# Ordering of Thin Diblock Copolymer Films

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The ordering in thin films of symmetric diblock copolymers has been studied by neutron reflectivity as a function of temperature and film thickness. Exponentially damped oscillatory variations in the concentration are shown to propagate into the specimens from both surfaces with decay lengths increasing with decreasing temperature. No distinguishable order-to-disorder transition is observed; only a transition from a partially to a fully ordered state is found. The temperature of this transition is found to depend in a power-law manner on the film thickness.

Ordering induced by the presence of a surface has been of recent interest [1,2]. For example, surface ordering phenomena have been studied in detail for binary fluid mixtures [1,2], liquid crystals [3], as well as homopolymer blends [4-6]. Diblock copolymers represent an interesting class of materials from the point of view of surface ordering. Because of connectivity of two chemically distinct polymer chains comprising the blocks, a different surface behavior is expected in films of diblock copolymers as compared to simple mixtures of homopolymers. For miscible homopolymer blends, the concentration profile of one of the components decays monotonically into the bulk, whereas for phase-mixed diblock copolymers an oscillatory concentration profile is expected near the surface [7].

In the bulk, symmetric diblock copolymers undergo a weak first-order phase transition at a temperature $T_{ODT}$ from an ordered lamellar microdomain morphology to a phase-mixed morphology [8,9]. This occurs [10] when $\chi N = 10.5$, where $\chi$ is the Flory-Huggins segmental interaction parameter and $N$ is the total number of segments in the copolymer chain. Near an interface the preferential affinity of one of the blocks to the interface has been shown to induce an ordering of a phase-mixed copolymer far from $T_{ODT}$ [11]. This ordering decays exponentially from the surface in agreement with mean-field arguments. For thin copolymer films in the ordered state, the interactions of the blocks with the interfaces have been shown to induce a near perfect orientation of the lamellar microdomains parallel to the film surface producing a multilayered structure [12-14]. In this Letter the temperature and film thickness dependence of the ordering of symmetric diblock copolymers is presented. It is shown that an order-disorder transition does not exist in thin films. However, the films are shown to undergo a transition from a partially to a fully ordered state at a temperature which depends in a power-law manner on the film thickness.

The copolymer used in this study was a symmetric diblock copolymer of polystyrene and perdeuterated polymethylmethacrylate, designated P(S-*b*-D-MMA), which

had total weight average molecular weight $M_w$ of 29 700 and a weight to number average molecular weight ratio of 1.1. Removal of unreacted PS homopolymer was achieved by successive extraction in cyclohexane. The molecular weights of the PS and D-PMMA blocks were 14 700 and 15 000, respectively, with a total number of segments, $N$, of 281 and a PS fraction of 0.50. Films of the copolymer were prepared with thicknesses ranging from 952 Å to 1.6 μm by spin coating a solution of the copolymer in toluene onto polished Si substrates (10 cm in diameter, 0.48 cm thick). Specimens were first dried at 80 °C under vacuum for 48 h to remove residual solvent. The samples were then annealed at the desired temperature for a period of at least 12 h and then quenched to room temperature. It should be realized that the thin film on the surface of the Si cools much more rapidly than the entire substrate and within seconds the temperature of the film is below the glass transition temperature of the copolymer. Within this time no significant changes in the state of the copolymer could occur; therefore, the structure at the annealing temperature is effectively frozen-in. Both decreasing and increasing annealing temperature cycles were used to ensure reversibility and reproducibility of the results. Reflectivity experiments were performed at room temperature on a neutron reflectometer at beam line BT7 in the reactor hall of the National Institute of Standards and Technology. A monochromatic beam of 2.35 Å neutrons, 75 μm (horizontal) ×2.5 cm (vertical) in size with a divergence of 0.01° and 2°, respectively, at an incidence angle of 0.05°, was used for the reflectivity measurements. The horizontal width of the beam was increased with angle $\theta$ to enhance flux. $\Delta\theta/\theta$ did not remain constant with $\theta$ and was accounted for in the calculations. Details of the reflectivity measurements including data fitting procedures can be found elsewhere [14,15].

Independent small-angle neutron-scattering studies on P(S-*b*-D-MMA) in the phase-mixed state yielded the temperature dependence of $\chi$ as [16]

$$\chi = (0.029 \pm 0.002) + (3.2 \pm 0.04)/T, \tag{1}$$

where $T$ is the absolute temperature. It should be noted that this differs from the result of the P(D-S-$b$-MMA) diblock where the isotopic labeling of the blocks is reversed [17]. The weak temperature dependence of $\chi$ makes a precise evaluation of $T_{ODT}$ from Eq. (1) difficult. However, we can estimate that $T_{ODT}$ occurs in the range of $157 \pm 8\,°C$ which serves as a basis for these studies.

Reflectivity measurements for the diblock copolymers are typified by the data shown in Fig. 1 which are for a 5232-Å-thick specimen at temperatures of 185, 176, 174, 165, and 135 °C. In all cases, the reflectivity drops markedly above a critical neutron momentum $k_{z,0} \simeq 6.8 \times 10^{-3}$ Å$^{-1}$ [$k_{z,0} = (2\pi/\lambda)\sin\theta$, where $\lambda$ is the wavelength and $\theta$ is the incidence angle]. At all temperatures, a distinct first-order reflection is observed at $k_{z,0} \simeq 0.02$ Å$^{-1}$. No significant temperature dependence of the position of this reflection was observed [18]. For experiments at the lowest temperature, distinct, higher-order reflections are seen at $\sim 0.038$ and $\sim 0.056$ Å$^{-1}$. These reflections become more narrow and intense with increas-

ing film thickness. As the temperature is increased, the first-order reflection broadens and diminishes in intensity whereas the higher-order reflections are gradually lost, and only a ridge in the reflectivity is seen between the positions of the second- and third-order reflections. This ridge becomes less pronounced with increasing film thickness and increasing temperature.

In general, an analytic solution of the reflectivity profile is not possible and one is required to develop a model for the scattering length density profile normal to the film surface from which the reflectivity can be calculated. Fredrickson [7] has developed a mean-field treatment which describes the concentration profile of a diblock copolymer near an isolated surface which has been shown [11] to describe experimental observations of diblock copolymer films far removed from $T_{ODT}$. Here, however, is a situation where two surfaces are in proximity to one another and the measurements were performed in the vicinity of $T_{ODT}$. Consequently, only the functional form of the concentration profile will be used as a model. Thus,

$$\phi_{PS}(z) = \max \left[ \phi_A e^{-z/\xi} \cos\left(\frac{2\pi z}{\bar{L}}\right), \phi_s e^{-(E-z)/\xi} \cos\left(\frac{2\pi(E-z)}{\bar{L}}\right) \right] + \bar{\phi}_{PS}, \tag{2}$$

where $\phi_{PS}(z)$ is the volume fraction of PS segments a distance $z$ from the surface in a film with a total thickness $E$. $\phi_A$ and $\phi_S$ are the excess concentrations of PS at the air and substrate interfaces, $\bar{L}$ is the average period of the diblock copolymer, and $\bar{\phi}_{PS}$ is the average concentration of PS in the copolymer. For diblock copolymer films in the ordered state, $E = (n + \frac{1}{2})\bar{L}$, where $n$ is an integer [12–14].

Several points need to be made concerning the use of Eq. (2). First, it is simply one model that has been found to suitably describe the reflectivity results. Other models with similar variations in the concentration could yield as good agreement with the experimental data. Second, $\phi_S$ was always found to be $-0.5$, reflecting the strong interaction of the PMMA block with the substrate, whereas $\phi_A$ was variable but found in good agreement with independent x-ray photoelectron spectroscopy studies. Third, with the exception of the lowest temperatures, the period $L$ was not constant through the film thickness and an empirical variation about an average value $\bar{L}$ of the form $L(z) = \bar{L} + \Delta L \sin[2\pi(E-z)/E]$ with $\Delta L \simeq 3$ Å was used. Omission of this slight variation in $L$ resulted in a marked dip in the reflectivity at $k_{z,0} = 0.037$ Å$^{-1}$ which is not observed. This variation in $L$ suggests that there is a depth-dependent phase term in the cosine argument. An average value of $\bar{L} = 168$ Å was found in agreement with neutron-scattering measurements on bulk specimens. Finally, $\xi$ determined from Eq. (2) in cases where the decaying profiles overlap will contain contributions from the fields at both surfaces.

The analysis of the reflectivity profile, thus, reduces

primarily to varying $\xi$ to obtain the best fit to the observed data. Roughnesses at the air/polymer and polymer/substrate interfaces were found, in general, to be $\sim 7 \pm 3$ Å. However, near $T_{ODT}$ the roughness at the air surface was found to increase significantly and then return to $\sim 7 \pm 3$ Å when the film was fully ordered. This variation in the roughness results from the formation of islands or terraces on the film surface as discussed elsewhere [12–14,19,20].

Typical fits to the reflectivity profile are shown as the solid lines in Fig. 1 where the scattering length density profiles shown in the insets, derived from Eq. (2), were used for the calculations. As can be seen, the agreement between the calculated and experimental profiles is quite good throughout the entire $k_{z,0}$ range. It should be noted that variation of $\xi$ by more than 20% would produce unacceptable fits to the observed data. In particular, the intensity of the first-order reflection is sensitive to the magnitude of $\xi$.

At higher temperatures the scattering length density profiles are characterized by oscillations in the concentration which are rapidly damped away from the surface. Since the decay length is much smaller than the film thickness, one then reaches a point where the oscillations are fully damped and, to within experimental uncertainty, a constant composition, equal to the average composition of the copolymer, is attained. By definition such specimens are in the disordered state. With decreasing temperature $\xi$ increases such that at 174 °C oscillations are seen to propagate through the entire specimen. Hence, at

FIG. 2. The decay length, $\xi$, characterizing the damping of the concentration oscillations from either the air or substrate interface as a function of temperature. Inset: $1/\xi^2$ as a function of $1/T$. The temperature at which the films become fully ordered, $T_{\infty,t}$, is indicated by the arrow.
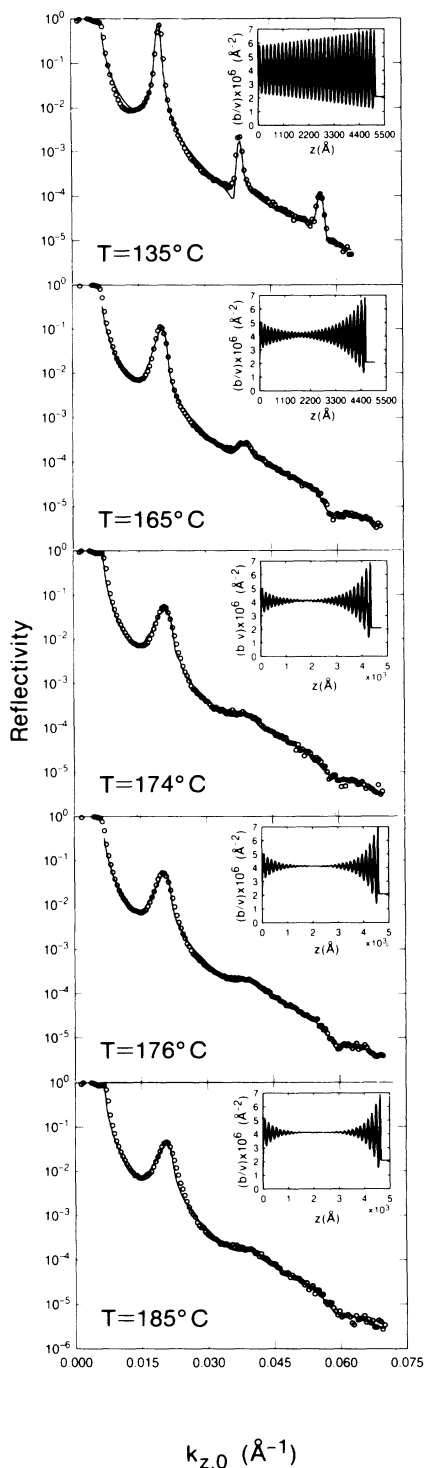


FIG. 1. Neutron reflectivity profiles for a 5232-Å film of P(D-S-$b$-MMA) symmetric, diblock copolymer as a function of the neutron momentum normal to the surface at the temperatures indicated. The scattering length density $b/V$ profiles as a function of depth $z$, where $z = 0$ is the air surface, shown in the insets were used to calculate the reflectivity profiles drawn as the solid lines in the figures.
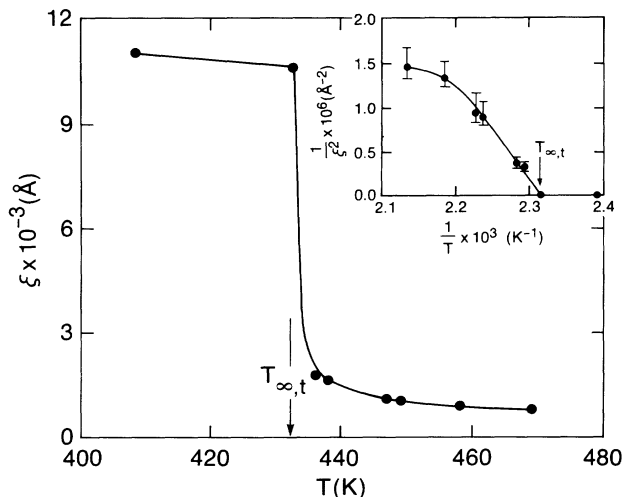
174 °C the thin film is ordered. However, it is impossible to define 174 °C as even a lower bound for $T_{\text{ODT}}$. This would be arbitrary since, with better resolution capabilities, the data at 185 °C or higher would, according to Eq. (2), show oscillations in the concentration through the entire film. Thus, for all temperatures, films of finite thickness are partially ordered and $T_{\text{ODT}}$ cannot be defined.

With decreasing temperature $\xi$ is seen to increase further and undergo an abrupt change at $T_{\infty,t}$, i.e., the temperature where $\xi \rightarrow \infty$ for a given thickness $t$. At $T_{\infty,t}$ the copolymer film undergoes a transition from a partially to a fully ordered film forming a well-defined multilayered morphology [14]. To define $T_{\infty,t}$ more precisely, $1/\xi^2$ was plotted as a function of $1/T$ since at $T_{\infty,t}$ $1/\xi \rightarrow 0$. This is shown in the inset of Fig. 2. For a second-order transition this plot would be linear extrapolating to the transition temperature when $1/\xi = 0$. Marked curvature is seen over the entire temperature range due in part to the proximity of the two surfaces. Nonetheless, a very reasonable estimate of $T_{\infty,t}$ can be made. Similar types of results were found for all thicknesses studied.

It was found that $T_{\infty,t}$ increased as the film thickness decreased down to thicknesses of $\sim$900 Å. For thinner specimens, either the samples were fully ordered or the morphology of the copolymer was altered by the constraints of the air and substrate interfaces. This will be discussed in a subsequent publication. On the opposite extreme, $T_{\infty,t}$ approaches an asymptotic value of 157.7 °C as $t \rightarrow \infty$. This value corresponds to the value of $T_{\text{ODT}}$ for a bulk specimen, $T_{\text{ODT},B}$, and, in fact, has
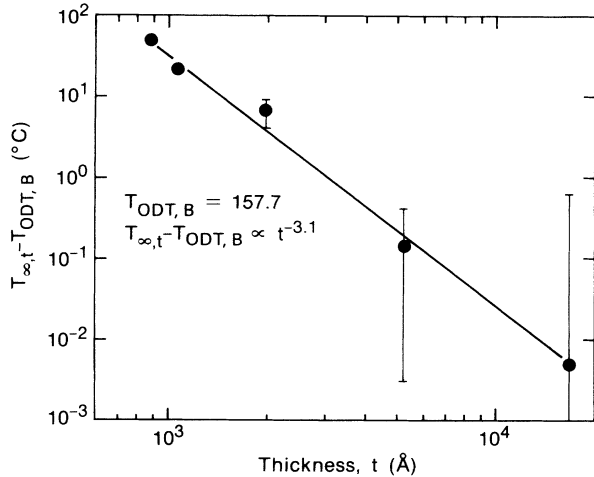
FIG. 3. A log-log plot of the difference between $T_{\infty,t}$ and the bulk value of $T_{ODT,B}$ as a function of film thickness using the value of $T_{ODT,B}$ extrapolated from the neutron reflectivity measurements.

provided a more precise measure of this transition temperature. What is surprising is the strong dependence of $T_{\infty,t}$ upon thickness. Shown in Fig. 3 is a plot of $T_{\infty,t} - T_{ODT,B}$ as a function of film thickness (using the extrapolated value of $T_{ODT,B}$ determined from the reflectivity measurements). As can be seen, a power-law behavior is observed with an exponent of $-3$. While one must be cautious of the exact value of the exponent, the results are clear. The proximity of two surfaces and the fields associated with the surfaces have induced an ordering in otherwise disordered copolymers. This effect becomes more important as the distance between the surfaces is decreased. Basically the surfaces pin concentration fluctuations normal to the film surface and suppress those in other directions. These, in turn, are reinforced by the proximity of the second surface. It is most important to note that for the situation discussed here the air surface is not really a hard wall since the copolymers can form islands and terraces on the free surface to accommodate any phase mismatch in the two oscillatory fields. In the case of truly solid boundaries the effect of the two surfaces may be quite different than that observed here.

In conclusion, it has been shown that for thin films of symmetric diblock copolymers there is no true order-to-disorder transition. In addition, it has been shown that thin-film copolymers undergo a transition from a partially to a fully ordered state. The temperature at which this transition occurs depends in a power-law manner on the film thickness.

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