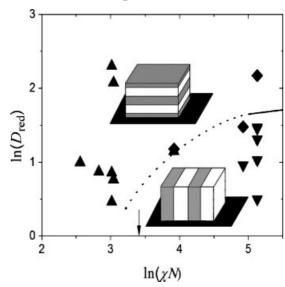# Effect of the Molecular Weight of AB Diblock Copolymers on the Lamellar Orientation in Thin Films: Theory and Experiment

Igor I. Potemkin,* Peter Busch, Detlef-M. Smilgies, Dorthe Posselt, Christine M. Papadakis

We propose a theoretical explanation of the parallel and perpendicular lamellar orientations in free surface films of symmetric polystyrene-*block*-polybutadiene diblock copolymers on silicon substrates (with a native SiO_x layer). Two approaches are developed: A correction to the strong segregation theory and a qualitative analysis of the intermediate segregation regime. We show that the perpendicular orientation of the lamellae formed by the molecules of high molecular weight is stabilized by A–B interfacial interactions. They are weaker in the case of the perpendicular orientation of the lamellae, whereas the surface tension coefficient of the A–B interface decreases with the increase of the molecular weight.

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Introduction

Microphase separation of compositionally symmetric diblock copolymers in the bulk results in the formation of a lamellar microstructure.[1,2] This bulk morphology is also generated in relatively thin films of the diblock copolymers. However, the presence of two boundaries introduces additional degrees of freedom. Most notable is the thermodynamic stability of two different orientations of the lamellae: parallel and perpendicular with respect to the boundaries. Crucial for many applications is the ability to

control the orientation.[3] It was shown in many experiments[4–7] and supported theoretically[8] that primarily a difference in the affinity of the blocks toward the substrate(s) is responsible for the parallel orientation of the lamellae, while similar interactions of both blocks with the substrate(s) can promote a perpendicular orientation of the lamellae.[9–12] Recently we have shown that in the case of free surface films, the interaction parameters of the blocks with the boundaries are not the only means to control the lamellar orientation. Depending on the overall molecular weight, symmetric polystyrene-*block*-polybutadiene [PS-*b*-PB] diblock copolymers on silicon substrates (with a native SiO$_x$ layer) reveal two distinct orientations of the lamellae toward the substrate: parallel (low molecular weight) and perpendicular (high molecular weight).[13] In this paper we will present the orientation diagram of the PS-*b*-PB film, which was obtained using atomic force microscopy[13] and grazing-incidence small-angle X-ray scattering (GISAXS),[16] and propose a theoretical explanation of the observed phenomenon.

Experimental Part

The films were prepared from symmetric PS-*b*-PB diblock copolymers.[2,14] The volume fraction of PB in all the samples was 0.49 ± 0.01. Nine copolymers with molar masses between 13.9 and 183 kg·mol^{-1} and with bulk lamellar thicknesses in the range between 138 and 839 Å were used. The Flory–Huggins interaction parameter is $\chi = A/T + B$ with $A = (21.6 \pm 2.1)K$ and $B = -0.019 \pm 0.005$.[14] In the bulk, we have identified the strong segregation limit where the lamellar thickness scales with the overall number of the statistical segments in the chain N as $N^{0.61}$ and the lamellar interfaces are sharp with nearly no mixing of different monomers, to be reached only above $\chi N \approx 30$.[2] Below this value, only intermediate segregation is encountered, i.e. the concentration profile is not rectangular, but rather sinusoidal, partial mixing of the two types of monomers takes place, and the lamellar thickness scales as $N^{0.83}$.[14]

The films were prepared by dissolving the polymers in toluene and spin-coating films onto Si wafers covered with a native silicon oxide layer. The film thickness was controlled by varying the concentration of the solutions (polymer concentration 0.1–7 wt.-%) and was determined by spectroscopic ellipsometry. For details of the film preparation see ref.[13] Samples with molar masses ≥ 54.5 kg·mol^{-1} were annealed at 150 °C while samples with molar masses below 54.5 kg·mol^{-1} were dried at room temperature in order to avoid dewetting. The AFM images of the films show a clear molar mass dependence of the lamellar orientation at the film surface: Low molar mass films (13.9–54.5 kg·mol^{-1}) show terraces at the surface having a height similar to the bulk lamellar thickness. High molar mass samples (148 and 183 kg·mol^{-1}), on the other hand, show meandering surface textures with repeat distances similar to the bulk lamellar thickness. These results point to a parallel and a perpendicular lamellar orientations near the film surface for low and high molar masses, respectively. This behavior is independent of the reduced film thickness in the range studied, i.e., the ratio between the film thickness and the bulk lamellar thickness.[13] More insight into the lamellar orientation in the interior of the films could be gained using grazing-incidence small-angle X-ray scattering (GISAXS[15–17]). Experiments were carried out at the synchrotron beamlines ESRF ID 10B and at CHESS D-line. The incident angle of the X-ray beam, α_i, is chosen to be slightly above the critical angle of external reflection of the polymer film, α_{cP}, which is 0.15° for PS-*b*-PB. The incident angle is below the critical angle of the substrate. Under these conditions, the X-rays penetrate the film completely, and absorption by the substrate is minimized. Scattering in the plane of incidence, i.e. with scattering vector normal to the film surface, together with the scattering out of the plane of incidence, i.e. with scattering vector parallel to the film surface, is recorded simultaneously by means of a two-dimensional detector. The resulting 2D reciprocal space maps were analyzed in the framework of a model based on the distorted-wave Born approximation (DWBA).[18]

The resulting lamellar orientations inside the films as determined using GISAXS are compiled as a function of χN and the reduced lamellar thickness, D_{red}, which is the ratio between the film thickness and the bulk lamellar thickness, see Figure 1. Low molar mass films have a parallel orientation (the only exception being ultrathin films where no distinct orientation can be defined), whereas two highest molar masses show a perpendicular orientation. Thick high molar mass films approach the bulk limit, i.e. in addition to the perpendicular lamellar orientation, other orientations are observed. Below, we propose a theory explaining the transition of the lamellar orientation as a function of molar mass.
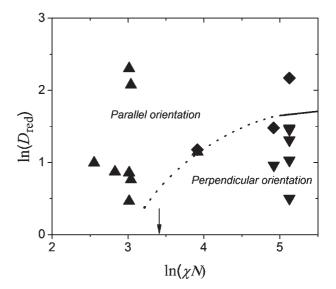

Figure 1. Lamellar orientation in thin films of symmetric polystyrene-*block*-polybutadiene diblock copolymers as observed using GISAXS. The orientations are given in double-logarithmic representation as a function of χN and of the reduced film thickness, D_{red}, which is the ratio between the film thickness and the bulk lamellar thickness. Triangles pointing up: parallel; triangles pointing down: perpendicular; diamonds: coexisting orientations. The solid and dotted curves correspond to the theoretical estimates of the boundary between the orientations. The arrow marks the value of the cross-over between intermediate and strong segregation regime identified for the P(S-*b*-B) system in the bulk (ref.[2],[14]).

Theoretical Part

An important feature determining the behavior of the free surface films is the presence of only one confining solid surface. Therefore, the thickness of the film with parallel orientation of the lamellae is not a fixed parameter. It is determined by the condition of thermodynamic equilibrium: if the amount of polymer in the film does not conform to the optimum (equilibrium) periodicity of the lamellae, the film is macroscopically separated into two films (phases) differing in thickness but each having the equilibrium period of the structure.

Theoretical predictions for the lamellar orientation in the free surface films were formulated in ref.[19] in the strong segregation approximation, $\chi N \gg 1$. The strong segregation theory is asymptotically exact in the limit $\chi N \to \infty$. The finite number of segments introduces corrections to the total free energy which can be taken into account similar to the case of microphase separation in the bulk.[20] Combining the approaches of ref.[19,20] we can write the free energy of the symmetric structure of the parallel lamellae (both boundary layers comprise the same kind of blocks) in the following form:

$$f_{\parallel} = \frac{\pi^2}{12} \frac{L_{\parallel}^2}{Na^2} + \frac{Na\sqrt{\chi}(1-x_{\mathrm{A}})}{2L_{\parallel}} + \ln\left(\frac{16N\sqrt{\chi}a}{\pi L_{\parallel}}\right) \quad (1)$$

Here the first term corresponds to the elastic free energy of the blocks forming brush layers of thickness $L_{\parallel}$, in Figure 2, a and N are the length and the number of the segments in the chain, respectively. The second term is the energy of the various interfaces.[19] The choice of the symmetric structure in comparison with asymmetric (the boundary layers are comprised of different kinds of blocks) is done for determination and does not affect the general conclusions of the calculations. In Equation (1), $a\sqrt{\chi} = \gamma_0$ is the main contribution to the surface tension coefficient of the A–B interface, and x_{A} is the ratio of the spreading

parameter of polymer A, S_{A}, to γ_0 and to the number of layers, $n+1$, each of the thickness $2L_{\parallel}$, $x_{\mathrm{A}} = S_{\mathrm{A}}/\gamma_0(n+1)$.[19] The spreading parameter S_{A} is known to be a combination of the surface tension coefficients of the substrate–air (γ_{sa}), polymer–air (γ_{Aa}), and polymer–substrate (γ_{As}) interfaces, $S_{\mathrm{A}} = \gamma_{\mathrm{sa}} - \gamma_{\mathrm{Aa}} - \gamma_{\mathrm{As}}$. The third term of Equation (1) contains two contributions coming from the correction to the surface tension coefficient of the A–B interface due to localization of the junction points of the blocks at the interface, and from the entropy of the chain ends.[20] The equilibrium value of the free energy is found by minimization with respect to $L_{\parallel}$ which can be done using a perturbation theory

$$f_{\parallel} \approx f_0(1-x_{\mathrm{A}})^{2/3} + \ln\left(\frac{64f_0}{3\pi(1-x_{\mathrm{A}})^{1/3}}\right),$$

$$f_0 = \frac{(3\pi)^{2/3}}{4}(\chi N)^{1/3} \gg 1$$

$$L_{\parallel} \approx L_0(1-x_{\mathrm{A}})^{1/3}\left(1 + \frac{1}{2f_0(1-x_{\mathrm{A}})^{2/3}}\right),$$

$$L_0 = \left(\frac{3}{\pi^2}\right)^{1/3} a\chi^{1/6}N^{2/3} \quad (2)$$

where f_0 and L_0 are the asymptotic values ($\chi N \to \infty$) of the free energy and of the layer thickness in the bulk, respectively. Note that our model does not take into account the difference in the stretching of the blocks in the boundary layers and in the internal ones. This correction has a smaller order of magnitude[21] than the logarithmic term of Equation (2), and can be neglected.

The free energy of the film with perpendicular orientation of the lamellae toward the substrate has a similar form:[19]

$$f_{\perp} = \frac{\pi^2}{12} \frac{L_{\perp}^2}{Na^2} + \frac{Na\sqrt{\chi}}{2L_{\perp}} - \frac{N(S_{\mathrm{A}}+S_{\mathrm{B}})}{2D}$$
$$+ \ln\left(\frac{16N\sqrt{\chi}a}{\pi L_{\perp}}\right) \quad (3)$$

where D is the thickness of the film and S_{B} is the spreading parameter of the blocks B.[19] Minimization of Equation (3) gives

$$f_{\perp} \approx f_0 - \frac{N(S_{\mathrm{A}}+S_{\mathrm{B}})}{2D} + \ln\left(\frac{64f_0}{3\pi}\right)$$

$$L_{\perp} \approx L_0\left(1 + \frac{1}{2f_0}\right)$$
$$(4)$$

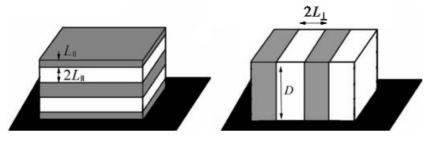where the thickness of the brush layer $L_{\perp}$ coincides with that in the bulk. A condition for the transition between

Figure 2. Schematic representation of parallel and perpendicular lamellar orientations in thin films of symmetric diblock copolymers. $L_{\parallel}$ and $L_{\perp}$ denote the corresponding thicknesses of the brush layers. It is assumed that each internal layer of A (gray) or B (white) type of the parallel lamellae has thickness $2L_{\parallel}$ (approximation of impenetrable brush layers) whereas the boundary layers are half this thickness. The total number of internal layers is denoted by n. The thickness of A and B layers of the perpendicular lamellae is $2L_{\perp}$.

the parallel and perpendicular structures can be found by equating the free energies, $f_\parallel = f_\perp$, considering that the film thickness $D = 2(n+1)L_\parallel$:[19]

$$3 + (\alpha - 2)x_A - 3(1 - x_A)^{1/3}$$
$$= \frac{1}{f_0}\left[(1 - x_A)^{1/3}\ln(1 - x_A) + \frac{x_A(\alpha + 1)}{2(1 - x_A)^{2/3}}\right],$$
$$\alpha = \frac{S_B}{S_A} \tag{5}$$

This condition determines the relation between the surface tension coefficients, the film thickness and the length of the blocks at the transition. The phase diagram of the film in the limit $f_0 \to \infty$ is presented in ref.[19] To fit the experimental data, let us find the dependence of the reduced film thickness (i.e. the ratio of the film thickness to the period of the lamellar structure in the bulk), D_{red}, on N at the condition given by Equation (5):

$$D_{red} \equiv \frac{D}{4L_\perp} = \frac{(n+1)L_\parallel}{2L_\perp}$$
$$\approx \frac{S_A}{2a\sqrt{\chi}}$$
$$\times \frac{(1 - x_A)^{1/3}}{x_A}\left(1 + \frac{1}{2f_0(1 - x_A)^{2/3}} - \frac{1}{2f_0}\right) \tag{6}$$

This parameter as a function of f_0 has the form $J + H/f_0 + \ldots$. Numerical calculations demonstrate that the coefficient H is always negative which means that D_{red} is an increasing function of N. A very simple expression for D_{red} can be found for the case of thick enough films (or small values of the spreading parameters), $|x_A| \ll 1$. In this case the orientational transition occurs at

$$1 + \frac{1}{f_0} \approx \frac{x_A}{3(1 - \alpha)} \equiv \beta^*, \quad 1 - \alpha \ll 1 \tag{7}$$

see Equation (5), and

$$D_{red} \approx \frac{S_A}{6a\sqrt{\chi}(1 - \alpha)}\left(1 - \frac{1}{f_0}\right) \tag{8}$$

Equation (7) means that the perpendicular orientation of the lamellae is stable at $1 + 1/f_0 < \beta^*$ while the parallel lamellae are formed at $1 + 1/f_0 > \beta^*$. Therefore, the transition from the parallel to the perpendicular lamellae can be induced by increasing the number of segments of the chain, $N(f_0 \sim N^{1/3})$.

To clarify the physical meaning of the lamellar reorientation upon variation of the molecular weight, let us compare the different contributions to the total free energies of both structures: the elastic energy, f_{el} [the first term of Equation (1) and (3)], A–B interfacial energy, f_{AB}

[the first part of the second term of Equation (1) and the second term of Equation (3)], the surface energy of the boundaries of the film, f_b [the second part of the second term of Equation (1) and the third term of Equation (3)], and the penalty in the free energy accounting for localization of the junction points of the blocks at the interfaces and the entropy of the chain ends, f_{je} [the last term of Equation (1) and (3)]

$$\frac{f_{el}^\parallel}{f_{el}^\perp} \approx 1 - \frac{2\overline{x}_A}{3}, \quad \frac{f_{AB}^\parallel}{f_{AB}^\perp} \approx 1 + \frac{\overline{x}_A}{3}, \quad \frac{f_b^\parallel}{f_b^\perp} \approx \frac{2}{1 + \alpha}$$
$$\frac{f_{je}^\parallel}{f_{je}^\perp} \approx 1 + \frac{\overline{x}_A}{3\ln(64f_0/3\pi)}, \quad |\overline{x}_A| = \frac{|x_A|}{(1 + 1/f_0)} \ll 1 \tag{9}$$

Under wetting conditions (both spreading parameters are positive) $f_{el}^\parallel/f_{el}^\perp < 1, f_b^\parallel/f_b^\perp < 1$ and $f_{AB}^\parallel/f_{AB}^\perp > 1, f_{je}^\parallel/f_{je}^\perp > 1$. Therefore, we can say that the A–B interfacial interactions and localization of the junction points stabilize the perpendicular lamellar orientation. Increasing N (i.e. $\overline{x}_A$) results in decreasing $f_{el}^\parallel/f_{el}^\perp$ and $f_{je}^\parallel/f_{je}^\perp$ but increasing $f_{AB}^\parallel/f_{AB}^\perp$. Since the contribution $f_{AB}^\perp$, which is responsible for the stability of the perpendicular structure, decreases on increasing N (compared to $f_{AB}^\parallel$), the A–B interfacial interactions are the driving forces for the reorientation. Indeed, the dependence on N can be included in the effective surface tension coefficient $\gamma = \gamma_0(1 + 1/f_0)$ which, when decreasing, leads to the thinning of the parallel lamellae, $L^\parallel/L^\perp \approx 1 - \overline{x}_A/3$, and to the increase in the A–B interfacial area, i.e. of $f_{AB}^\parallel$.

As we mentioned above, the strong segregation regime can be reached only above $\chi N \approx 30$.[2,14] Below this value, $10 < \chi N < 30$, only intermediate segregation is encountered. Indeed, in this range of values of χN, the main correction to the strong segregation theory $\sim 1/f_0$ is not negligible (for example, $1/f_0 \approx 0.33$ at $\chi N = 20$) and the perturbation theory has to be modified. It was predicted theoretically[22–24] and confirmed experimentally[2,14,25] that in the intermediate segregation regime, the domain spacing in the bulk has a stronger dependence on N compared to the strong segregation regime. Let us assume that in the intermediate segregation regime the stretching of the blocks (the end-to-end distance) follows a power law, $R_\delta \approx a\chi^{1/6}N^{2/3}(\chi N)^\delta, \delta \geq 0$. Here the parameter δ is not a constant: With increasing χN, it gradually decreases from a certain, positive value to 0. To calculate the free energy of the lamellar structure in the bulk in the intermediate segregation regime, let us refer to the blob picture. Each chain can be considered as a sequence of blobs, each of size ξ and with a number of segments g. The relation between ξ and g is chosen from the condition that the chain is not stretched at length scales smaller than ξ, i.e. $\xi \approx ag^{1/2}$. Then the free energy of the chain is proportional to the number

of the blobs $f_\delta \approx N/g \approx R_\delta/\xi \approx (\chi N)^{1/3+2\delta}$. To apply the results of the strong segregation theory to the case of the intermediate segregation regime, let us substitute the real chains by virtual ones having M segments of the size a. We assume that the end-to-end distance of the virtual chain coincides with the one of the real chain and follows exactly the same power law as in the strong segregation regime, $R_\delta \approx a\overline{\chi}^{1/6}M^{2/3}$. Here $\overline{\chi}$ differs from χ to provide the strong segregation condition. Equating the free energy of the virtual chain to f_δ, $(\overline{\chi}M)^{1/3} \approx f_\delta$, we get $\overline{\chi} \approx \chi(\chi N)^{6\delta}$ [or $\overline{\gamma} \approx \gamma_0(\chi N)^{3\delta}$ for the surface tension coefficient]. Therefore, D_{red} of the system with the virtual chains at the condition of the transition from the parallel to the perpendicular lamellae [Equation (5) at $f_0 \to \infty$) has the form

$$
\begin{aligned}
D_{\mathrm{red}} &\approx \frac{S_A}{2a\sqrt{\overline{\chi}}} \frac{(1-x_A)^{1/3}}{x_A} \\
&\approx \frac{S_A}{2a\sqrt{\chi}(\chi N)^{3\delta}} \frac{(1-x_A)^{1/3}}{x_A}
\end{aligned}
\tag{10}
$$

i.e., D_{red} of the real system in the intermediate segregation regime depends on N.

In order to fit the experimental data of Figure 1, let us rewrite Equation (10) in the form

$$
\begin{aligned}
\ln(D_{\mathrm{red}}) &= c - 3\delta \ln(\chi N),\ c \\
&= \ln\left(\frac{S_A}{2a\sqrt{\chi}} \frac{(1-x_A)^{1/3}}{x_A}\right)
\end{aligned}
\tag{11}
$$

where parameters c and δ are considered as the fitting parameters. The dependence of δ on χN can be found in the limit $\chi N \gg 1$ if we use the result for the surface tension coefficient in the strong segregation regime,[20] $\gamma \approx \gamma_0[1 + 0.9\ln(\chi N)/(\chi N)^{1/3}]$, $\delta \approx 0.3/(\chi N)^{1/3}$. Relying on the experimental results for the parameter δ in the intermediate segregation regime,[14] $\delta \approx 0.22$ at $\chi N = 25$, we choose $c \approx 2.5$. The solid part of the boundary curve in Figure 1 corresponds to Equation (11) with $\delta \approx 0.3/(\chi N)^{1/3}$. The dotted part of the curve has an expected monotonic behavior of the boundary whose δ varies with χN, and $\delta \approx 0.22$ at the point $\ln(\chi N = 25) \approx 3.22$ and $\ln(D_{\mathrm{red}}) \approx 0.376$. The physical reason for the lamellar reorientation in the intermediate segregation regime can also be found in the decrease of the effective surface tension coefficient ($\overline{\gamma}$) with increasing N.

Conclusion

In conclusion, we demonstrate that depending on the molecular weight of the compositionally symmetric PS-*b*-PB diblock copolymers, both the parallel and the perpendicular orientation of the lamellae in thin films can be stable. The transition from the parallel to the perpendicular orientation with increasing molecular weight is driven by A–B interfacial interactions which are weaker for longer molecules in the perpendicular orientation of the lamellae.

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