicular Lamellar-within-Lamellar Structure

With increasing N , additional separation between the A and B blocks inside of the AB layer will occur, resulting in the formation of more complicated lamellar structures such as parallel lamellar-within-lamellar (LL_{||}, Figure 2a) or perpendicular lamellar-within-lamellar (LL_⊥, Figure 2b). First, we consider the perpendicular lamellar-within-lamellar structure. In this case, thin A and B layers are arranged perpendicularly

Figure 3. Conformation of the A-b-(B-b-A)_n-b-C copolymer chain in the perpendicular lamellar-within-lamellar structure.

with respect to the thick C layers. We denote the thickness of the C layer as $2H$ (along the z -axis) and the thickness of the A and B layers as $2d$ (along the x -axis). In the perpendicular lamellar-within-lamellar structure, both A and B layers have the same thickness since we assume that their volume fractions are equal. The period of the lamellar structure in the x -direction is $L_x = 4d$, and in the z -direction, it is $L_z = 4H$. For further calculation, we consider the volume containing half of the periods along the z - and x -directions and take the origin of the (x, z) plane on the line where the A, B, and C layers intersect (see Figure 3). The y -axis is perpendicular to the (x, z) plane. The junction points between the A and C blocks are located on a strip of width $2d$ and are characterized by the distribution function $\rho(x)$.

We start with the elastic stretching energy of the C blocks which are extended inside of the C layers so that their conformations can be described by trajectories. For simplicity, we assume that these trajectories are straight lines characterized by a bending angle $\theta(x)$ with the x -axis (Figure 3).

On average, a C block occupies a box of size $2dHl$, where $l = (N_C v / 2dH)$ is its dimension along the y -axis. The length of the trajectory which starts at the point x is equal to $(d+x)/(\cos \theta(x))$ if $0 \leq \theta \leq \theta^*$ and $0 \leq x \leq x^*$ and $(H/\sin \theta(x))$ if $\theta^* \leq \theta \leq \pi/2$ and $x^* \leq x \leq d$, where $\tan \theta^* = H/(d+x^*)$. Coordinate x^* can be found from the incompressibility condition. The number of C blocks that start on the surface area $dx dy$ in the vicinity of point x is $dQ = \rho(x) dx dy$, and the volume occupied is given by $dV = v N_C dQ$. This volume can also be obtained using the incompressibility condition and simple geometrical arguments

$$\begin{aligned} dV &= \frac{d+x}{\cos \theta} \left(\sin \theta + \frac{d+x}{2 \cos \theta} \frac{d\theta}{dx} \right) dx dy & 0 < \theta < \theta^* \\ dV &= \frac{H}{\sin \theta} \left(\sin \theta + \frac{H}{2 \sin \theta} \frac{d\theta}{dx} \right) dx dy & \theta^* < \theta < \frac{\pi}{2} \end{aligned} \quad (7)$$

Thus, we arrive to the following equations

$$\begin{aligned} \frac{d\theta}{dx} &= \frac{\sin 2\theta}{d+x} \left(\frac{v N_C \rho(x)}{(d+x) \tan \theta} - 1 \right) & 0 \leq \theta \leq \theta^* \\ \frac{d\theta}{dx} &= \frac{2 \sin^2 \theta}{H} \left(\frac{v N_C \rho(x)}{H} - 1 \right) & \theta^* \leq \theta \leq \frac{\pi}{2} \end{aligned} \quad (8)$$

The solutions to these equations can be written in the form

$$\begin{aligned} \tan \theta(x) &= \frac{2v N_C}{(d+x)^2} \int_0^x \rho(x') dx' & 0 \leq x \leq x^* \\ \cot \theta(x) &= \frac{2}{H} \left(d+x - \frac{v N_C}{H} \int_0^x \rho(x') dx' \right) & x^* \leq x \leq d \end{aligned} \quad (9)$$

The normalization condition implies that $\int_0^d \rho(x') dx' = (2dH/v N_C)$. For $0 \leq \theta(x) \leq \theta^*$, the z -coordinate of the free end of the trajectory is $z_N(x) = (d+x) \tan \theta(x)$, and its x -coordinate is $x_N(x) = -d$. Similarly, for $\theta^* \leq \theta(x) \leq \pi/2$, the free end has coordinates $x_N(x) = x - H \cot \theta(x)$ and $z_N(x) = H$.

The local stretching of the C block can be obtained from similar arguments. The number of segments that are inside of the interval dr at a distance r along the trajectories starting at the point with coordinate x is $dN = (1/v)(\sin \theta + r(d\theta/dx)) dx dy dr$. Therefore, the number of segments belonging to one block equals $dn = (dN/dQ) = (1/v\rho(x))(\sin \theta + r(d\theta/dx)) dr$. The equation for the local chain stretching is given by

$$E(x, r) = \frac{3}{2a^2} \frac{dr}{dn} = \frac{3v\rho(x)}{2a^2} \left(\sin \theta + r \frac{d\theta}{dx} \right)^{-1} \quad (10)$$

The elastic energy of stretching for the C block can be written as

$$F_C = 2 \frac{v N_C}{4dH} \left[\int_0^{x^*} dx \rho(x) \int_0^{(d+x)/\cos \theta} dr E(x, r) + \int_{x^*}^d dx \rho(x) \int_0^{H/\sin \theta} dr E(x, r) \right] \quad (11)$$

Using eq 10, we get

$$F_C = \frac{3v^2 N_C}{4a^2 dH} \left[\int_0^{x^*} dx \frac{\rho^2(x)}{\theta'_x} \ln \left(1 + \frac{(d+x)\theta'_x}{\sin \theta \cos \theta} \right) + \int_{x^*}^d dx \frac{\rho^2(x)}{\theta'_x} \ln \left(1 + \frac{H\theta'_x}{\sin^2 \theta} \right) \right] \quad (12)$$

θ'_x can be eliminated from the last equation using eq 8 and the results in

$$F_C = \frac{3v^2N_C}{4a^2dH} \left[\int_0^{x^*} dx \frac{(d+x)\rho^2(x)}{\sin 2\theta \left(\frac{vN_C\rho(x)}{(d+x)\tan\theta} - 1 \right)} \times \right. \\ \left. \ln \left(\frac{2vN_C\rho(x)}{(d+x)\tan\theta} - 1 \right) + \int_{x^*}^d dx \frac{H\rho^2(x)}{2\sin^2\theta \left(\frac{vN_C}{H}\rho(x) - 1 \right)} \times \right. \\ \left. \ln \left(\frac{2vN_C}{H}\rho(x) - 1 \right) \right] \quad (13)$$

To simplify further calculations, we assume that the junction points between the A and C blocks are distributed homogeneously on the AC interface. This implies that $\rho(x) = \rho_{0x} = (2H/vN_C) = (4H/vN)$. From the incompressibility condition, we get $x^* = d/3$, and after some calculations, the final equation for the elastic energy of the C block becomes

$$F_C = 2.65 \frac{H^2}{a^2N} + 5.29 \frac{d^2}{a^2N} \quad (14)$$

The situation is more complicated for the short period AB lamellar structure, where the blocks are stretched both in the x - and z -directions and their ends located at the AB interface. Here, we use a simple approach assuming that the blocks are stretched homogeneously. An AB multiblock occupies the volume $2dHl = vN/2$. Therefore, its average end-to-end distance along the z -axis is H , and the average stretching force of the multiblock along the z -direction is $E_z = (3/a^2)(H/N)$. The internal A and B blocks form either bridge or loop conformations. Assuming that the energies of a bridge and a loop are the same, which implies that the middle of a loop is located on a distance d from the interface, the average tension of the A and B blocks are $E_{x,A} = (12(n+1)d)/(a^2N)$ and $E_{x,B} = (12nd)/(a^2N)$, respectively. The total elastic energy of the AB multiblock is given by

$$F_{AB} = E_z H + 2(n+1)E_{x,A}d + 2nE_{x,B}d = \frac{3}{a^2N} [H^2 + 8((n+1)^2 + n^2)d^2] \quad (15)$$

The interfacial energy is determined by the Flory–Huggins interaction parameters χ_{AB} , χ_{AC} , and χ_{BC} and is given by

$$F_{inf} = \frac{a}{v\sqrt{6}} (\Sigma_{AB}\sqrt{\chi_{AB}} + \Sigma_{AC}\sqrt{\chi_{AC}} + \Sigma_{BC}\sqrt{\chi_{BC}}) \\ = \frac{aN}{4H\sqrt{6}} \left[\frac{H}{d}\sqrt{\chi_{AB}} + \sqrt{\chi_{AC}} + \sqrt{\chi_{BC}} \right] \quad (16)$$

Here, $\Sigma_{AB} = (vN_C/2d)$ and $\Sigma_{AC} = \Sigma_{BC} = (vN_C/2H)$ are the areas of contact between the different components per copolymer chain. The total free energy is equal to the sum of the elastic energies of the C, A, and B blocks and the interfacial energy.

$$F_{LL\perp} = 5.65 \frac{H^2}{a^2N} + 48(n(n+1) + 0.61) \frac{d^2}{a^2N} + \\ \frac{aN}{4d\sqrt{6}} \sqrt{\chi_{AB}} + \frac{aN}{4H\sqrt{6}} [\sqrt{\chi_{AB}} + \sqrt{\chi_{BC}}] \quad (17)$$

Further minimization of this energy with respect to H and d is trivial. The periods of the structure are

$$L_z = 4H \cong 0.84R_0(\sqrt{N\chi_{AC}} + \sqrt{N\chi_{BC}})^{1/3} \\ L_x = 4d \cong 0.41 \frac{R_0(N\chi_{AB})^{1/6}}{(n(n+1) + 0.61)^{1/3}} \quad (18)$$

The final equation for the free energy is given by

$$F_{LL\perp} = \frac{3}{2}(n(n+1) + 0.61)^{1/3}(N\chi_{AB})^{1/3} + 0.73(\sqrt{N\chi_{AC}} + \sqrt{N\chi_{BC}})^{2/3} \quad (19)$$

This energy scales as $F_{LL\perp} \propto N^{1/3}$. Comparison of the energies F_L (eq 4) and $F_{LL\perp}$ (eq 19) shows that the perpendicular lamellar-within-lamellar becomes stable when N exceeds some critical value N_{c1} . For the terpolymer A–B–A–B–A–C consisting of poly(cyclohexylethylene) (A), poly(ethylene) (B), and poly(ethylene-*alt*-propylene) (C) blocks, this value turns out to be $N_{c1} \cong 2200$.

Parallel Lamellar-within-Lamellar Structure

Next, we address the parallel lamellar-within-lamellar structure where the thin A and B layers are parallel to the thick C layers. We assume that two neighboring C layers are separated by $m+1$ A layers and m B layers (the total number of thin layers inside of the AB multiblock domain is $k = 2m+1$; Figure 4). A similar structure has been considered before for copolymer chains with the chemical structure C-*b*-(A-*b*-B)_{*n*}-*b*-A-*b*-C.^{19–21}

We denote the thickness of the B layers as $2d_B$ and the thickness of the C layers as $2H$. Among the A layers, we will distinguish between the boundary layers which are in a contact with C layers and have thickness $h + d_A$ and the internal A layers having thickness $2d_A$. Homogeneous stretching of the blocks in the proposed structure imply that the stretching force of the C blocks is $E_C = (3H/a^2N)$, the stretching force of the B blocks is $E_B = (12nd_B/a^2N)$, and the stretching force of the A blocks is $E_{A1} = (12(n+1)d_A/a^2N)$. The exception is the first half of those A blocks that are directly connected to C blocks and occupy a domain of thickness h in the boundary A layer. The stretching force of this section is $E_{A2} = (12(n+1)h/a^2N)$. If the interfacial area per copolymer chain equals Σ , incompressibility implies

$$\frac{vN}{2} = H\Sigma \quad 2md_B\Sigma = \frac{vN}{4} \quad h\Sigma = \frac{vN}{8(n+1)} \\ 2md_A\Sigma = \frac{vN(2n+1)}{8(n+1)} \quad (20)$$

Figure 4. Conformation of the A-*b*-(B-*b*-A)_{*n*}-*b*-C copolymer chain in the parallel lamellar-within-lamellar structure.

The total free energy per multiblock copolymer chain includes the local stretching energy of A, B, and C blocks, AB and AC interfacial energy, and a combinatorial term which takes into account the different ways that the AB multiblock chain can pass through the m AB interfacial layers.

$$F_{\text{LL}_{\parallel}} = \frac{12(n+1)h^2}{a^2N} + \frac{12(n+1)(2n+1)d_A^2}{a^2N} + \frac{24n^2d_B^2}{a^2N} + \frac{3H^2}{a^2N} + \frac{a\Sigma}{\nu\sqrt{6}}[m\sqrt{\chi_{AB}} + \sqrt{\chi_{AC}}] + F_{\text{comb}} \quad (21)$$

The combinatorial term F_{comb} can be estimated from imagining the extended multiblock conformation as a one-dimensional random walk consisting of $2n$ steps²¹ (this is the total number of AB links) drifting on a distance m , that is, the number of steps in the positive direction is $(2n+m)/2$, and that in the opposite direction is $(2n-m)/2$

$$F_{\text{comb}} \cong \left(\frac{2n+m}{2}\right) \ln\left(\frac{2n+m}{2}\right) + \left(\frac{2n-m}{2}\right) \times \ln\left(\frac{2n-m}{2}\right) - 2n \ln(n) \quad (22)$$

After minimization of $F_{\text{LL}_{\parallel}}$ with respect to Σ using eq 20, we get

$$F_{\text{LL}_{\parallel}} = \frac{3}{2}(m\sqrt{N\chi_{AB}} + \sqrt{N\chi_{AC}})^{2/3} \left(\frac{m^2 + (2n+1)^3}{16m^2(n+1)} + \frac{n^2}{2m^2} + \frac{1}{4} \right)^{1/3} + F_{\text{comb}} \quad (23)$$

The period of the structure is given by

$$L_z = 4H \cong 0.82R_0(m\sqrt{N\chi_{AB}} + \sqrt{N\chi_{AC}})^{1/3} \times \left(\frac{m^2 + (2n+1)^3}{16m^2(n+1)} + \frac{n^2}{2m^2} + \frac{1}{4} \right)^{1/3} \quad (24)$$

For large N , the free energy scales as $F_{\text{LL}_{\parallel}} \propto N^{1/3}$. The transition between the simple lamellar phase (L) and the parallel lamellar-within-lamellar structure occurs when the energies (eqs 4 and 23) are equal. Turning back to the terpolymer A–B–A–B–A–C consisting of poly(cyclohexylethylene) (A), poly(ethylene) (B), and poly(ethylene-*alt*-propylene) (C) blocks, we find that $N_{c2} \cong 2040$. The transition occurs to a structure with $k = 5$ thin layers.

Discussion and concluding remarks

The above analysis of poly(cyclohexylethylene-*b*-ethylene-*b*-cyclohexylethylene-*b*-ethylene-*b*-cyclohexylethylene-*b*-ethylene-*alt*-propylene) hexablock terpolymer, which is based on the strong segregation theory approach, shows that for large chain lengths N , the parallel lamellar-within-lamellar structure is more preferable than the perpendicular lamellar-within-lamellar structure (the transition to the lamellar-within-lamellar structure occurs first for $N_{c2}\chi_{AB} \cong 110 < N_{c1}\chi_{AB} \cong 119$). This result is in contradiction with the experimental observations.^{11,12} However, we note that these two transition points are very close to each other, and using a more rigorous approach in the part concerning the calculation of the energy of the terminal A blocks may well change this sequence.

When the number of blocks in the multiblock is large ($n > 1$), the contribution of the terminal A blocks to the free energy is small, and the transition between the different lamellar structures can be done using the approach presented. In this limiting case, the dominating contribution to the free energy of the complex lamellar structures appears to be due to the AB multiblock. This energy is the same for both the parallel and perpendicular lamellar-within-lamellar structures. Expansion of the free energies (eqs 19 and 23) with respect to the small parameter $1/n \ll 1$ with the additional assumption that $1 \ll m \ll n$ (this inequality should be verified after the calculations) results in

$$F_{\text{LL}_{\perp}} \cong \frac{3}{2}n^{2/3}(N\chi_{AB})^{1/3} + 0.73(\sqrt{N\chi_{AC}} + \sqrt{N\chi_{BC}})^{2/3} \quad (25a)$$

$$F_{\text{LL}_{\parallel}} \cong \frac{3}{2}n^{2/3}(N\chi_{AB})^{1/3} \left(1 + \frac{2}{3m} \left(\frac{\chi_{AC}}{\chi_{AB}} \right)^{1/2} + \frac{m^2}{12n^2} \right) + \frac{m^2}{4n} \quad (25b)$$

In the last equation, we used the approximation $F_{\text{comb}} \cong (m^2/4n)$. Minimization of the free energy (eq 25b) with respect to m gives

$$m \cong (2n)^{2/3} \left(\frac{\chi_{AC}}{\chi_{AB}} \right)^{1/6} \quad (26)$$

After substitution of this value in eq 25b, we get the final formula for the free energy of the parallel lamellar-within-lamellar structure

$$F_{\text{LL}_{\parallel}} \cong \frac{3}{2}n^{2/3}(N\chi_{AB})^{1/3} + \frac{3}{2^{5/3}}(N\chi_{AC})^{1/3} + \frac{1}{2^{2/3}}n^{1/3} \left(\frac{\chi_{AC}}{\chi_{AB}} \right)^{1/3} \quad (27)$$

The last term is connected with the combinatorial energy and is small since $\chi_{AB}(N/2n) \gg 1$. Here, the parameter $\chi_{AB}(N/2n)$ determines the energy of the (A–B) diblock. In our case, this parameter is responsible for the transition between the simple lamellar and the complex lamellar structures. Comparing the free energies of eqs 4 and 25a, 25b gives the range of stability of the complex lamellar structures

$$\chi_{AB} \left(\frac{N}{2n} \right) > \chi^*M = 6 \cdot \sqrt{12} \cong 20.8 \quad (28)$$

Here, $M = N/2n$ is the length of AB diblock. This value exceeds the critical value $\chi^*M = 15.1$ of the lamellar phase formation in AB multiblock copolymers obtained using the random phase approximation approach.^{24,25} The essential discrepancy between these two values appears because in the present approach, loops and bridges have the same energy. The separation line between the parallel and perpendicular lamellar-within-lamellar structures can be found by equating the energies eqs 25a and 27. The perpendicular lamellar-within-lamellar structure becomes stable when

$$\frac{\chi_{BC}}{\chi_{AC}} < 0.22 \quad (29)$$

Figure 5. Phase diagram of A-b-(B-b-A)_n-b-C for $n = 2$ (top) and 10 (bottom) with $\chi_{AB} = \chi_{AC}$. In the parallel lamellar-within-lamellar structure $LL_{||}(\cdot)$, the number in the parentheses denotes the number of thin layers.

According to this criterion, the transition to the perpendicular lamellar-within-lamellar phase for the terpolymer A-b-(B-b-A)_n-b-C consisting of poly(cyclohexylethylene) (A), poly(ethylene) (B), and poly(ethylene-*alt*-propylene) (C) blocks with $n \gg 1$ should occur before the transition to the parallel lamellar-within-lamellar phase as long as $\chi_{BC}/\chi_{AC} \approx 0.16 < 0.22$. Contrary to the direct calculations, the formal application of this criterion to the case when $n = 2$ is in agreement with the experimental observations.^{11,12}

Different phase diagrams for $n = 2$ and 10 for $N\chi_{AB} = N\chi_{AC}$ with $n = 2$ and 10 and for $N\chi_{AB} = 1.6 N\chi_{AC}$ (this corresponds to the experimental system^{11,12}) with $n = 10$ are shown in Figures 5 and 6, respectively.

The figures clearly show how the perpendicular lamellar-within-lamellar structure occurs for relatively small values of χ_{BC} . In the case of $\chi_{AB} = 1.6\chi_{AC}$, even smaller values of χ_{BC} are required than in the case of $\chi_{AB} = \chi_{AC}$. A comparison between eqs 25a and 27 shows that this is mainly due to the effect of the ratio χ_{AC}/χ_{AB} on the free energy of the parallel lamellar-within-lamellar structure. When χ_{BC} is very small, that is, $\chi_{BC}(N/n) \leq 1$, the B blocks start to penetrate inside of the C

Figure 6. Phase diagram of A-b-(B-b-A)_n-b-C for $n = 10$ with $\chi_{AB} = 1.6 \chi_{AC}$. In the parallel lamellar-within-lamellar structure $LL_{||}(\cdot)$, the number in the parentheses denotes the number of thin layers

layers, and the BC interface is destroyed. In this case, we expect stabilization of the parallel lamellar-within-lamellar structure.

The self-consistent field method appears to be the most appropriate way to analyze terpolymers with small numbers of blocks in the AB multiblock chain. Very recently, Wang et al.²⁶ performed real-space self-consistent field calculations on slightly different C-b-(A-b-B)_n multiblock copolymers for small n and established the transition from parallel to perpendicular lamellar-within-lamellar structures for C-b-(A-b-B)₃ in the case of $N\chi_{CA} = 100$ and 150.

Acknowledgment. Financial support from Netherlands Organization for Scientific Research (NWO) within the Dutch–Russian scientific cooperation program is gratefully acknowledged.

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JP9113943