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Static and Kinetic Aspects of the Ordering Transition in Thin Films of Diblock Copolymers

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ABSTRACT: Using time-resolved X-ray reflection experiments, we have investigated the surface structure of thin films of a symmetric diblock copolymer of polystyrene-*b*-polyisoprene (M_W = 15 700). The film thickness ranges from 20 to 80 nm. The ordering transition is observed in a temperature-driven experiment. We find the transition temperature to be raised above its bulk value. It is close to the transition temperature of the ideal mean-field system. The evolution of order proceeds through a roughening of the film surface and subsequently the formation of an incomplete top layer. In atomic force microscopy measurements this layer is shown to consist of islands and depressions. The thickness of this layer is precisely one bulk lamellar period L = 16.2 nm. The lamellae are oriented parallel to the substrate. The base layer is expanded in thickness to 20 nm. The formation of the ordered structure follows the same time constants that were found for the long-range ordering process in the bulk of this polymer.

1. Introduction

The ability of block copolymers to form ordered mesophases has attracted considerable attention in recent years. The rich variety of ordered morphologies has been explored, and the factors determining their stability are defined. Whereas the basic phenomenon of mesophase formation is generally understood, there are suggestions that the phase diagram discussed today may still be incomplete.[1,2] The transition between the ordered and the disordered state of block copolymers, the microphase separation transition (MST), may be observed in scattering experiments or by measuring the rheological properties of the material. It is governed by the balance of the entropy of mixing on one side and the—mostly—repulsive interaction between the different blocks of the polymer on the other side. This interaction is parametrized by the Flory–Huggins parameter χ which serves as a control parameter in the fundamental mean-field theory of the MST by Leibler.[1] Only if χ is strongly dependent on temperature can one expect to observe the MST in a temperature-driven experiment. In such experiments it has been shown[3,4] that concentration fluctuations play an important role in the thermodynamics of block copolymers near the disorder-to-order transition. In particular, for symmetric diblock copolymers the MST was characterized as a fluctuation-induced first-order phase transition. Only recently the kinetics of the MST in bulk block copolymers has been investigated using time-resolved scattering experiments[5,6] or the time dependence of the dynamic shear modulus.[7–9] The interesting observation here was that the structure formation at the transition from disorder to order obviously proceeds on two well-separated time scales[5] which are interpreted as a local demixing and a subsequent ordering on long range.[6]

The present work focuses on the static and the kinetic aspects of the MST in thin films of diblock copolymers. We present results from X-ray reflection experiments on films of a polystyrene/polyisoprene diblock copolymer. The bulk properties of the MST in this polymer have been extensively studied, and we can therefore separate the influence of the thin film geometry on the MST. Previous experiments have shown that the ordering in thin films comprising only a few lamellar layers leads to a rough surface structure that has been described as consisting of islands and depressions.[10] This feature is a consequence of the film thickness D being incommensurate with the lamellar thickness L that is essentially defined by the composition and the molecular weight of the block copolymer.[11] In ultrathin films with a thickness less than one lamella a stable layer was found for $D = L/2$.[12] We have investigated a series of films ranging in thickness between one and four lamellae and characterized the surface structure of the ordered films with reflection experiments and atomic force microscopy. The variation of film thickness with temperature is studied across the bulk transition temperature T_{MST} and an instability is observed above T_{MST} that is interpreted as the order-to-disorder transition of the film. Finally we have investigated the kinetics of ordering in the thin films and compared it to the ordering kinetics in the bulk.

2. Experimental Section

2.1. Sample Description. The polystyrene/polyisoprene diblock copolymer used in this study is the same as the one in ref 4. Its molecular weight is 15 700, and the polydispersity M_W/M_N = 1.04. The volume fraction of polystyrene has been determined with NMR to be f = 0.44. The ordered state is of lamellar symmetry, and the bulk lamellar thickness is 16.2 nm. The phase transition temperature in the bulk was determined using small-angle X-ray scattering (SAXS) and measurements of the dynamic shear modulus G^*. It was consistently found to be T_{MST} = 362 K (±2).[4] Thin films of the block copolymer were prepared by dissolving it in toluene at concentrations ranging from 6 to 18 mg/mL. The solution was then spin cast onto a microscope slide.

2.2. X-ray Reflection Camera. The X-ray reflection experiments were carried out in a Kratky compact camera (Paar, Graz, Austria) which has been modified to operate in reflection geometry.[13,14] The source of radiation is a rotating-anode generator with a copper anode. The wavelength used is Cu Kα: λ = 0.1542 nm. The sample table is 35 mm long and 33 mm wide and is located in the evacuated camera. Its temperature may be controlled with a stability of ±0.1 K. It can be tilted with respect to the primary beam with an angular resolution of 0.0175 mrad. The reflected intensity is mono-

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chromatized with a graphite crystal and analyzed with a scintillation counter. This detection unit may be positioned automatically with a resolution of the scattering angle 2Θ of 0.025 mrad. The reflected beam is scanned through 2Θ at a fixed position of the sample table. It is then possible to determine the background scattering and to obtain the corrected integrated intensity of the reflected beam. Using a series of calibrated attenuators in the primary beam, this setup allows the measurement of the reflection coefficient R in a range of 6 orders of magnitude.

3. Discussion of Results

In the following we will focus on the process of structure formation at the MST in thin films of a symmetric diblock copolymer. An important prerequisite for this investigation is a detailed study of the MST in the bulk of the same polymer. Results of this work have been published previously,[4,6] and only the results that are relevant for our present topic shall be summarized. SAXS experiments measure the structure factor of concentration fluctuations and therefore allow a determination of the phase state as well as of the transition temperature T_{MST}. As was mentioned in the Experimental Section $T_{\mathrm{MST}} = 362$ K was observed in a discontinuity of the scattered X-ray intensity at the maximum of the structure factor located at a scattering vector $q^* = 0.41\ \mathrm{nm}^{-1}$. A further source of information on the bulk phase transition are experiments that probe the segmental and chain dynamics of diblock copolymers. Dielectric normal-mode spectroscopy clearly showed the change of the local composition at the ordering transition.[15] It was found to occur in a rather broad transition regime ($\Delta T \approx 30$ K) around T_{MST}. Also the center of mass diffusion of the polymer chain as observed in field gradient NMR measurements[16] revealed a gradual disappearance of barriers caused by the structure of the ordered state when traversing T_{MST} from order to disorder. These findings support the notion of a fluctuation-controlled temperature regime above T_{MST}. For our polymer the limit for the validity of mean-field theory is given in terms of the spinodal temperature $T_{\mathrm{s}} = 388$ K. T_{S} was determined from an extrapolation of the temperature dependence of the X-ray intensity at q^* at temperatures above 390 K. The MST in the symmetric diblock copolymer is accordingly described as a fluctuation-induced first-order phase transition. The fact that the actual ordering transition occurs below T_{s} is caused by a stabilization of the disordered state due to concentration fluctuations.

The X-ray reflection measurements on thin films of the diblock copolymer are unable to directly detect the internal structure of the film as the electron-density difference between polystyrene and polyisoprene is only 10%. The signal is dominated by the interference of the waves reflected from the substrate and the surface of the sample, respectively. This interference leads to an oscillating behavior (Kiessig fringes) of the reflection curve $R(\Theta)$ as is seen in Figure 1. The thickness D of the film shows up as the period of the Kiessig pattern:[17]

$$R = \frac{R_{\mathrm{F}}}{\varrho_{\mathrm{s}}^2}[\varrho_{\mathrm{f}}^2 \mathrm{e}^{-\sigma_{\mathrm{f}}^2 q_z^2} + (\varrho_{\mathrm{s}} - \varrho_{\mathrm{f}})^2 \mathrm{e}^{-\sigma_{\mathrm{s}}^2 q_z^2} + 2\varrho_{\mathrm{f}}(\varrho_{\mathrm{s}} - \varrho_{\mathrm{f}}) \mathrm{e}^{-(\sigma_{\mathrm{f}}^2+\sigma_{\mathrm{s}}^2) q_z^2/2} \cos q_z D] \quad (1)$$

The electron densities of the film and substrate are ϱ_{f} and ϱ_{s}, respectively, and the Fresnel reflectivity of the neat substrate is

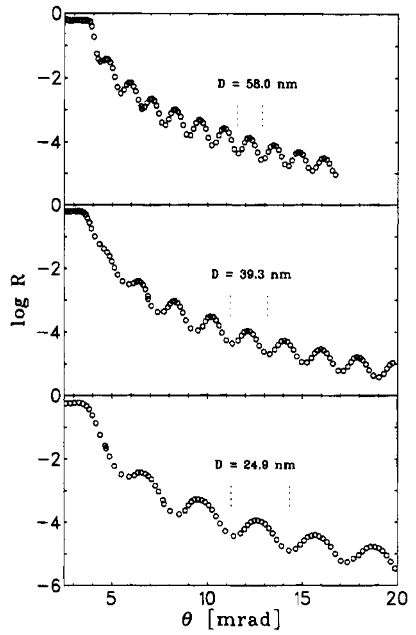

Figure 1. X-ray reflection measurement of spin-cast films with varying thickness D. The period of the Kiessig pattern is a direct measure of the film thickness.

$$R_{\mathrm{F}} = \left(\frac{\Theta_{\mathrm{c}}}{\Theta + (\Theta^2 - \Theta_{\mathrm{c}}^2)^{1/2}}\right)^4 \quad (2)$$

with the critical angle for total reflection $\Theta_{\mathrm{c}} \propto \sqrt{\varrho_{\mathrm{s}}}$. For the glass substrate used in our experiment we find $\Theta_{\mathrm{c}} \approx 4$ mrad (cf. Figure 1) corresponding to an electron density $\varrho_{\mathrm{s}} \approx 7.4 \times 10^{23}\ \mathrm{cm}^{-3}$ which is in accord with the known density of the material. The angle Θ is between the X-ray beam and the plane of the reflecting surface and therefore half the scattering angle 2Θ. Correspondingly, $q_z = (4\pi/\lambda) \sin \Theta$ is the component of the scattering vector perpendicular to the plane of reflection, and for specular reflection the scattering vector has no lateral component.

The roughness of the film surface and substrate is included in eq 1 by the mean-squared displacement of the reflecting surface σ_{f}^2 and σ_{s}^2, respectively. It appears as Debye–Waller factors, effectively damping the interference pattern with increasing length of the scattering vector q_z.

Equation 1 is written for the condition $\Theta \gg \Theta_{\mathrm{c}}$ which is the regime of validity for Born's approximation[18] and shows the correspondence between the reflection experiment and the small-angle scattering experiment. However, this is not a necessary simplification in the interpretation of X-ray reflection data. Close to Θ_{c} the effect of refraction may be taken into account in the calculation of the scattering vector. Alternatively, the problem of calculating the reflection profile $R(\Theta)$ for a given electron-density profile $\varrho(z)$ may be solved exactly by making use of numerical methods based on matrix methods.[19,20] In the following we will use both methods in parallel for an analysis of the experimental data.

3.1. Surface Structure of Disordered and Ordered Films. In Figure 1 we show the results of reflectivity measurements on several of the thin films. The curves drawn through the data are a fit of eq 1, with the film thickness D and the roughness σ being the only adjustable parameters. σ is found to be 5 Å and of the same value as for the neat surface. The film thickness may be obtained from these measurements

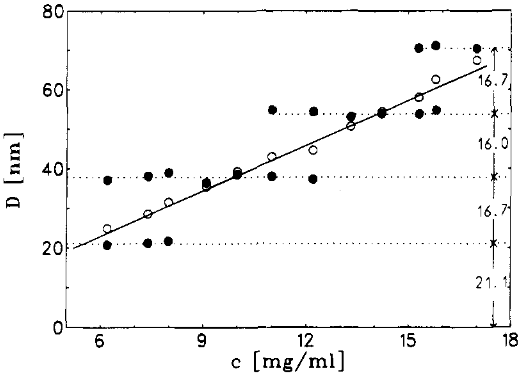

Figure 2. Initial film thickness (○ and full line) depending linearly on the concentration of the solution c in the spin-casting process. During annealing the film surface breaks into the island and depression structure. Two periods appear in the Kiessig pattern resulting in two film thicknesses (●). The broken lines mark completely filled lamellae. Their thickness is given in the figure. The base lamella is expanded in thickness over the bulk value.

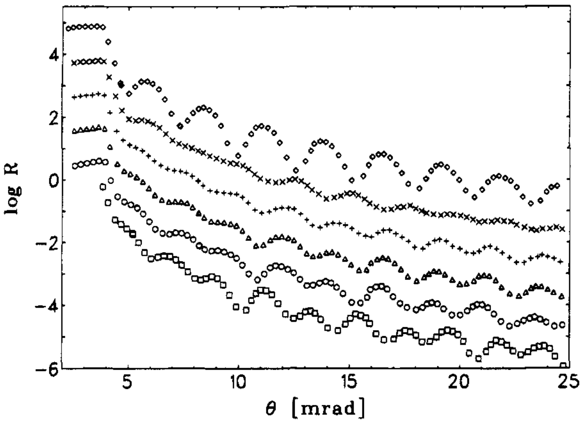

Figure 3. Reflection curves during the annealing at $T = 333$ K. The curves have been shifted vertically. The data refer to the as-cast film (◇) and annealing times of 10 (×), 20 (+), 30 (△), 50 (○), and 80 min (□).

with good precision. Figure 2 displays these results. Obviously D varies nearly linearly with the concentration of the solution in the spin-casting procedure

$$D/[\mathrm{nm}] = 3.82\ (\pm 0.02)c/[\mathrm{mg/mL}]$$

We are thus able to prepare films with a predefined thickness.

The spin-casting process will leave the diblock copolymer in a state of no long-range order. This may be concluded from the slow structure formation observed in this material,[6] which takes place on the scale of minutes up to hours. Also annealing at room temperature will not change the structural state of the block copolymer as the glass transition temperature of the polystyrene domain is $T_g = 330$ K. Annealing the film just above T_g, however, will start the process of structure formation, and we will now discuss the changes of the film structure resulting from the ordering transition in the diblock copolymer. The annealing was done in an evacuated oven or in the evacuated Kratky camera. Figure 3 shows the reflection data for the example of an annealing temperature of 333 K. The data were obtained by subsequently annealing the film for 10 min. Then it is cooled to room temperature and the reflection profile is registered, which takes about 1 h for each set of data. Within the first 10 min the film shows a strong roughening which leads to a disappearance of the Kiessig fringes. In the subsequent measurements one observes a revival of the flat surface structure as indicated by the increasing amplitude of the Kiessig fringes. However, their period is no longer described by the single cosine of eq 1, as was the case for the initial state of the experiment. With increasing annealing time one clearly discerns two periods in the reflection pattern of Figure 3, indicating the existence of two lengths giving rise to interference in the reflected X-ray beam.

In order to quantitatively analyze these data, we extend eq 1 to the case of a reflecting film consisting of areas that refer to two different film thickness D_1 and D_2. Such a structure was recently observed in ref 21 using neutron reflection experiments. Assuming the coherence length of the X-ray beam to be larger than the lateral size of this structure of islands and depressions, one obtains

$$R = R_F\left[\frac{\varrho_f^2}{\varrho_s^2}\{\alpha^2 + (1-\alpha)^2 + 2\alpha(1-\alpha)\cos q_z(D_2 - D_1)\}e^{-\sigma_f^2 q_z^2} + \left(\frac{\varrho_s - \varrho_f}{\varrho_s}\right)^2 e^{-\sigma_s^2 q_z^2} + 2\frac{\varrho_f(\varrho_s - \varrho_f)}{\varrho_s^2}e^{-(\sigma_f^2+\sigma_s^2)q_z^2/2}\{(1-\alpha)\cos q_z D_1 + \alpha\cos q_z D_2\}\right] \quad (3)$$

The new parameter entering eq 3 is the area fraction α that is covered with islands giving rise to the film thickness D_2, whereas the remaining surface fraction $1 - \alpha$ belongs to a film thickness D_1. The detailed form of eq 3 depends on the coherence assumption quoted above. In the incoherent case the term $\propto\cos q_z(D_2 - D_1)$ is dropped. However, it modulates the reflection pattern only weakly.

A practical method for the evaluation of the coverage α and the film thicknesses D_1 and D_2 from the experimental reflection profile is to determine the properties of the substrate in a separate measurement. The reflection coefficient of the sample is then divided by this data. This procedure removes the strong angular dependence of R due to the Fresnel reflection coefficient. The Debye–Waller factors are nearly cancelled. The quantity left corresponds to the expression in square brackets in eq 3. It is the structure factor of the film S_{film}.

$$S_{\mathrm{film}} = \frac{\varrho_f^2}{\varrho_s^2} + \left(\frac{\varrho_s - \varrho_f}{\varrho_s}\right)^2 + 2\frac{\varrho_f}{\varrho_s}\left(\frac{\varrho_s - \varrho_f}{\varrho_s}\right)\{(1-\alpha)\cos q_z D_1 + \alpha\cos q_z D_2\} \quad (4)$$

It is evident from eq 4 that the surface structure of the film is only visible for sufficiently large electron-density differences between film and substrate. In the present case we have $(\varrho_s - \varrho_f)/\varrho_f \approx 1.46$ and $\varrho_s/\varrho_f \approx 2.46$. The desired values for α, D_1, and D_2 may be extracted from eq 4 by a least-squares fitting procedure or a Fourier transformation (see below).

Whereas eq 3 is expected to hold for the regime of large scattering angles, the full curve is described in the same structural model, with the matrix method assuming a density profile

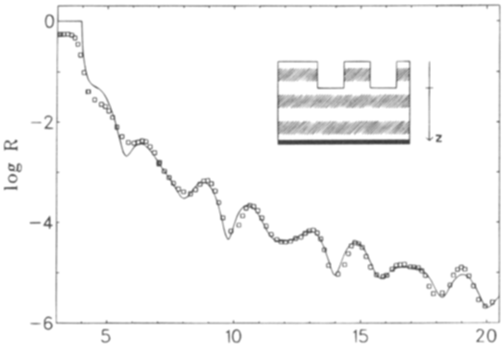

Figure 4. Reflection profile of a film with island and depression structure. The initial film thickness was 30 nm. The film was annealed at $T = 358$ K for 1 h. The full curve is a fit using the matrix method according to eq 5. The inset schematically shows a cut through the film with the incomplete top layer.

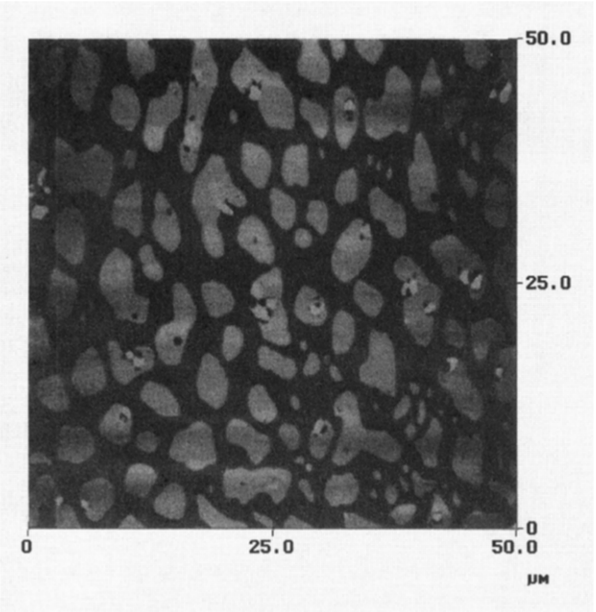

Figure 5. Atomic force microscopy measurement of a thin film of the diblock copolymer after annealing to attain the ordered state. The difference in height between light and dark areas is just one lamellar period. The surface is covered with depressions, giving rise to an incomplete coverage of the top layer.

$$\varrho(z) = \alpha\varrho_f\vartheta(z,\sigma_f) + (1-\alpha)\varrho_f\vartheta(z-d,\sigma_f) + (\varrho_s - \varrho_f)\vartheta(z\text{-}D_2,\sigma_s) \quad (5)$$

$\vartheta(z,\sigma)$ describes the smooth variation of the electron density at the film surface and the substrate on a length scale of σ. It is expressed in terms of the error function as $\vartheta(z,\sigma) = 1/2\,[1 + \mathrm{erf}(z/\sqrt{2}\sigma)]$.

Equation 5 yields the result of 3 within Born's approximation. The structural model is depicted in the inset of Figure 4.

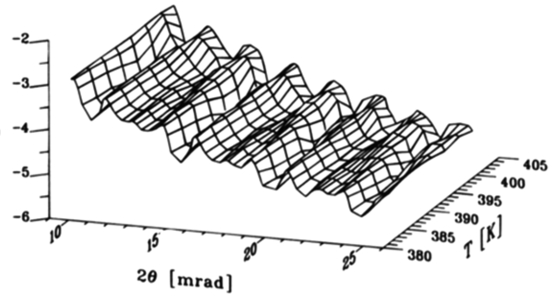

Figure 6. Temperature-dependent reflection experiment of a film with initial thickness $(2 + \alpha)L$. Heating leads to the disappearance of the second period in the Kiessig pattern corresponding to a thinner film of thickness $2L$.

Figure 4 demonstrates that this model is in very good accordance with the experimental data. The data deviate at very small angles due to a waviness of the sample on a long length scale that becomes more effective at small angles due to the then large reflecting area of the sample. The thickness D_1 and D_2 of the block copolymer films differ by just one bulk period L. The formation of islands and depressions may therefore be considered as a result of the competition between the film thickness as defined in the spin-casting process and the internal length L of the ordered microphase-separated state. It leads to a rather orderly structure as opposed to the intermediate state observed after short annealing times. In order to display the effect of this competition for films of thicknesses between $1L$ and $4L$, we refer back to Figure 2. Whereas the open symbols here display the thickness of the initial, disordered film, the full symbols are the thicknesses D_1 and D_2 characterizing the equilibrium state of the film after annealing. Obviously the ordering causes a partitioning of the surface into two states that are integral multiples of the lamellar thickness L. The model suggested in the inset of Figure 4 assumes the substrate and the free surface to be the same component. This is supported by the fact that no thickness of type $(n + {}^1\!/_2)\,L$ could be observed for our system. The detailed internal structure, i.e., the variation of the electron density between polystyrene and polyisoprene, has a negligible effect on the data. It is therefore not possible to decide on the basis of these measurements which component is enriched at the interfaces of the film. The base layer of the films comprising between one and four lamellae is extended in its thickness by nearly 30%. We ascribe this increased layer thickness to the strong affinity of one component to the glass substrate. This causes a strong segregation of polystyrene from polyisopropene.

The lateral structure of the ordered diblock copolymer film may be studied with atomic force microscopy (AFM).[22] Figure 5 displays the surface structure of a film that had an initial thickness of 45 nm. It orders into a film of thickness $2L$ which is covered with islands and depressions of an average lateral size of 4 μm. The depth of the depressions is one lamellar thickness L within experimental error. The AFM measurements confirm the picture of an incomplete surface layer. For a quantitative discussion of the coverage α, we return to the reflection experiment which intrinsically provides an average over the film surface. In AFM experiments these averages have to be performed numerically and they are limited by the small area of observation.

3.2. Disordering of Ordered Films. We now turn to the question of the stability of the ordered film structure when temperature is raised and the system crosses the phase transition between the ordered and the disordered state. Figure 6 presents a series of reflection data of a film that had been annealed at $T = 348$ K to attain its ordered structure. No significant change of the reflectivity profile is found between room temperature and 380 K. The data in Figure 6 therefore start at 380 K. Data were taken in steps of 2−3 K, and the sample was annealed for 30 min before each measurement. It is seen in the figure that the original

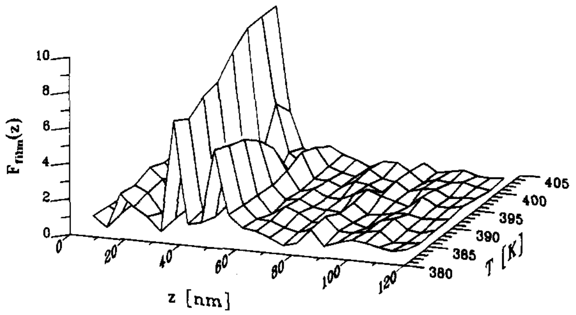

Figure 7. Fourier transform of the film structure factor (cf. eq 4) shows the change of film thickness above $T_c = 390$ K.

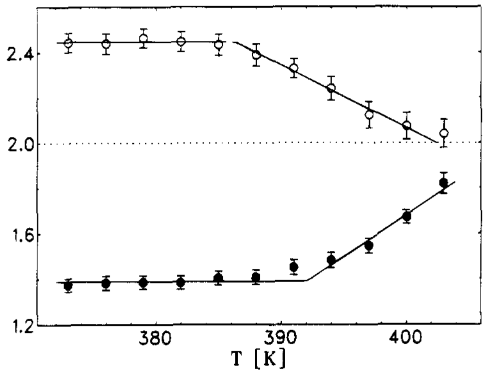

Figure 8. Heating (○) and cooling (●) runs of a film with initial thickness $2L$ with an incomplete top layer with coverage $\alpha = 0.42$.

Kiessig pattern consisting of two periods continuously transforms into a one-period pattern characteristic of a film with a flat surface. This feature becomes even more evident if the reflection data are corrected for the Fresnel term R_F and the Debye–Waller factor (cf. eq 4) as described above and subsequently Fourier transformed with respect to q_z resulting in $F_{film}(z)$. According to eq 4, the transform should exhibit peaks at positions D_1 and D_2, with intensities corresponding to the coverage α and $1 - \alpha$, respectively. The initial structure clearly shows two periods that are $2L$ and $3L$, respectively (see Figure 7). The film consists of two complete lamellae and is covered with islands of again one lamellar period thickness and a large lateral extent. The coverage α of the base film with islands is determined with a fit of eq 4 to be $\alpha = 0.42$. With increasing temperature the peak at $D_2 = 3L$ in Figure 7 decreases in intensity and disappears abruptly above 390 K. At the same temperature there is an increase in intensity of the peak at $D_1 = 2L$.

In Figure 8 we show the temperature dependence of the effective film thickness $n + \alpha$ for the heating and the subsequent cooling run of the sample. n is the number of complete lamellae in the film. The above-described loss of the coverage occurs at a well-defined temperature of 386 K.

Subsequent cooling of the film does not take us back to the same initial state. Whereas the heating ends with a thickness of $2L$ and a vanishing coverage, the cooling then leads to formation of a film of thickness $1 + \alpha$. Its surface again breaks into the island and depression structure, and this process stabilizes below 392 K. The evolution of the island and depression structure continues during the two subsequent measurements at $T = 403$ K.

The transition temperature of the bulk has no effect on the observed process. Instead, a significantly higher temperature T_c marks the limit of stability of the ordered state. Above T_c the tilting of the sample during the reflection experiments suffices to induce lateral flow which destroys the surface structure of the film and causes a continuous decrease of its thickness. The maximum tilt angle during a reflection measurement is 3°. This process is stopped below T_c. In the bulk one finds a decrease of the shear modulus G' at T_{MST}. This suggests to relate T_c to the ordering transition temperature of the thin film.

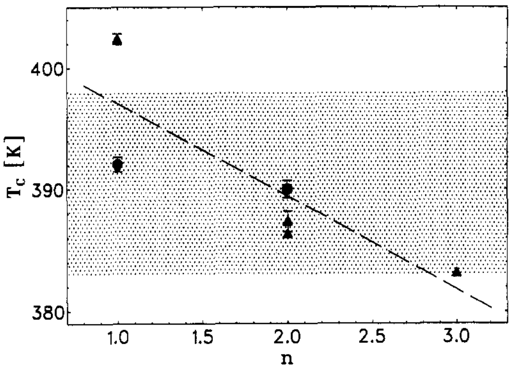

Figure 9. Transition temperatures of the thin block copolymer films. n is the number of complete lamellae (▲, heating; ●, cooling). The shaded area marks the regime of the spinodal temperature T_s determined in the bulk of the same polymer.

T_c depends strongly on the number of lamellae constituting the film, as is seen in the heating and cooling cycle of Figure 8. For films with thicknesses between one and three lamellae T_c varies by 20 K, as is shown in Figure 9. The straight line in the figure is only intended to demonstrate the monotonic decrease of T_c with film thickness. It is on the order of the spinodal temperature T_s that marks the limit of stability for the disordered state in the bulk if mean-field theory is assumed to be a valid description.

The reason for the shift of the transition temperature from its bulk value T_{MST} to the mean-field spinodal value T_s lies in the suppression of concentration fluctuations in the thin film as compared to the bulk.[11] The existence of a stable disordered state below T_s in the bulk is due to the formation of concentration fluctuations which allow polystyrene and polyisoprene segments to separate without the formation of long-range order. Such a shift of T_{MST} has already been observed earlier for thick films consisting of 100–1000 lamellae.[23] In the case of less than three lamellae, concentration fluctuations appear to be completely suppressed.

3.3. Kinetics of Structure Formation in Thin Block Copolymer Films. We now discuss the kinetics of the formation of the ordered structure in the thin diblock copolymer films. We focus here on the development of an island and depression structure. The variation of the lateral size distribution (see Figure 5) has been studied with interference microscopy.[24] The starting point is the film as prepared in the spin-casting process. It shows no island and depression structure. For these experiments we choose films of a thickness that is incommensurate with the lamellar period L such that the ordering process may be observed in the evolution of a reflection pattern due to two film thicknesses as shown above Figure 3. On the basis of eqs 4 and 5, we can evaluate the coverage α of the homogeneous film with islands. α is consistently obtained using the method of Fourier transformation as described above or the matrix algorithm based on eq 5. The coverage may be measured in time intervals of 10 min.

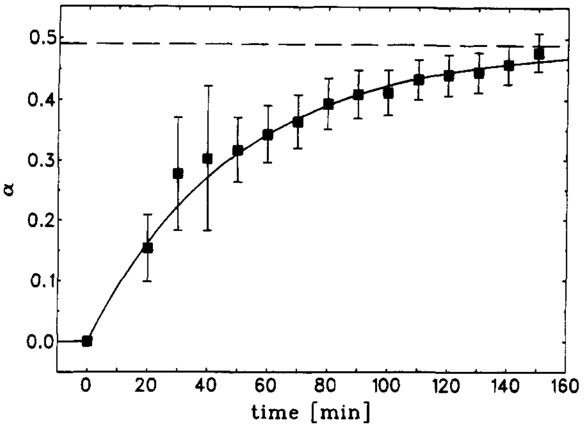

Figure 10. Time dependence of the development of an island and depression structure at $T = 331$ K.

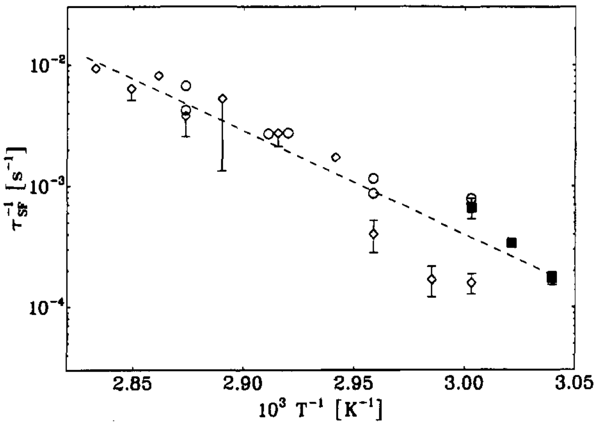

Figure 11. Temperature dependence of the structure formation times in thin films (■) in comparison with results from measurements on bulk samples (◇, ref 5; ○, ref 6).

The films are annealed in the horizontal positioned. They are then quenched to room temperature, and the reflection experiment is carried out.

Figure 10 displays the results for a time-resolved reflection experiment during annealing at 331 K. It is seen that α increases exponentially with time. At long times it approaches a limiting value of $\alpha = 0.49$ in Figure 10. The rise time τ for the full curve in Figure 10 is 49 min. The time constant for the formation of the island and depression structure depends strongly on temperature. Decreasing the temperature by 2 K changes τ to 92 min. This drastic variation of τ with temperature is shown in Figure 11 in an Arrhenius representation. The figure also includes the time constants for the formation of long-range order in the bulk of the same diblock copolymer. They were obtained by time-resolved small-angle scattering.[5,6] All three sets of data agree even in their absolute value and correspond to the same activation energy of ≈300 kJ/mol. We are therefore led to conclude that the underlying microscopic process is the same in both cases. The ordering transition leads to the formation of a lamellar structure which in the thin film case is forced to be oriented parallel to the surface. The driving force for this orientation lies in the affinity of the substrate for one of the components of the diblock copolymer. In films comprising 50–100 lamellae of the block copolymer the process of orientation is decoupled from the ordering transition and proceeds on a much slower time scale.[14] In the case of the thin film, orientation is induced from the boundaries and comprises all three lamellae at once. The ordered structure leads, in general, to a film thickness that is incommensurate with the original film thickness. This conflict causes the top layer to break into the observed island and depression structure. Lateral transport of chains is needed in order to accomplish this structural change in addition to the separation of polystyrene and polyisoprene blocks on local scale. The surprisingly slow time τ found in both experiments for the perfection of the structure of the ordered state results from the combination of two factors. First, the diffusion constants of the block copolymer chains are small due to the proximity of the glass transition of the polystyrene domains. The diffusion constants determined in ref 16 allow diffusion over distances that are just the size of the islands and depressions on the surface of the copolymer film.

Second, the thermodynamic driving force for the transition into the ordered state is only given by the free energy difference between the locally ordered and the perfectly ordered state. This results in a time τ_{SF} for structure formation[25]

$$\tau_{SF} = \tau_0 \exp\{(c_0 kT\chi)^{2/3}\}$$

c_0 is a constant of order 1. We would therefore expect the temperature dependence of τ_{SF} to be that of the diffusion coefficient alone as represented by τ_0. In particular, according to this picture, τ_{SF} should increase with lowering T. This is indeed the case, as is seen in Figure 11.

4. Conclusions

The transition from a disordered block copolymer film with a flat surface to the ordered film consisting of lamellae oriented parallel to the substrate proceeds in two steps. The first process causes a local demixing of polystyrene and polyisoprene and is observed in the X-ray reflection experiment as a roughening of the film surface. Subsequently the system orders into lamellae that laterally extend over macroscopic dimensions. The conflict between the lamellar period L on one side and the film thickness D on the other side results in the breaking of the top layer into an island and depression structure. The existence of two processes participating in the ordering kinetics is equivalent to previous observations on the bulk system.

The transition temperature in the thin films is observed indirectly in the ability of the disordered state to allow lateral flow which causes a loss of the partially filled top layer. This temperature is the same as the extrapolated spinodal temperature of the bulk. It may be considered as the transition temperature of the block copolymer system without concentration fluctuations. The latter are suppressed in the thin film geometry but contribute significantly to the ordering transition of the bulk.

The kinetics of the ordering transition is observed in the development of the incomplete top layer of the film. The observed rates are slow and depend strongly on temperature which is a consequence of the small thermodynamic driving force for the finishing of the ordered structure.

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