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Lamellar Orientation in Thin, Supported Diblock Copolymer Films: Strong Segregation Theory

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ABSTRACT: The parallel and perpendicular orientation of lamellae in free-surface thin films of symmetric diblock copolymers is studied in the strong segregation approximation. In contrast to films, which are confined between two hard walls, the period of the parallel lamellar structure in the free-surface films is determined from the equilibrium conditions. As a result, the period depends on the surface tension coefficients (spreading parameters). Both wetting and nonwetting conditions are considered. We have shown that the perpendicular orientation of the lamellae can be stable even in thick films if the different blocks interact with the substrate and air similarly, i.e., when the values of the spreading parameters of both polymers are close to each other. Also stability of the perpendicular lamellae is predicted for thin enough films with dissimilar spreading parameters under wetting conditions for both species (attractive interactions between film and substrate). Otherwise, the lamellae have the parallel orientation.

Introduction

Thin diblock copolymer films have been found to represent an interesting class of materials for nanostructuring surfaces. Because of their ability to self-organize into regular structures having inherent length scales in the submicrometer range, they can be used as templates for a number of applications, for instance, for data storage.[1] Depending on block copolymer and substrate used, different structures of the films have been detected.[2] Compositionally symmetric PS−PMMA block copolymers have repeatedly been found to form lamellae that are parallel to the film surface, if the film thickness is larger than the lamellar thickness.[3−6] This has been attributed to the strong affinity of PMMA to the substrate (silicon oxide). If the substrate surface is modified such that it is very close to neutral, the PS−PMMA lamellae are perpendicular to this surface.[7,8] In studies of thin films of polystyrene−polyisoprene diblock copolymers, different lamellar orientations have been found near the free film surface.[9,10] In lamellae-forming polystyrene−polybutadiene (PS−PB) diblock copolymers, the lamellae were found to be tilted near the free film surface.[11] A molar-mass dependence of the lamellar orientation in PS−PB films was detected in recent experiments.[12] In this system, the selectivities of the substrate (silicon with a native oxide layer) and of the film/air surface toward the two blocks are weak. In films of low molar mass, the lamellae are preferentially parallel to the film surface, and it was found that high molar mass samples form lamellae that are perpendicular to the film surface.

Intensive theoretical investigations of lamellar orientation in thin films of diblock copolymers have been started in the past decade.[13−20] However, most theoretical studies treat the case of a diblock copolymer being confined between two hard walls; i.e., the film thickness is imposed by the distance between the walls. Turner developed a strong segregation theory,[13] which considers symmetric (the same polymer is in contact with both surfaces) and antisymmetric lamellar morphologies oriented parallel to the confining surfaces. It was predicted that, depending on the interfacial energy of the confining surfaces, the free energy of the symmetric and antisymmetric morphologies attains its minimum if the film thickness D conforms to an integer or half-integer number of the bulk lamellar period d, respectively. This theory was extended by Walton et al. to analyze the conditions of stability of the perpendicular orientation of lamellae.[14] It was shown that the perpendicular structure is possible where the lamellar period of the bulk is realized. A critical number of layers was derived, below which the morphology can be either perpendicular or parallel symmetric, depending on the extent of chain deformation. Above this critical number of layers, only a parallel symmetric morphology is predicted.[14] It has also been shown that the parallel antisymmetric morphology can be stable only for dissimilar substrates.[14] Further generalization of the theories[13,14] was done by Turner et al.[15] where mixed morphologies of the film (various combinations of parallel an perpendicular lamellae) was shown to be unstable while pure parallel and perpendicular structures can be formed both at small and high distances between the walls depending on the surface tension. Kikuchi and Binder performed Monte Carlo simulations where surface interactions were repulsive for one of the blocks.[16] It was shown that, depending on the compatibility of the film thickness D and the lamellar thickness d, different orientations are possible. For cases when D and d are compatible (integer number of lamellae), a parallel orientation is indicated. Otherwise, a perpendicular orientation or a coexistence of the two orientations is observed. Recent simulations with attractive interactions between the confining surfaces and one of the polymers[17] have shown that the perpendicular structure can be stable at high incompatibility of the monomer units or at small film thicknesses. Also, computer simulations of Sommer et al. predicted that lamellae orient perpendicular to perfectly neutral walls.[18] Phase diagrams of the film, whose thickness is equal to or below the bulk equilibrium lamellar thickness, d,

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were constructed by Tang[19] and Fasolka et al.[20] using self-consistent-field calculations following the approach of Scheutjens and Fleer.[21] In particular, it was found that the perpendicular morphology in films of thickness d can be stable within a wide range of values of polymer−surface interfacial energies.[19]

As stated above, most of the theoretical approaches and computer simulations have in common that the block copolymer film is confined between two hard walls, i.e., the film thickness is fixed.[13−18] On the other hand, many experiments deal with supported films which are able to spread on the substrate and to tune the thickness to the equilibrium value. Turner et al. developed also a theory of the wetting behavior of thin diblock copolymer films deposited on the solid substrate.[15] They found that the equilibrium spreading of the film can result in the formation of either single or double layers far from the wetting edge and of the perpendicular structure (parallel orientation of the chains) in the vicinity of the edge, i.e., where the film is thinner.

If the spreading of diblock copolymers on the surface can be stopped due to lateral obstacles, multilayer films can be formed. One of the experimental methods, which allows one to create multilayer films with equilibrium internal structure, is slow solvent-casting.[12] In this case a substrate is wet with the polymer solution and placed in a closed, shallow pan (Petri dish). Slow evaporation of the solvent (usually a few days) promotes relaxation of the structure, and we can expect that the period of the structure can reach the equilibrium value and tune it during evaporation. Final thickness of the dry film is determined by the polymer concentration of the solution. Depending on polymer concentration, the upper layer of the film with parallel lamellae can be either complete (homogeneous surface area) or incomplete (holes and terraces).[4,12,25]

The objective of this paper is to modify the strong segregation theories of thin films confined between two hard walls[13−15] to describe equilibrium, supported films. We will consider films on a substrate having one free surface and assume that the period of the parallel lamellar structure with a *fixed number of lamellae* is determined from the balance between elastic forces of stretched blocks and interfacial interactions, i.e., by the minimization of the total free energy of the film. This gives the period of the film structure as a function of various surface tension coefficients and the number of layers. Note that in the previous theories the period was considered to be restricted within a certain interval of values[14] or determined by the equating of the free energies of the films having n and $n + 1$ number of layers.[13,15] We will study both wetting (positive spreading parameter) and nonwetting (negative spreading parameter) conditions. In this way, we will show that the perpendicular orientation of the lamellae is stable not only for thin films (few lamellar periods) but, under certain conditions, also for thicker films (many lamellar periods). The phase diagram of the film will be constructed.

Theoretical Model

Let us consider a dry incompressible film of symmetric AB diblock copolymers with $N_A = N_B = N/2 \gg 1$ segments per block, each of size a (a being the only microscopic size in the problem) in the strong segregation regime, i.e., when the interaction (Flory−Huggins) parameter χ_{AB} between A and B segments satisfies the inequality $N\chi_{AB} \gg 1$. In this case the shape of the lamellae is pronounced, and the interfaces are narrow. The free energy of the film in such a regime can be written as a sum of two terms[22]

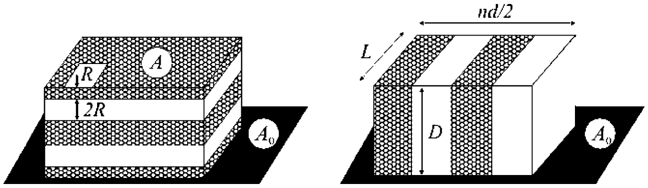

Figure 1. Schematic representation of the film with parallel (a) and perpendicular (b) orientation of lamellae.

$$F = F_{el} + F_{int}, \tag{1}$$

namely, the elastic free energy F_{el} of the stretched blocks and the interfacial energy F_{int} of various interfaces. Note that in diblock copolymer films the contribution of long-range interactions between the two film surfaces[23,24] is small in comparison with the elastic free energy of the copolymers and can be neglected. Let us consider separately two different orientations of lamellae in the film.

(1) Parallel orientation. We will analyze the case when the amount of polymer in the film conforms to the perfect symmetric or antisymmetric structure. Otherwise, the film generally separates upon annealing into regions of different thickness, each of them has perfect structure (the formation of holes and terraces).[4,12,25] From the theoretical point of view this case is equivalent to the consideration of two films having equilibrium thicknesses and different number of the layers. This more complicated situation will be analyzed elsewhere.

In a lamellar morphology each half of the diblock forms a planar brush. These brushes do not interpenetrate.[22] Denote by R the end-to-end distance of one block of the diblock copolymer and by d the lamellar thickness in the film. Then the thicknesses of the boundary and the internal A and B layers are approximately equal to $R = d/4$ and $2R = d/2$, respectively, Figure 1a. The elastic energy of the stretched blocks can then be written as

$$F_{el} = 4k_BTQ\frac{R^2}{a^2N} = k_BTQ\frac{d^2}{4a^2N}, \tag{2}$$

where k_BT is the thermal energy, and Q the number of the molecules (diblock copolymers) in the film. The interfacial energy can be presented as a sum of four terms, Figure 1a

$$F_{int} = \gamma_{As}A + \gamma_{A,Ba}A + \gamma_{AB}(n + 1)A + \gamma_{sa}(A_0 - A) \tag{3}$$

Here the first term is the energy of the polymer A/substrate interface. The second term is the surface energy of the polymer (A or B) which is in contact with air. γ_{As} and $\gamma_{A,Ba} = \gamma_{Aa}$ (or γ_{Ba}) are the corresponding surface tension coefficients; A is the surface area of the film. The third term is the energy associated with the polymer A/polymer B contacts in the film; n is the total number of internal A and B layers of the film, each with the thickness $d/2$. The thickness of the film D is expressed through n as $D = (n + 1)d/2$. Finally, the last term in eq 3 is the energy of the substrate/air interface, where A_0 is the total surface area of the substrate. The space filling condition for a dry film takes the form

$$(1 + n)Ad/2 = NQa^3 \tag{4}$$

Minimization of the total free energy (eq 1) per chain, F/Q, with respect to the period d, where the area A is expressed through d using condition 4, enables us to find both the equilibrium values for the period $d_{||}$ and for the free energy $F_{||}$

$$d_{||} = d_0\left(1 - \frac{\bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{As}} - \bar{\gamma}_{\mathrm{A,Ba}}}{(n+1)\bar{\gamma}_{\mathrm{AB}}}\right)^{1/3} \quad d_0 = 4a\bar{\gamma}_{\mathrm{AB}}^{\;1/3}\left(\frac{N}{4}\right)^{2/3}$$

$$f_{||} = \frac{F_{||}}{Qk_{\mathrm{B}}T} = f_0\left(1 - \frac{\bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{As}} - \bar{\gamma}_{\mathrm{A,Ba}}}{(n+1)\bar{\gamma}_{\mathrm{AB}}}\right)^{2/3} \qquad f_0 = \frac{3}{2}(2N)^{1/3}\bar{\gamma}_{\mathrm{AB}}^{\;2/3} \tag{5}$$

Here $\bar{\gamma}_{ij} = \gamma_{ij}a^2/k_{\mathrm{B}}T$ are dimensionless surface tension coefficients; d_0 and f_0 are the period and the free energy of the lamellae in the bulk.[22] We omit the constant contribution to the free energy, which is proportional to the substrate area A_0. Similar to microphase separation in the bulk under strong segregation conditions, the period $d_{||}$ of parallel lamellae scales with the length of the blocks as $N^{2/3}$. However, the presence of additional interactions with the substrate and with air results in the change of the lamellar thickness in comparison to the case in the bulk. The increase or decrease of the thickness depends on the sign of the combination of surface tension coefficients $S = \bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{As}} - \bar{\gamma}_{\mathrm{A,Ba}}$. Positive values of S correspond to the wetting of the substrate, i.e., the polymer film tends to be spread on the substrate to minimize substrate/air contacts. In this case the lamellar thickness is smaller than that in the bulk. In the opposite case (negative values of S) the lamellae are thicker.

(2) Perpendicular Orientation. The elastic energy of laterally ordered lamellae in the film has the same form as for the case of parallel orientation, eq 2. The interfacial energy can be written as

$$F_{\mathrm{int}} = nLD\gamma_{\mathrm{AB}} + ndL(\gamma_{\mathrm{Aa}} + \gamma_{\mathrm{As}})/4 + ndL(\gamma_{\mathrm{Ba}} + \gamma_{\mathrm{Bs}})/4 + \gamma_{\mathrm{sa}}(A_0 - ndL/2), \quad L, n \to \infty \tag{6}$$

where we denote by L and D one of the linear sizes of the film and its thickness, respectively, Figure 1b. The first term in eq 6 is the energy of polymer A/polymer B contacts, the second and third terms describe interactions of the polymers with the substrate and air while the last term is the energy of the air/substrate interface. The space-filling condition for such a film is

$$nLDd/2 = NQa^3 \tag{7}$$

Minimization of the free energy of the film having a laterally ordered lamellar structure gives the following result:

$$d_\perp = d_0,$$
$$f_\perp = \frac{F_\perp}{Qk_{\mathrm{B}}T} = f_0 - \frac{Na}{2D}(2\bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{As}} - \bar{\gamma}_{\mathrm{Aa}} - \bar{\gamma}_{\mathrm{Bs}} - \bar{\gamma}_{\mathrm{Ba}}) \tag{8}$$

where the period of the structure, $d_\perp$, coincides with that of the bulk, d_0, while the free energy can be higher or lower, depending on the sign of the combination of the surface tension coefficients in the brackets. This combination can be presented as a sum, $S_{\mathrm{A}} + S_{\mathrm{B}}$, of the two spreading parameters of polymers A and B: $S_{\mathrm{A}} = \bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{As}} - \bar{\gamma}_{\mathrm{Aa}}$and $S_{\mathrm{B}} = \bar{\gamma}_{\mathrm{sa}} - \bar{\gamma}_{\mathrm{Bs}} - \bar{\gamma}_{\mathrm{Ba}}$. If both coefficients are positive, i.e., if there is a tendency for spreading on the substrate of both components, then the free energy $f_\perp$ is lower than the free energy f_0. In the opposite case of a nonwetted substrate, both coefficients are negative, and the free energy of lateral structure exceeds the free energy of lamellar structure in the bulk.

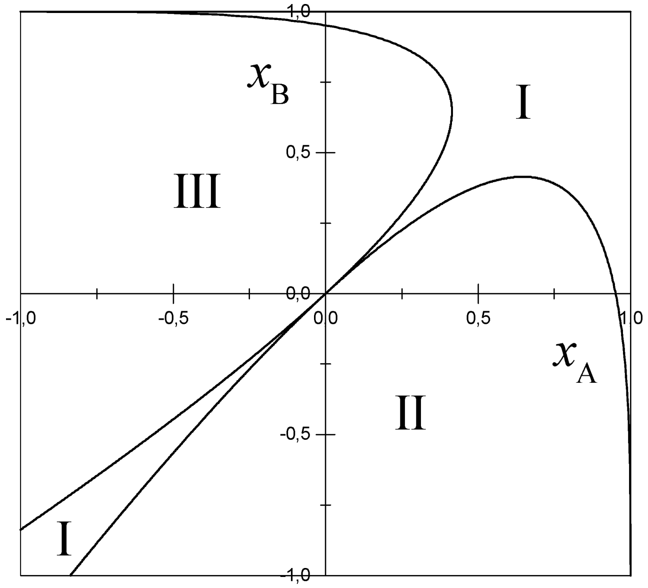

Figure 2. Phase diagram of a supported, lamellar diblock copolymer film in variables $x_{\mathrm{A}} = S_{\mathrm{A}}/[\bar{\gamma}_{\mathrm{AB}}(n + 1)]$ and $x_{\mathrm{B}} = S_{\mathrm{B}}/[\bar{\gamma}_{\mathrm{AB}}(n + 1)]$, where S_{A} and S_{B} are the spreading parameters of polymers A and B, $\bar{\gamma}_{\mathrm{AB}}$ is the dimensionless surface tension coefficient of A−B interfaces, and n is the total number of internal A and B layers of the film, each with the thickness $d/2$. Roman numbers denote regions of stability of various structures: perpendicular lamellae (I), symmetric structure of parallel lamellae with boundary A layer (II), and symmetric structure of parallel lamellae with boundary B layer (III).

Discussion

Let us compare the free energies of the different structures of the film. For this purpose we consider films having the same thickness, i.e., the parameter D in eq 8 should be equal to $d_{||}(1 + n)/2$. First, we analyze the case where polymer A (or B) forms both boundary layers in the film with parallel orientation of the lamellae, i.e., when n is odd (symmetric structure). It becomes favorable when conditions $\gamma_{\mathrm{As}} < \gamma_{\mathrm{Bs}}$ and $\gamma_{\mathrm{Aa}} < \gamma_{\mathrm{Ba}}$ (or $\gamma_{\mathrm{Bs}} < \gamma_{\mathrm{As}}$ and $\gamma_{\mathrm{Ba}} < \gamma_{\mathrm{Aa}}$) are satisfied. The equality of the free energies $f_{||} = f_\perp$ can be presented as

$$x_{\mathrm{B}} = 3(1 - x_{\mathrm{A}})^{1/3} - 3 + 2x_{\mathrm{A}}, \quad \text{boundary layer of A type}, \quad x_{\mathrm{A}} > x_{\mathrm{B}},$$
$$x_{\mathrm{A}} = 3(1 - x_{\mathrm{B}})^{1/3} - 3 + 2x_{\mathrm{B}}, \quad \text{boundary layer of B type}, \quad x_{\mathrm{A}} < x_{\mathrm{B}}, \tag{9}$$
$$x_{\mathrm{A}} = \frac{S_A}{\bar{\gamma}_{\mathrm{AB}}(n+1)}, \quad x_{\mathrm{B}} = \frac{S_{\mathrm{B}}}{\bar{\gamma}_{\mathrm{AB}}(n+1)}$$

The solution of eq 9 is presented in the phase diagram shown in Figure 2. We can see that for fixed values of the number of layers n and the surface tension coefficient $\bar{\gamma}_{AB} \approx \sqrt{\chi_{AB}}$, a laterally ordered structure of the film (region I) is favorable mainly for positive values of the spreading parameters S_A and S_B or when their values are close to each other. The parallel structure of the film (regions II and III) remains stable in very wide ranges of values of parameters S_A and S_B. To understand what is the driving force of lamellar reorientation, let us compare different contributions to the free energies of both structures. Elastic (f_{el}), A/B interfacial (f_{AB}) and polymer/surrounding medium (substrate and air) (f_{med}) free energies per one chain can be written as follows:

$$\begin{array}{ll} \text{parallel lamellae} & \text{perpendicular lamellae} \\ f_{el} = \frac{1}{3}f_0(1 - x_A)^{2/3}, & f_{el} = \frac{1}{3}f_0, \\ f_{AB} = f_0\frac{2}{3(1 - x_A)^{1/3}}, & f_{AB} = \frac{2}{3}f_0, \\ f_{med} = -f_0\frac{2x_A}{3(1 - x_A)^{1/3}} & f_{med} = -f_0\frac{x_A + x_B}{3(1 - x_A)^{1/3}} \end{array} \qquad (10)$$

These expressions are presented for the case when polymer A forms both boundary layers ($x_A > x_B$). Let us consider the wetting and the nonwetting conditions. In the first case, x_A, $x_B > 0$; f_{el} and f_{med} of parallel lamellae are smaller than those of perpendicular lamellae. Therefore, the elasticity of the diblock copolymer and the preferential interactions of one of the components with the substrate and with air stabilize the parallel lamellar orientation under wetting conditions. Indeed, a tendency of the film to occupy as much as possible of the substrate area can be considered as an action of an external normal force resulting in a compression of the film and in a decrease of the block stretching (see eq 5). However, the area (per molecule) and the corresponding free energy f_{AB} of polymer A/polymer B contacts is increased at the spreading on the surface of parallel lamellae, which is unfavorable and can result in lamellar reorientation. This means that the interactions of A and B monomer units stabilize the perpendicular orientation under wetting conditions. Such a stabilization mechanism is in good agreement with recent computer simulations[17] where the perpendicular structure was found to be stable at high incompatibility of monomer units.

Under nonwetting conditions, x_A, $x_B < 0$, and f_{AB} and f_{med} of parallel lamellae are smaller than that of perpendicular lamellae. Therefore, all interfacial interactions stabilize parallel lamellae. On the other hand, the stretching of molecules in perpendicular lamellae is smaller than in parallel lamellae. Therefore, elastic forces can stabilize the perpendicular structure under nonwetting conditions.

We can see in Figure 2 that perpendicular lamellae can be stable even in thick films containing a large number of layers, $n \gg 1$ (small values of x_A, x_B). This becomes possible when the difference in the spreading parameters of two polymers $\delta S = S_A - S_B$ is small, $\delta S \ll |S_A|$, $|S_B|$. Expanding the total free energies of different morphologies, eq 10, into a power series of x_A and x_B, we find the following criterion for the stability of perpendicular lamellae in thick films:

$$n < n^*, \quad n^* = \frac{{S_A}^2}{3\bar{\gamma}_{AB}\delta S} - 1 \gg 1 \qquad (11)$$

I.e., the thickness of the film should be smaller than some large threshold value. This prediction is consistent with the results obtained for the films confined between two hard walls[15] in the sense that n^* increases with the decrease of the difference in the spreading parameters. In our notations the value of n^* in ref 15 takes the form $n^* = 3\bar{\gamma}_{AB}/\delta S$. However, it is seen that the dependence of n^* on other parameters is different for these two cases.

In the opposite limit of thin films ($n = 1$ corresponds to one period) or large values of spreading parameters, when $|x_A|$, $|x_B| \sim 1$, the region, occupied by perpendicular lamellae, becomes wider, Figure 2, especially under wetting conditions, x_A, $x_B > 0$. These results are in good agreement with recent self-consistent-field calculations[19] and computer simulations.[17]

Now let us consider the case when different polymers form boundary layers of the film with parallel lamellae, i.e., when the number of internal A and B layers, n, is even (antisymmetric structure). It becomes favorable when inequalities $\gamma_{As} < \gamma_{Bs}$ and $\gamma_{Ba} < \gamma_{Aa}$ (or $\gamma_{Bs} < \gamma_{As}$and $\gamma_{Aa} < \gamma_{Ba}$) are held. The condition for the transition between the parallel and perpendicular lamellae can be reduced to eq 9, if we introduce new variables

$$\bar{x}_A = \frac{\bar{\gamma}_{sa} - \bar{\gamma}_{As} - \bar{\gamma}_{Ba}}{\bar{\gamma}_{AB}(n + 1)}, \quad \bar{x}_B = \frac{\bar{\gamma}_{sa} - \bar{\gamma}_{Bs} - \bar{\gamma}_{Aa}}{\bar{\gamma}_{AB}(n + 1)} \qquad (12)$$

Therefore, the phase diagram for antisymmetric structure in variables $\bar{x}_A$ and $\bar{x}_B$ looks like the diagram in Figure 2.

Some of the results of this paper are in good agreement with the predictions of Walton et al. for the films confined between two solid walls.[14] In their theory, the vertical morphology was shown to be occur, if (i) the number of layers in the film is less than some critical value and if (ii) the ratio of the period of parallel lamellae $d_{||}$ to the period of lamellae in the bulk d_0, $\lambda = d_{||}/d_0$, is less or higher than some threshold values, $\lambda < \lambda_-$, $\lambda > \lambda_+$. Note that λ is an external parameter of the theory[14] whose value is not fixed: it is restricted between two boundary values. In our theory the parameter λ has a certain fixed value $\lambda = \lambda_0$, which depends on the surface tension coefficients, eq 5. It turns out that in the region, where perpendicular lamellae are stable, λ_0 always satisfies inequalities $\lambda_0 < \lambda_-$ (under wetting conditions) and $\lambda_0 > \lambda_+$ (under nonwetting conditions), i.e., these results are consistent. On the other hand, the theory[14] cannot predict explicit conditions for the stability of various morphologies because of unfixed value of λ.

It has to be noted that the expressions for the free energy of parallel lamellae, eq 5, are equivalent to those of the film confined between two hard walls whose thickness corresponds to the absolute minimum of the free energy of the parallel structure (film with “happy” thickness).[15] However, the authors concluded that in this case the only structure with the lowest free energy is the parallel lamellae. On the other hand, Figure 2 shows that the perpendicular lamellae can be stable as well.

Conclusions

We developed a strong segregation theory to describe the lamellar orientation in thin, free-surface films of symmetric diblock copolymers. In contrast to the films confined between two hard walls, the period of the parallel lamellae in the free-surface film can reach its equilibrium value. Phase diagram of the film is constructed in variables which are dependent only on the surface tension coefficients of various interfaces and on the number of layers in the film. It was shown that the perpendicular lamellae are stable mostly when interactions of polymers (A and B) with the substrate are attractive (wetting conditions). They can be stable even in thick enough films if the character of interactions of both polymers with the substrate is similar (similar spreading parameters for polymers A and B). We have shown that under wetting conditions, when the film tends to be spread on the substrate, the stretching of the chains in the parallel lamellae is less than in the perpendicular lamellae, while the surface area of A–B contacts (per chain) has a smaller value in the perpendicular lamellae. Therefore, in this regime, the incompatibility of A and B monomer units is responsible for the stability of the perpendicular lamellae. On the other hand, under nonwetting conditions, when the contacts polymers/substrate are unfavorable, the stability of the perpendicular lamellae is connected with lower stretching of the chains compared to the stretching in the parallel lamellae.

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