Kinetics of layer hopping in a diblock copolymer lamellar phase

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Abstract. In the ordered state, symmetric diblock copolymers self-assemble into an anisotropic lamellar morphology. The equilibrium thickness of the lamellae is the result of a delicate balance between enthalpic and entropic energies, which can be tuned by controlling the temperature. Here we devise a simple yet powerful method of detecting tiny changes in the lamellar thickness using optical microscopy. From such measurements we characterize the enthalpic interaction as well as the kinetics of molecules as they hop from one layer to the next in order to adjust the lamellar thickness in response to a temperature jump. The resolution of the measurements facilitate a direct comparison to predictions from self-consistent field theory.


Often the most fascinating features of nature are rooted in the complexity and order found in self-assembling patterns. The innate interest in self-assembly, coupled with the technological need for simple cost-effective templates results in a significant research effort to understand pattern formation [1]. Of the many self-assembling nanoscale polymeric structures, some of the most remarkable are formed by block copolymers [2, 3]. Block copolymers are long chain molecules made up of segments of different chemical constituents joined together by a covalent bond. In the simplest case, a block of $fN$ segments is attached to another block of $(1 − f)N$ segments to form a diblock copolymer. Because of the general incompatibility of the chemically distinct blocks, the molecules exhibit amphiphilic properties: that is, the blocks tend to segregate into structures that minimize contact between unlike segments. These molecules will typically self-assemble into long-range periodically ordered morphologies composed of nanosized domains, when cooled below an order-disorder transition (ODT). The composition of the molecule, $f$, sets the preferred curvature of the internal interfaces which, in turn, controls the geometry of the resulting morphology; symmetric diblocks ($f \sim 1/2$) prefer zero curvature resulting in a simple lamellar phase, where the incompatible domains form flat alternating layers. The repeat period, $L$, is on the order of the relaxed molecular size (i.e., the polymer radius of gyration, $R_g \sim 10\text{ nm}$), but the precise value of $L$ is controlled by the product, $\chi N$, where the Flory-Huggins parameter, $\chi$, is a temperature-dependent quantity that specifies the incompatibility of the unlike segments.

Here we examine thin films of a symmetric diblock copolymer, which form a stack of lamellae oriented parallel to the substrate. Using a simple optical measurement, we are able to monitor changes in the domain size, $L$, in situ with an unprecedented sensitivity. By comparing the measured $L$ with predictions from self-consistent field theory (SCFT), we extract the temperature dependence of $\chi$ and verify the technique. With the methodology established, we measure the equilibration of $L$ as the lamellae respond to a sudden temperature jump. The resolution of the experiments facilitates a direct comparison of the data with SCFT, which provides a quantitative, parameter-free measure of the kinetic energy barrier, $\Delta \epsilon$, for an individual molecule to hop between adjacent layers.

The kinetics of molecular motion in structured morphologies is of wide interest [4–7]. It is relevant to virtually all complex liquids and biological systems; such as the exchange of molecules between layers in smectic liquid crystals and between the inner and outer layers of lipid membranes. In the model system of block copolymer melts, Lodge and co-workers have tried to differentiate between lateral diffusion where the molecules move with their junction point on the same interface, and perpendicular diffusion where the junction point jumps between neighboring interfaces [8]. In our experiment, the rate of change in the...

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domain spacing of our defect-free thin films is controlled solely by the rate at which the molecules hop between layers, since lateral diffusion does not contribute to changes in $L$. A decrease in $L$, for example, requires molecules to move upward through the layers eventually adding to the topmost incomplete layer—a reservoir, which adjusts its area accordingly.

The main difficulty in quantitatively relating theory to experiment is obtaining the temperature dependence of $\chi$. This dependence is often determined by measuring the ODT of symmetric diblock copolymers of different $N$, and matching to Leibler’s mean-field prediction, $(\chi N)_{\text{ODT}} = 10.495$, with $\chi = A/T + B$ expressed in terms of the fitting parameters, $A$ and $B$. However, it is known that fluctuations play an important role in the location of the ODT, and additional theory is used to supplement the prediction of $(\chi N)_{\text{ODT}}$ [9,10]. Another common approach is to perform the comparison on symmetric binary blends, but unfortunately this does not always produce a consistent result [11]. Regardless of the methodology, the comparison should be performed on some quantity for which both the experiment and theory are accurate. Our use of the domain size $L$ is particularly ideal [12], because not only can we measure it accurately, it is also considered to be one of the most reliable predictions of SCFT.

The molecule used in our experiment is a monodisperse (polydispersity index of 1.09), symmetric ($f = 0.50$), diblock copolymer polystyrene-poly(2-vinyl pyridine), with a molecular weight of $M = 16.5 \text{ kg/mol}$ (Polymer Source). Thin films of various thicknesses were prepared by spin-coating the polymer from toluene or chloroform solution onto silicon substrates with the native oxide layer present, which were cleaned by super-critical CO$_2$ (Applied Surface Technologies) and UV-ozone. Upon annealing the sample below the ODT temperature, a surface topography results due to the lamellar confinement—the molecules must exist within lamellae of a preferred thickness, $L$. If an integer number of $n$ lamellae happens to be commensurate with the film thickness ($i.e.', h = nL$), then the film adopts a flat featureless surface. When there is a small amount of extra material, the film creates a topography of isolated islands of height $L$ on top of the $n$ complete layers. Further material causes the islands to grow eventually merging into an interconnected bicontinuous structure. As the low areas are gradually filled in, the topography is best described as a film of thickness $h = (n + 1)L$ with isolated holes of depth $L$. Ultimately, the holes fill in producing a flat uniform film, but now with $(n + 1)$ complete layers [13]. These surface topographies: islands, bicontinuous networks and holes, are readily observed with simple optical microscopy.

Even with a fixed amount of material, the topography of the film surface varies with temperature because of the effect that the temperature dependence of $\chi$ has on the preferred lamellar thickness, $L$. The equilibrium thickness results from a delicate balance between the energy penalty of the internal interfaces separating the unlike domains (favoring large $L$) and the entropic cost of stretching the blocks so as to fill the center of each domain (favoring small $L$). A decrease in temperature, for example, causes an increase in $\chi$, which in turn amplifies the interfacial tension resulting in thicker domains. Because the polymer melt can be treated as incompressible, the increase in $L$ among the complete layers must be accommodated by removing molecules from the topmost layer, thus reducing its area (see Fig. 1(a)). The change in area can be calculated by writing the volume of film within some large field of view as $V = \chi L(nA_f + a(T))$, where $n$ is the number of complete layers each of area $A_f$ and $a(T)$ is the total area of the upper incomplete layer within the field of view. Since the thermal expansion is a small contribution [14], $V$ can be treated as constant, and the lamellar thickness can be written with respect to a reference temperature, $T_0$, as

$$\frac{L(T)}{L(T_0)} = \frac{nA_f + a(T_0)}{nA_f + a(T)}$$

(1)

Using the observed area in this way, we can accurately infer tiny variations in $L$, because the topography of the topmost surface results from the change in thickness of all the lamellae in the film [15].

In our experiment, samples are placed on a hot stage in a nitrogen atmosphere and an optical microscope is used to observe any changes in the area of the topmost layer as the temperature is slowly changed. After each change in temperature, the sample is allowed to equilibrate for as long as is necessary for the surface topography to stop changing. Figure 1(b) shows the change in area of the topmost layer as the temperature is decreased from 468 K to 413 K. Over this range in temperature the area of the islands is seen to vary linearly with a slope of $106 \mu\text{m}^2/\text{K}$. Analogous measurements were conducted for film thicknesses ranging up to $n = 7$ and with surface topographies ranging from islands to holes. Figure 2 shows the data from all these films scaled according to equation (1); there

![Fig. 1. a) Schematic cross-section of a film illustrating the decrease in island area and increase in lamellar thickness upon cooling the film. b) Total area of surface structures as a function of temperature for a film with $n = 2$ layers. Optical images in the inset collected at 433 K and 463 K for a film with $n = 7$ layers (20 µm scale bar).](image)
is a near perfect collapse of the data onto a single master curve. This implies that the substrate interface has a negligible effect on $L$ —more precisely, we can infer that the thickness of each and every layer is indicative of the bulk lamellar spacing despite its proximity to the substrate. We note that this result is in complete agreement with SCFT predictions [16].

Although the optical measurements of the area are very sensitive to the ratio $L/L_0$, they do not provide an absolute value for $L$. AFM is used here to set the absolute scale for $L_0$, we use $L(453\, K) = 13.1$ nm as this reference. This absolute reference is obtained from AFM measurements of a number of lamellae. The very small change in thickness of lamella makes the AFM measurement extremely error prone, as indicated by the relatively large error bars in Figure 2. Another disadvantage of the AFM measurement is that lamellae that are parallel to a substrate can only be measured at a lamellar edge. An edge is where one would expect to see the most deviation from the “bulk” lamellar thickness. This highlights the advantages of the optical measurement —it is simple and very accurate, as one can average the change over many surface domains of different sizes and furthermore the $n$-layers amplify the effect on the topmost feature.

Numerical solutions of the self-consistent field theory show that $L/R_g$ is an increasing function of $\chi N$, which is extremely well fit by

$$L/R_g = 2.8 + \sqrt{0.15(\chi N - 9.2)}, \quad (2)$$

shown in Figure 3(a) by the solid curve. Note that the conventional power law fit, $L/R_g \sim (\chi N)^m$, is a relatively inaccurate approximation, which may explain the wide range of exponents, $m$, quoted in the literature. Fitting equation (2) to the experimental results in Figure 2 with $R_g = 3.44$ nm (since both blocks are structurally similar, $R_g$ is obtained from polystyrene parameters [17]), we obtain

$$\chi = \frac{(97 \pm 2)\, K}{T} + (-0.11 \pm 0.01), \quad (3)$$

in close agreement with previous measurements [10,18].

Further insight into the process by which lamellae form and adjust their length scale with temperature is available through experiments which probe the dynamics of the transition from equilibrium at $T_i$, and a quench to $T_f$. Molecules from one lamella can penetrate into another lamella by overcoming an energy barrier $\Delta \epsilon$ —roughly, the energy associated with a block entering a matrix of the unfavorable block [19]. Figure 4 shows the response of the area of the topmost layer $(n+1)$ as the temperature is dropped from $T_i = 453\, K$ to $T_f$ for a film with $n = 7$. With the drop in temperature, the lamella becomes more
strongly segregated, and \( L \) increases resulting in a pressure difference that is equilibrated by molecules hopping from one lamella into another. This results in a decrease in \( a(t) \) with time as molecules from the topmost layer, which acts as a reservoir, empty into the \( n \) layers below.

A model can be constructed to describe the decay of the area of the islands, \( a(t) \), from \( a_i \) to \( a_f \) resulting from the temperature quench. For modest temperature jumps, it is natural to assume that the rate of change is \( a'(t) \propto [a(t) - a_f] \), which leads to exponential decay,

\[
a = (a_i - a_f) \exp(-t/\tau) + a_f .
\]  

(4)

In Figure 4, we fit the data to equation (4) plus an additional long-time exponential relaxation. The additional relaxation is attributed to the gradual Ostwald ripening of the islands or holes, and occurs on a time scale that is independent of and much larger than that of the hopping mechanism.

The symbols in Figure 5 denote the time constants, \( \tau \), extracted from our fits at the various temperatures, \( T \). The changes in \( \tau \) are dictated by two important temperature-dependent contributions. The first contribution, the frequency with which molecules attempt to pass between layers, is represented by the temperature dependence of molecular motion, and is given by the Vogel-Fulcher expression, \( \exp[-T_A/(T - T_V)] \). Because the chemical structures of polystyrene and poly(2-vinyl pyridine) are so similar [20], we use the values, \( T_A = 1250 \) and \( T_V = 320 \), of polystyrene homopolymer [17]. The second contribution, the success rate with which the molecules diffuse across lamellae, is a thermally activated process \( \tau \propto \exp(\Delta \epsilon/kT) \), where \( \Delta \epsilon \) is the energy barrier associated with molecules hopping between layers. Thus the time constant can be expressed as

\[
\tau = \tau_0 \exp[T_A/(T - T_V)] \exp(\Delta \epsilon/kT),
\]  

(5)

where \( \tau_0 \) is a temperature-independent quantity that depends on details such as the total number of layers, \( n \). Returning to the SCFT, we calculate \( \Delta \epsilon \) by examining the free energy of a single polymer in the self-consistent fields as its junction point is dragged from one interface to another. Note that the SCFT automatically accounts for changes in the block copolymer conformation as the molecule passes between layers. The theoretical result, plotted in Figure 3(b) as a function of \( \chi N \), is then converted to a function of \( T \) using our fit of \( \chi \) in equation (3) with \( N = 158 \). The solid curve in Figure 5 shows the theoretical expression in equation (5) fit to the data using only one free parameter (\( \tau_0 = (1.3 \pm 0.1) \times 10^{-4} \) s). The excellent agreement between the theory and experiment provides a useful consistency check between the information gained from the static and kinetic experiments.

In conclusion, we have used a simple optical technique to measure the area of the surface structure of symmetric diblock copolymer lamellae. As the temperature is varied, the balance between the entropic stretching of chains and the enthalpic repulsion between the two chemically distinct polymer blocks results in a change in the thickness of the lamellae. When the lamellar thickness changes, material from the topmost layer acts as a reservoir changing its area accordingly. This reservoir responds to all the layers thus amplifying any change in the lamellar thickness. Because of this amplification, the simple area measurement of the top layer can extract changes in the lamellar thickness with unprecedented resolution. Our study begins by comparing the equilibrium thickness of lamellae as a function of temperature to predictions from self-consistent field theory; from this, we obtain the temperature dependence of the Flory-Huggins \( \chi \) parameter (see Eq. (3)). In the second part of our study, we switch from equilibrium measurements to dynamics; by measuring the rate with which the area of the topmost layer changes in response to a temperature jump, we obtain a time constant associated with molecules passing over the energetic barrier as they hop from one layer to the next. The relaxation data is fit with a simple model, which verifies both the model and the consistency between the results obtained for both the equilibrium and dynamic measurements. For both sets of experiments, a simple optical microscopy observation is used to obtain parameters describing the motion of the diblock chains on a molecular level.

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References

14. Thermal expansion opposes and contributes less than 10% of the measure effect, i.e. lamellae decrease in thickness with increasing temperature.