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Phase Coherence and Microphase Separation Transitions in Diblock Copolymer Thin Films

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ABSTRACT: In thin films of diblock copolymers it was found that microphase separation and the establishment of phase coherence can occur as two distinct events in diblock copolymer thin films, at widely separated temperatures. At temperatures far removed from the bulk microphase separation transition temperature increasing overlap of the decaying concentration profiles from the substrate and air interfaces leads to a sharp onset of phase coherence throughout a thin film and the discretization of the film thickness, despite only weak microphase separation in the center of the film. A further transition to a fully microphase separated state occurs at temperatures close to the microphase separation transition temperature, but this transition becomes broader and less distinct with decreasing film thickness. In thicker films, on the other hand, phase coherence is not established until the ordering transition temperature is reached, due to the first-order nature of the transition and the finite coherence length in the disordered state. In thick films, phase coherence throughout the film is established either simultaneously or after complete microphase separation has occurred.

Introduction

While thin films of microphase-separated block copolymers have been extensively studied over the past 10 years,[1] the disordered state and the order−disorder transition in thin films have received much less attention. These systems are of interest due their similarity to other simple and complex fluids undergoing ordering transitions in confined spaces (e.g., in thin films[2] or nanoporous media[3]). In addition, block copolymer films are being investigated for their potential as nanofabrication templates.[4] Passing a film through its order−disorder transition (ODT) in the presence of a symmetry-breaking field is a potentially useful method for improving and controlling in-plane and out-of-plane order. However, it is important to understand how surface-induced ordering affects the ODT in thin films so as to develop such strategies.

As predicted by Fredrickson,[5] and later confirmed by Anastasiadis et al.,[6] a bounding surface with a preference for one of the two blocks can induce order in a diblock copolymer melt. Menelle and co-workers[7] studied the ODT in films of a P(S-*b*-dMMA) diblock copolymer using neutron reflectivity and found evidence for an increase in the ODT temperature as the film thickness was reduced. This was ascribed to the overlap of the partially ordered regions originating at the two film surfaces, so that material even in the center of the film was influenced by the presence of the walls. However, these studies were limited in scope due to the relatively low neutron flux available at reflectometer sources at the time.

A more detailed study of the behavior of diblock copolymer thin films is reported as the bulk ordering temperature is approached from the disordered state. The order−disorder transition is first order in bulk block copolymer melts,[8] involving a discontinuous jump in the magnitudes of both the order parameter amplitude $\Phi_A - \Phi_B$, i.e., the degree of phase segregation where Φ_I is the concentration of component *i*, and the correlation length ξ, characterizing the decay of concentration fluctuations (which is large or infinite in a periodic ordered phase) at ODT temperature, T_{ODT}. Because microphase separation and long-range order occur simultaneously in the bulk, the terms order−disorder transition (ODT) and microphase separation transition (MST) are often used interchangeably.

In thin films of block copolymers preferential interactions of the two blocks at the air and substrate interfaces will result in oscillatory concentration profiles from each interface that propagates into the film. At temperatures well removed from the microphase separation temperature, the decaying fields will overlap. While the periods of these oscillations are identical, the thickness of the sample in relation to this period may cause a phase mismatch. For perfectly hard interfaces, any phase mismatch should result in a destructive interference and induce disorder, whereas if the thickness is commensurate with the period, an amplification of the ordering should occur. However, in cases where one of the interfaces is air, even a slight overlap of the two fields is sufficient to bring about a phase coherence throughout the film, as evidenced by the formation of a terraced surface topography, i.e., islands or holes on the surface. Thus, the order−disorder transition occurs abruptly at a temperature far removed from the MST when the center of the film is only weakly microphase separated. We shall call this the phase coherence transition (PCT) for the thin film.

Such films, although already “ordered,” in the sense that the time-average order parameter is not zero anywhere in the sample, undergo a further transition at a temperature near T_{MST} to a microphase separated morphology throughout the film. The MST becomes progressively weaker and broader as the film thickness

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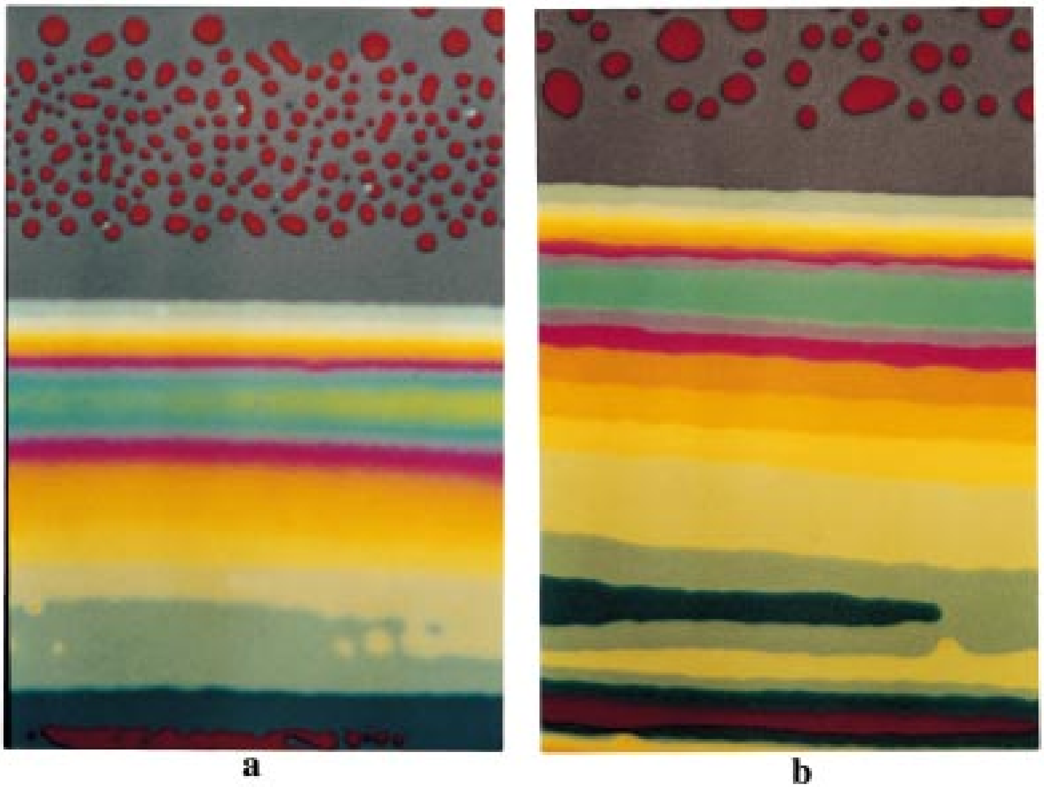

Figure 1. Reflection optical micrographs of edge regions of two spin-coated films of P(dS-*b*-nBMA), with MW = 85 000. The samples were annealed for 18 h at (a, left) 125 °C and (b, right) 175 °C, temperatures which are below and above the bulk LCOT temperature for this polymer, respectively, and correspond to bulk disordered and ordered states, respectively. The films' thickness have a maximum thickness of approximately 3500 Å at the center of the "ridge" and drop to approximately 1200 Å at the edges of the micrographs. The "disordered" film (a) shows a continuous variation in the film thickness in the thickest regions of the film, but the film thickness still takes on discrete values in the thinner regions. In contrast, the thickness of the "ordered" film (b) is discrete in all parts of the film.

is reduced since the decay length is comparable to the film thickness well below the MST. In thick films, on the other hand, phase coherence is not established before the MST is reached; this is due to the first-order nature of the transition where the decay length ξ changes *discontinuously*. The MST in the center of a thick film, sufficiently far from the influence of the walls, is thus bulklike, and the transition in thick films is extremely sharp. Thus, in thick films, phase coherence is established either simultaneously with or after microphase separation.

Experimental Section

The experiments reported here were performed using two symmetric poly(d_8-styrene-*block*-*n*-butyl methacrylate) diblock copolymers, denoted P(dS-*b*-nBMA).[9] The molecular weight, polydispersities, and styrene fractions of the copolymers were $M_w = 68\,000$ g/mol, $M_w/M_n = 1.03$, $f_{PS} = 0.51$ and $M_w = 85\,000$ g/mol, $M_w/M_n = 1.04$, $f_{PS} = 0.47$. These will be referred to as the 68K and 85K polymers, respectively. The P(S-*b*-nBMA) system is somewhat unusual in that it shows a lower disorder-to-order transition, termed the lower critical ordering transition (LCOT), where the copolymer microphase separates as the temperature is *raised*, i.e., opposite the behavior observed in most block copolymers.[9] The ordering transition temperatures for the polymers used here are ~150 °C for the 85K polymer and ~235 °C for the 68K polymer. A detailed study of the microphase separation transition is most easily accomplished with the 85K material, because of the relatively low value of the ordering temperature. The phase coherence transition occurs at temperatures far below the bulk ordering transition temperature, however, and the 68K polymer presents a much wider temperature range between the glass transition temperature of polystyrene and the ordering transition temperature of the block copolymer. Consequently, this copolymer was used for detailed studies of the PCT.

Results and Discussion

LCOT behavior in general is driven dominantly by entropic forces.[11,12] Aside from the difference in the temperature dependence, however (increased segregation on heating instead of on cooling), thin films of diblock copolymers exhibiting an LCOT behave in a manner highly similar to thin films of copolymers that have a classical order-to-disorder transition. The effects reported here have also been observed in more conventional diblock copolymers, such as poly(styrene-*block*-isoprene) and poly(styrene-*block*-methyl methacrylate).[14]

The distinction between microphase separation and phase coherence in diblock copolymer films is illustrated in Figure 1. Figure 1 shows optical micrographs of two films of the 85K polymer. The films were spin-coated onto clean silicon wafers and were annealed in a vacuum for several hours at temperatures of 125 °C (a) and 175 °C (b), corresponding to the bulk disordered ($T < T_{LCOT}$) and ordered ($T > T_{LCOT}$) states of this block copolymer. The samples were removed from the vacuum oven and quenched rapidly to room temperature and were then examined under white light with a reflection optical microscope. The photomicrographs were taken at the edge of the wafer, where spin coating leads to a highly nonuniform film thickness, which causes strong variation of the reflection interference colors.

Although the film in Figure 1a was annealed at a temperature at which the bulk copolymer is disordered

(T < T_{LCOT}), the thinner regions of this film show discrete changes in the film thickness (terracing or island formation) which is well-known to occur in films of "ordered" diblock copolymers at temperatures where the bulk diblock copolymer is microphase separated.[15] The thicker regions of the film in Figure 1a, on the other hand, do not show terracing, indicating that the film thickness can take on any value. Longer annealing times at $T = 125$ °C did not produce terracing in the thicker regions of the film. In contrast, the film annealed at $T > T_{\mathrm{LCOT}}$ (Figure 1b) shows strong terracing in both the thick and thin regions. Therefore, even when $T < T_{\mathrm{LCOT}}$ and the bulk polymer is not microphase separated, ordering induced at both surfaces propagates through the entire film, producing a quantized surface topography.

Figure 2a shows a series of neutron reflectivity profiles (points) taken for a spin-coated film of the 68K polymer ($T_{\mathrm{LCOT}} = 235$ °C) at a series of evenly spaced temperatures from 100 to 200 °C, with $\Delta T \approx 15$ °C. All measurements were done at a temperature where the sample was heated in situ under vacuum (diffusion pump). The temperature was always increased from one scan to the next so the experiments began with the film in its most disordered state. Careful studies showed that annealing times of approximately 15 min following each temperature jump were more than adequate for equilibration of the structure within the film, as determined by reproducibility of the reflectivity data upon repeated scans at the same temperature. Structural equilibration following a temperature jump, and island formation and growth, in particular, are exceptionally rapid in P(dS-*b*-nBMA) block copolymer films. In keeping with this rapid ordering, topographic features (island or holes) were found to coarsen to sizes of hundreds of microns (visible to the naked eye) after only a few hours of annealing at elevated temperatures in comparison to the tens of microns typical of P(dS-*b*-MMA) and other copolymers.

The solid lines in Figure 2a are the reflectivities calculated from the best-fit scattering length density profiles shown in Figure 2b, which were obtained using a model and fitting procedure described previously.[15] As the temperature is raised, the correlation length ξ increases and the composition oscillations penetrate further into the film, resulting in an increasingly prominent reflection at $K_z \sim 0.013$ Å^{-1}, where $K_z = (2\pi/\lambda)\sin\theta$ is the neutron momentum normal to the substrate, λ is the neutron wavelength, and θ is the grazing angle of incidence. A steady compression of the Kiessig fringes is also apparent (indicated by the dashed line in Figure 2a, for $T \leq 159$ °C), due to thermal expansion of the film. Both of these phenomena are evident in the scattering length density profiles.

There is an abrupt change in the fringe spacing and the shape of the reflectivity profile between 159 and 173°. This can be seen most easily with reference to the dashed line in Figure 2a, which connects a particular fringe maximum from one scan to the next and thus represents smooth thermal expansion of the sample. The shift in the fringe spacing is accompanied by a loss of intensity in the total external reflection regime just below the critical edge (shown by the arrow in Figure 2a). Both of these features in the data are due to the onset of island formation on the sample surface.[17]

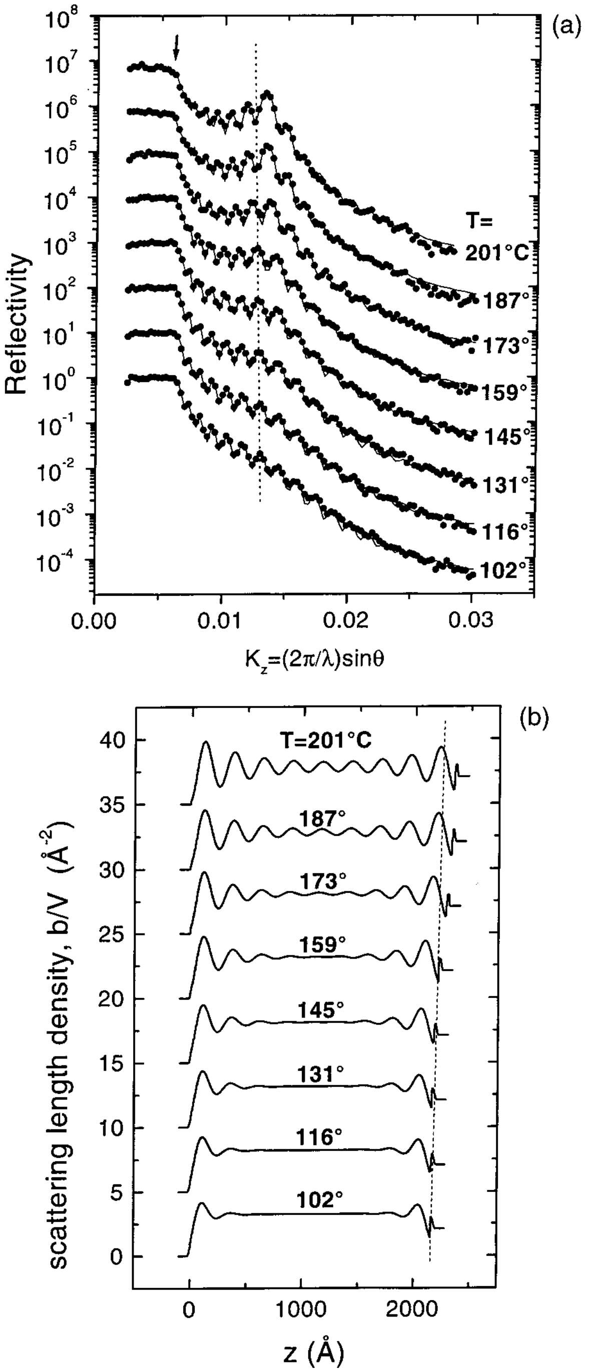

Figure 2. (a) Neutron reflectivity data (points) from a film of P(dS-*b*-nBMA), with $M_w = 68\,000$ g/mol, at a series of evenly spaced temperatures from 100 to 200 °C. The solid lines were calculated from the best-fit scattering length density profiles shown in (b). Dashed lines illustrate the contraction of the Kiessig fringes in (a) and the corresponding thermal expansion of the film in (b). The increasingly prominent peak at $Q = 0.012-0.013$ Å^{-1} is due to the increasing correlation length ξ of the composition oscillations. Note the reduced reflectivity at the critical edge above 173 °C (arrow) and the sudden additional contraction of the fringes between 159 and 173 °C. Both effects are due to the onset of coherence and island formation.

The reduced reflectivity below the critical edge results from the surface roughness associated with initial island formation that produces a significant off-specular scattering and, therefore, a reduction of the specular reflectivity. This can be seen more clearly in Figure 3a, where the reflectivity at the critical angle is shown as a function of temperature on a linear scale. The reflectivity is approximately unity below 160 °C but drops

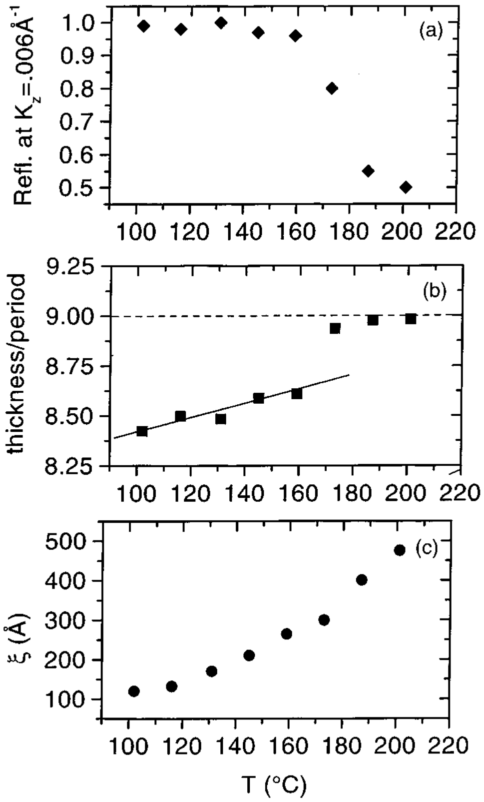

Figure 3. Summary of some key parameters obtained fit to the data in Figure 2. (a) The reflectivity just below the critical edge drops sharply between 159 and 174 °C, due to surface roughness associated with island formation. (b) The ratio of the fit film thickness to the fit period, t/L, undergoes a transition from an incommensurate to a commensurate value between 159 and 174 °C and remains locked at $t/L = 9.0$ above this temperature. (c) In contrast, the correlation length ξ varies smoothly throughout this temperature range, showing that there is no discontinuous change in the thermodynamic state of the copolymer.

sharply by a factor of 2 as the temperature is raised further.

The apparent shift in the fringe spacing appears to imply a discontinuous change in the total film thickness, but a closer examination of the data shows that this is not the case and that this is instead due to the onset of island formation. The ratio of the best-fit film thickness t and the best-fit copolymer period L is plotted against temperature in Figure 3b. At 160 °C, $t/L = 8.6$, a highly incommensurate value, while at 175 °C, t/L has jumped to approximately 9.0, a commensurate value, and remains locked at this value as the temperature is further increased.

The *average* film thickness cannot change discontinuously. The volume change associated with the ordering for P(dS-*b*-nBMA) is $\sim -0.1\%$,[18] much smaller than that suggested by the data in Figure 3b. The abrupt change in t/L is not indicative of a volume change but rather the onset of island formation in this film. Since $t/L \approx 8.7$, approximately 70% of the film area has thickness $t = 9L$ and 30% has $t = 8L$. The reflectivity is an incoherent sum of the reflectivities from these regions, resulting in the beating of the fringes which is observed clearly in the upper two data sets in Figure 2a; but the $t = 9L$ region dominates the fringe structure and "pulls" the fit. (Note that a more accurate fitting procedure would be to fit an incoherent sum of the reflectivities of $8L$ and $9L$ films, with the area fraction ratio as a fitting parameter. The current procedure gives a very good fit with $t = 9L$, because there is much more area with $t = 9L$ than with $t = 8L$. This approximate fitting procedure does not reproduce the beating of the fringes observed in the data though.)

The correlation length ξ obtained from the fits is plotted against temperature in Figure 3c and is seen to increase smoothly through the entire temperature range, even with the onset of island formation. Thus, the appearance of a surface topography is *not associated with any change in the thermodynamic state of the copolymer*. In fact, as can be seen in Figure 2b with the data for $T \geq 173$ °C, island formation occurs when the coupling between the ordered regions is very weak, and the order parameter (essentially the amplitude of the oscillations, propagating into the film from the air and substrate interfaces) is still quite small. More quantitatively, for this film with a thickness $t = 2300$ Å, when the decay or correlation length $\xi \approx 300$ Å, ~ 8 times smaller than the film thickness, there is a phase coherence of the ordering induced from both interfaces sufficient to induce the formation of a surface topography. At this point, the composition oscillation at the center is $|\Delta\Phi(z)| \approx 0.1$ (where $\Delta\Phi(z) = \Phi_A(z) - \langle\Phi_A\rangle$ is the local excess volume fraction of component A, relative to the average value $\langle\Phi_A\rangle$; $|\Delta\Phi(z)| = 0$ for complete phase mixing, and $|\Delta\Phi(z)| = 0.5$ for complete segregation). Any phase mismatch of the oscillatory profiles is corrected by the formation of a surface topography. The discretization of the film thickness clearly indicates that the film is "ordered" in the sense of being phase coherent across the entire thickness but is not ordered in the sense of being fully microphase separated.

While data from only one sample are presented here, the reduced specular scattering below the critical edge and the "locking" of the Kiessig fringe period to a commensurate value have been observed repeatedly, on many samples of the 68K polymer with a wide range of different film thicknesses. In general, thinner samples become phase coherent at lower temperatures, as the overlap of the surface ordered regions for a given temperature is larger if the surfaces are closer together. No detailed study has been done on the relationship between the phase coherence temperature and commensurability effects.

The $M_w = 85$K copolymer has a sharp bulk MST transition at approximately 150 °C, allowing detailed studies of this transition without risk of degrading the samples. Reflectivity profiles from ~2000 and ~3000 Å thick films of the 85K polymer are shown in Figure 4a, at a series of temperatures separated by $\Delta T = 10$ °C. For the thicker film, a sudden change in the reflectivity curves is apparent on passing through the transition; specifically, the first- and second-order Bragg peaks are sharply enhanced between 143° and 153°. Also noteworthy is a drop in the reflectivity below the critical angle, due to the surface roughness associated with the onset of island formation, which occurs simultaneously with the microphase separation transition for this film. In the 200 nm film, neither type of discontinuity is apparent with changing temperature, and the curves appear to vary smoothly in all respects.

It is difficult to carefully assess the sharpness of the transition by studying reflectivity data taken at such widely spaced temperatures. An alternative method is to measure the reflectivity at a fixed $K_{z,0}$, corresponding to the first-order Bragg peak maximum, as a function

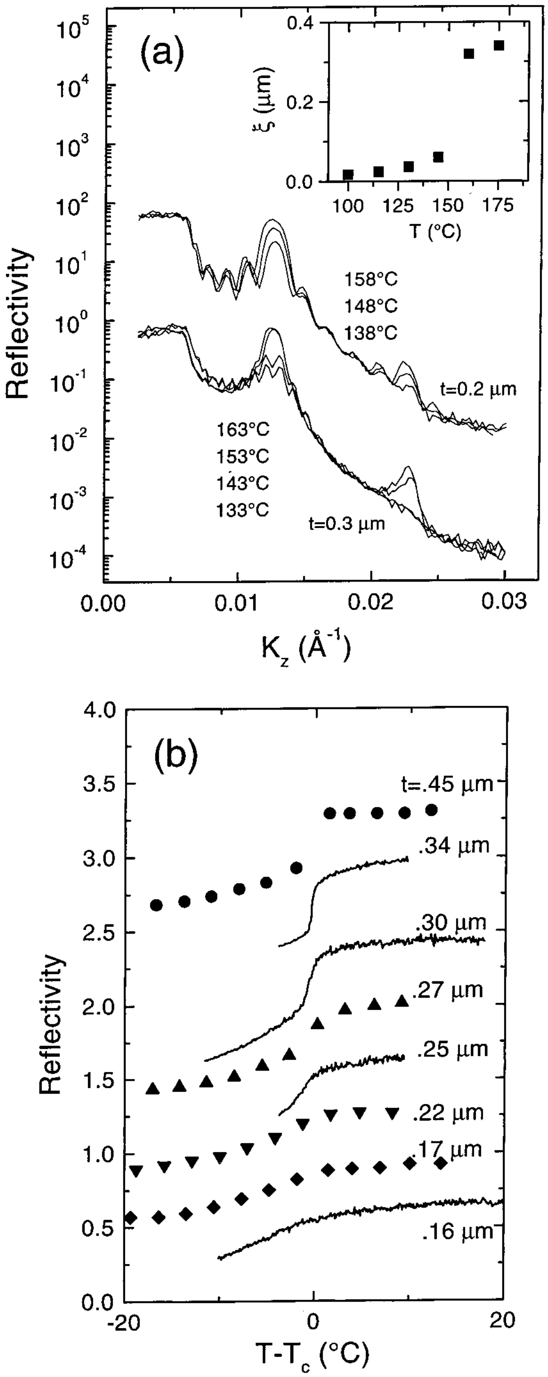

Figure 4. Detailed study of the microphase separation transition in films of P(dS-*b*-nBMA), with M_w = 85 000 g/mol, for various film thicknesses. (a) Studies of two film thicknesses at a discrete set of temperatures. A sharp increase in the Bragg peak intensities is evident between 143 and 153 °C in the thicker film, while the peak intensities for the thinner film appear to vary continuously in the same temperature range. Inset: fit values of ξ for the thicker film, showing the abrupt nature of the transition. (b) Reflectivity at the first-order Bragg peak maximum vs temperature, for films of the 85K polymer of various thicknesses. Data were taken both by sweeping temperature at fixed scattering angle (lines) and by making complete reflectivity scans over the Bragg peak at a series of closely spaced temperatures (points are the reflectivities at the Bragg peak maximum). The transition width for the 3400 Å film is approximately 1 °C.

of temperature. Data of this type are shown in Figure 4b for film thicknesses ranging from 160 to 340 nm (lines). The sample was aligned at the highest temperature of each scan, and the temperature was reduced smoothly at a rate of approximately 0.4 °C/min. In the thickest films, the transition is extremely sharp—less than 1 °C wide. As the films become thinner, the transition is seen to broaden and weaken. Eventually, only a gradual change in slope at the onset of the transition is visible, with no discontinuity in the intensity of the reflection.

To ensure that the above results were not significantly affected or compromised by changes in alignment during the temperature scans, due to thermal expansion of the substrate and heater assembly, complete reflectivity scans were taken at closely spaced temperature intervals ($\Delta T \approx 2.5$ °C) using a separate set of samples. Realignment at each temperature was performed. The intensity of the first-order peak from these experiments is also plotted in Figure 4b (points) for comparison. Both data sets have been offset and interleaved, to preserve the sequencing of the data according to film thickness. A comparison of the two types of data sets confirms that the MST becomes narrower and more pronounced as the film thickness is increased, although the extreme sharpness of the transition in thick films is not as apparent in the discrete data (points).

Because of the first-order nature of the order–disorder transition, the correlation length ξ undergoes a discontinuous change at the transition, from a finite to an essentially infinite value. Thus, thicker films are both disordered *and* phase-mixed at temperatures close to the bulk MST, and phase coherence can at best occur simultaneously with microphase separation.

Thinner films, on the other hand, can become "ordered" (phase coherent, with a discrete set of allowed thicknesses) at temperatures far removed from the bulk MST, as evidenced by the formation of islands and holes. The occurrence of such ordering depends on the ratio of the film thickness to the correlation length, t/ξ, and is likely to depend on the degree of frustration of the film, which is related to t/L. For the polymers studied here, the crossover occurs in the range $t/\xi \sim 10$. The order parameter in the center of the film remains small but finite, however, until the bulk ordering temperature is reached; at this point the film becomes fully microphase separated as well. This second transition becomes less distinct as the film thickness is reduced, however. In the phase coherent but microphase mixed state, the degree of surface-induced microphase separation increases as the film thickness decreases, reducing the amount of material which is available to undergo further microphase separation at the bulk MST temperature.

The above picture implies that perfect lamellar ordering occurs at the MST when $t \leq 10\xi$, and coherence is already established prior to the microphase separation transition. In thicker films, however, phase coherence is not established prior to microphase separation. Therefore, it is possible for ordered regions to nucleate in the center of very thick films with initially random orientations, without any guidance from the film surfaces.

Thus, it seems likely that upon passing through the transition, one will obtain a region in the film center in which the lamellae orientation is initially uncorrelated with the film surfaces. Only after further annealing in the microphase-separated state will order be established throughout the film. If the ordering transition were second order rather than first order, then the correlation length would diverge continuously as the transition was approached, and phase coherence would always be established prior to microphase separation. Thus, the thermodynamic nature of the transition can have a strong impact on the associated ordering processes in thin films.

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References and Notes

(1) Matsen, M. *Curr. Opin. Colloid Interface Sci.* **1998**, *3* (1), 40.
(2) Gao, J.; Luedtke, W. D.; Landman, U. *Phys. Rev. Lett.* **1997**, *79*, 705.
(3) Yoon, Y.; Chan, M. H. W. *Phys. Rev. Lett.* **1997**, *78*, 4801.
(4) Park, M.; Harrison, C. K.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.
(5) Fredrickson, G. H. *Macromolecules* **1987**, *20*, 2535.
(6) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852.
(7) Menelle, A.; Russell, T. P.; Anastasiadis, S. H.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1992**, *68*, 67.
(8) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 515.
(9) Russell, T. P.; Karis, T. E.; Gallot, Y.; Mayes, A. M. *Nature* **1994**, *368*, 729.
(10) Bidkar, V. R.; Sanchez, I. C. *Macromolecules* **1995**, *28*, 3963.
(11) Dudowicz, J.; Freed, K. F. *Macromolecules* **1993**, *26*, 213.
(12) Yeung, C.; Desai, R. C.; Shi, A.-C.; Noolandi, J. *Phys. Rev. Lett.* **1994**, *72*, 1834.
(13) Hino, T.; Prausnitz, J. M. *Macromolecules* **1997**, *10*, 681.
(14) Mansky, P.; Russell, T. P. Unpublished on P(S-*b*-I) and (S-*b*-MMA).
(15) Coulon, G.; Deline, V. R.; Green, P. F.; Russell, T. P. *Macromolecules* **1989**, *22*, 2581.
(16) Mansky, P.; Russell, T. P.; Hawker, C. J.; Mays, J.; Cook, D. C.; Satija, S. K. *Phys. Rev. Lett.* **1997**, *79*, 237.
(17) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171.
(18) Pollard, M.; Tsui, O. K. C.; Russell, T. P.; Ruzette, A. V.; Mayes, A. M.; Gallot, Y. *ACS Symp. Ser.*, in press.

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