

Self-assembly of block copolymers in thin films

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Block copolymers are recognized for their tendency to form well-ordered periodic microstructures, often with exceptionally intricate geometries. This class of molecule now promises to provide important commercial applications in the form of thin films. There have been many recent advances in the effort to create confined films, control surface potentials, probe and manipulate morphology, explain equilibrium behaviour, and understand kinetics. Such advances will be crucial in the development of applications for block copolymer films such as surface coatings, porous membranes, waveguides, and nanoscale templates.

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Introduction

Block copolymer molecules consist of chemically distinct polymer chains (i.e. blocks) covalently bonded together, and they self-assemble because of a general tendency for unlike blocks to phase separate. Most widely studied is the AB diblock copolymer composed of two amorphous, flexible blocks designated A and B. Even this simplest architecture exhibits a rich selection of ordered phases [1]. Its bulk equilibrium phase behaviour can be described in terms of the interfacial tension between the A- and B-rich microdomains and the entropic stretching energies of the two blocks [2]. The competition between the interfacial and stretching energies dictates the domain size. Any mismatch in the size and, hence, stretching energy of the A and B blocks generates a spontaneous curvature in the interface, which causes the minority domains to evolve from lamellae to cylinders to spheres as the diblock becomes increasingly asymmetric. Much attention has been focused on the region between lamellae and cylinders, where a number of complex morphologies compete for stability [1]. Subtle issues, such as complex phase selection and the symmetry of the cylindrical and spherical phases, are determined by the detailed shape of the microstructure [3•]. The block copolymer melt favours structures that possess small variations in the interfacial curvature and that provide uniformly thick domains, which minimize interfacial area and packing frustration (i.e. highly stretched chains), respectively.

New intriguing phenomena and the promise of various applications has spurred research in the area of block copoly-

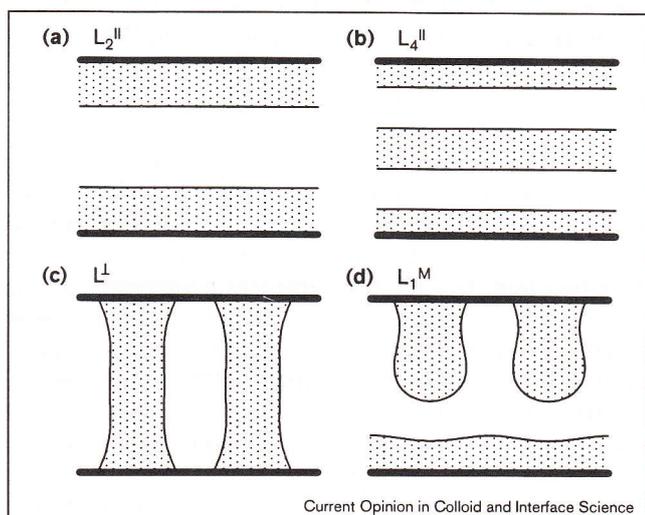
mer thin films. This introduces new parameters, film thickness and surface fields, which need to be controlled. New confinement techniques [4,5] allow us to prepare uniform films of a specified thickness, and surface coatings, such as random copolymer brushes [6•] or self-assembled monolayers [7•,8], permit us to finely tune the surface interactions. Other clever techniques [9•,10,11•,12,13•] provide the means to probe and manipulate the microstructure in ways not possible in bulk samples. This control will enable us to put block copolymers to important uses, such as surface coatings [14,15], porous membranes [16], waveguides [17] and templates [18–21,22•]. Furthermore, research into thin films is certain to greatly advance our general understanding of molecular self-assembly. Films represent an ideal system for examining segment distributions [23•,24–26,27•,28,29] surface effects [23•,24,30–32,65], electric field effects [9•,10,11•], packing frustration [4,5,33,34•], shear [35], and kinetics [36–40]. Below I discuss some of the recent advances involving block copolymer thin films and their applications without overlapping too much with reviews by Russell [41•] and by Binder [42•].

Confinement

To study the full range of thin film behaviour, it is essential to fix the film thickness. Without this constraint, a film will typically phase separate into two thicknesses, and all the behaviour between these two thicknesses will be unaccessible. So far, confinement studies have been limited to symmetric lamellae-forming diblock molecules.

Lambooy *et al.* [4] have confined films by depositing them on a silicon wafer and covering them with a thin protective polymer layer followed by a hard silicon oxide layer. The protective layer prevents the silicon oxide layer from bonding with the block copolymer film. Instead, it bonds with the polymer layer, which conveniently prevents intermixing with the block copolymer (P Mansky, personal communication). This confinement experiment produced parallel lamellae with periods modified to be commensurate with the film thickness; the expanded and compressed lamellar structures (Figure 1a and 1b, respectively) were separated by discontinuous phase transitions. More recently, Kellogg *et al.* [33] inserted random copolymer layers next to the hard walls to control the surface potentials. These studies produced a lateral structure consistent with a mixed-lamellar phase (Figure 1d) observed earlier in Monte Carlo simulations [43]. However, the lower random copolymer layer was not secured to the silicon wafer, and consequently it may have affected the results by partially mixing with the block copolymer (P Mansky, personal communication).

Figure 1



Parallel (L_v^{\parallel}), perpendicular (L^{\perp}), and mixed (L_v^M) lamellar structures for symmetric ($f=0.5$) diblocks confined between two walls with an equal affinity for the shaded domains. The index v refers to the number of parallel interfaces. These structures are all generated from actual self-consistent field calculations. Adapted with permission from [44**].

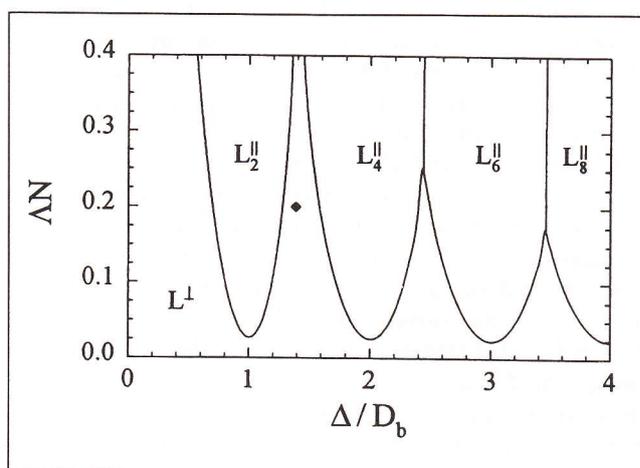
In the above studies [4,33], the polymer layers represent soft walls. Koneripalli *et al.* [5] introduced an alternative method in which a glassy polymer film provides the top confining wall. Not only can both surfaces now be considered hard walls, the glassy layer can easily be stripped off, which opens up important experimental opportunities (see section on Kinetics). Their confinement studies also revealed transitions between compressed and expanded lamellae [5] and provided the first compelling evidence for the mixed-lamellar phases [34**].

Recent self-consistent field calculations [44**] have provided the phase diagram in Figure 2 for symmetric diblock copolymers confined between equivalent walls. Only parallel and perpendicular lamellae are predicted to be stable; the mixed-lamellar phase is just metastable. Nevertheless, we can expect the mixed-lamellar structure to be observed in the perpendicular-lamellar region since the kinetics of microphase separation should favour its formation, as discussed in [44**]. Although somewhat counterintuitive, the mixed-lamellar phase is most metastable when the two confining walls have the same surface affinity. Also note that a small appropriate asymmetry in the diblock copolymer can stabilize this phase.

Behaviour characteristic of confinement, such as the formation of compressed parallel lamellae [45] and the mixed-lamellar structure [46], has been observed in some experimental studies on unconfined films. Morkved *et al.* [47] have, in fact presented theoretical as well as experimental evidence for a mixed-lamellar phase;

however, more accurate self-consistent field calculations (MW Matsen, unpublished data) disagree with their claim that it is stable for the film thickness and surface potentials in their experiment. At any rate, confinement effects are observed and several different mechanisms could be responsible. A strong preferential affinity at the free surface for one of the block copolymer components could cause the rapid formation of a flat uniform domain, which could effectively act as a confining layer. In ultrathin films, perhaps the lateral transport of material is sufficiently slow [48] that microdomain formation occurs on a much shorter time scale than terrace formation (i.e. the development of steps in the surface topography). Regardless, this behaviour clearly demonstrates the importance of kinetics in the self-assembly of thin films.

Figure 2



Phase diagram for intermediately-segregated ($\chi N=20$) symmetric ($f=0.5$) diblocks confined between identical walls plotted in terms of film thickness, Δ , relative to the bulk lamellar period, D_b , versus surface potential Δ . The diamond marks the location where the structures shown in Figure 1 were calculated. Adapted with permission from [44**].

Boundary effects

The proper boundary condition for a surface is that the polymer concentration should approach zero. Nevertheless, Silberberg [49] has explained that reflecting boundary conditions can be used [50,51*,52] in the case of flexible polymer chains. However, reflecting boundaries miss a variety of effects resulting from the finite width, ϵ , over which the polymer profile drops to zero.

Sikka *et al.* [30,31] have observed entropic surface segregation, which cannot be captured by reflecting boundary conditions. The Silberberg argument specifically rules out the nonlocal-entropic explanation suggested in [30]. The segregation, however, can be accounted for by the local-entropic penalty resulting from the decreasing polymer concentration at the surface. The penalty per

unit area of surface is proportional to $\rho_0 a^2/\epsilon$, where ρ_0 is the bulk segment density and a is the statistical segment length [44••]. This assumes that ϵ is large relative to the length scale on which the polymer chain be treated as Gaussian. While this may not be true at a hard wall, we can still expect an entropic penalty that increases with a . Thus the block copolymer component with the shorter a will be favoured next to the surface, in agreement with experiment. This same effect should occur for immiscible polymer blends, and is related to the predicted surface enrichment for miscible blends [53]. Note that Yethiraj [54] has predicted packing effects that could also explain the experimental results.

Calculations by myself [44••] and by Pickett and Balazs [55] reveal another effect that cannot be explained with reflecting boundary conditions. Both studies find a preference for the perpendicular orientation of lamellae, which accounts for the absence of parallel lamellae at small surface affinities in Figure 2 and implies that perpendicular lamellae can be stable in unconfined films [44••]. Pickett and Balazs [55] attributed their result to a nematic effect [52] involving the rigid segments in their lattice model, but I disagree, because the arguments of Silberberg will still apply when the segments are freely jointed. Instead, I suggest this effect originates from a drop in segregation near the surface. In [44••] the reduced segregation arises from the lower polymer concentration near the surface, and in [55] it occurs because lattice sites next to the surface have fewer nearest neighbours. This reduced segregation will decrease the A/B interfacial energy, producing a negative line tension, which will favour contacts between the A/B interface and the surface. Note that the reduction in nearest neighbours at the surface also explains why Pickett and Balazs [55] found a larger surface tension with neutral walls for unstrained parallel lamellae than for disordered films.

Surface fields

Russell and co-workers have made important strides in controlling the surface fields with random copolymers. In their initial experiments [33] they coated thin layers of random copolymer between the substrate and the diblock film. By changing the composition of the random copolymer, the preferential affinity of the surface was finely tuned. As noted above, intermixing between the random copolymer and the block copolymer film can be a concern. One solution for maintaining segregation would be to increase the molecular weight of the random copolymer as this reduces the entropy of mixing. Another is to chemically bond the random copolymer to the substrate to form a secure brush [6••,23••,46]. Even so, there is evidence that in some instances, the block copolymer penetrates the brush and interacts with the substrate [23••].

Up to this point, only AB random copolymers have been used to vary the surface potential of AB block

copolymer films. Assuming a well-segregated interface (so that $\gamma \propto \chi^{1/2}$, where χ is the usual interaction parameter), the surface tension between an A domain and the surface is $\gamma_{As} = f_{As} \gamma_{AB}$, where f_{As} is the A-segment content of the random copolymer and γ_{AB} is the interfacial tension between A and B domains, and similarly $\gamma_{Bs} = (1 - f_{As}) \gamma_{AB}$ [23••]. The preferential affinity of the surface is then $\Delta\gamma \equiv \gamma_{As} - \gamma_{Bs} = (2f_{As} - 1) \gamma_{AB}$. Thus a neutral surface should occur at $f_{As} = 1/2$, but in experiment, $\Delta\gamma = 0$ occurs at a somewhat asymmetrical composition [6••,23••,46]; the deviation from $f_{As} = 1/2$ may represent asymmetries in the system such as differences in the two statistical segment lengths, or it may be a result of significant penetration into the brush by the block copolymer [23••]. The latter will be particularly problematic when either $f_{As} \rightarrow 0$ or 1. In these instances, broad interfaces will occur and the simple expressions for γ_{As} , γ_{Bs} , and $\Delta\gamma$ will completely fail [6••]. This problem could be overcome by using an appropriate CD random copolymer. If γ_{AC} , γ_{AD} , γ_{BC} , and γ_{BD} were all reasonably large, the interfaces would remain narrow and well defined. Furthermore, there may be no need to bond the random copolymer to the substrate. If C and D had affinities for opposite components of the AB diblock, then the random copolymer composition could still be tuned to give a neutral surface.

Undoubtedly, other clever ways of controlling the surface affinity will be devised, such as the method introduced recently by Genzer and Kramer [7••]. They coat the substrate with a self-assembled monolayer consisting of a binary mixture of short chain molecules. The surface affinity can be varied by changing the composition of the monolayer. This method is not just restricted to homogeneous surfaces; Heier *et al.* [8] have, in fact, designed a periodic surface potential, which offers a new way to manipulate the morphology of the film [56].

Segment distributions

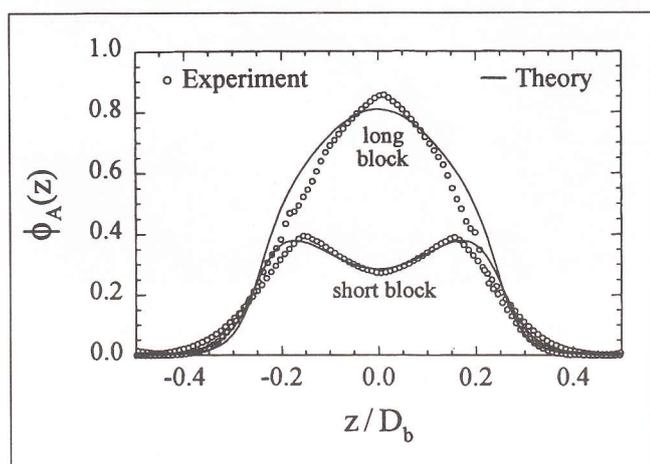
Pioneering work by Russell and co-workers [25,26] has established neutron reflectivity as a powerful tool in the study of block copolymer self-assembly. By deuterating specific segments, their distributions can be accurately measured. This now provides one of the most sensitive tests for block copolymer theories.

Anastasiadis *et al.* [25] used neutron reflectivity to measure segment distributions in a lamellar diblock film. Good agreement with theoretical predictions for the domain size and the shape of the interfacial profile was found in their study, but the interface was significantly wider than predicted. Later, Shull *et al.* [26] accounted for this discrepancy in terms of capillary wave fluctuations. Although there was little doubt that capillary waves significantly broaden the interface, it was satisfying to have this point clearly demonstrated in a recent study by Sferrazza *et al.* [27••].

Results from studies on diblock-homopolymer blends [26] and on binary diblock blends (N Koneripalli *et al.*,

unpublished data) have allowed detailed comparisons to be made with the self-consistent field theory of Helfand [57], which represents the state of the art in block copolymer theory. In both studies, all the measured segment profiles agreed beautifully with the theoretical predictions (e.g. Figure 3). The agreement is particularly impressive given that in both cases the experimental profiles were obtained without prior knowledge of the theoretical predictions, thus avoiding any unfair bias in the fitting procedure.

Figure 3



Segment distributions in a binary diblock copolymer blend. The two profiles are for slightly different conditions, but both roughly correspond to a 50:50 blend of complementary diblocks ($f_A \sim 0.3$ and ~ 0.7) with nearly equal molecular weights ($\chi N \sim 30$). One of the profiles provides the segment distribution for the long A block and the other represents the short A block. Open circles are obtained from experimental fits to neutron reflectivity data and solid curves are calculated using self-consistent field theory. Notice that the theoretical profiles are significantly steeper at the interfaces because they do not account for capillary wave fluctuations. Courtesy of N Koneripalli *et al.*

Other comparisons between theory and experiment [23••,24] have examined the surface enrichment in disordered AB diblock films. Theory [36,50,51•] predicts the A-segment profile in a disordered symmetric diblock melt next to a hard wall at $z=0$ to be

$$\phi_A(z) = 1/2 + \frac{c_0}{\text{Re}[\kappa]} \text{Re}[\kappa \exp(ikz)], \quad (1)$$

$$\approx 1/2 + c_0 \cos(q_0 z + \phi) \exp(-z/\xi) \quad (2)$$

where $\kappa = q_0 [1 + 2i(q_0 \xi)^{-1}]^{1/2} \approx q_0 + i\xi^{-1}$. The amplitude c_0 , wavevector q_0 , and correlation length ξ can all be related to the molecular parameters. These expressions are only valid for small c_0 (i.e. weak surface segregation), but it has not been established just how small c_0 has to be. Equation 2 is obtained by assuming $q_0 \xi \gg 1$. The

phase factor, $\phi \approx (q_0 \xi)^{-1}$, which was omitted in [23••,24,51•] emerges naturally and is required for the conservation of segments, expressed mathematically as:

$$\int (\phi_A(z) - 1/2) dz = 0$$

Nevertheless, in [23••,24] this damped harmonic form accurately modelled their reflection data even with $\phi=0$, values of $q_0 \xi$ often not much larger than 1, and rather large values of c_0 . However, the measured amplitudes, c_0 , in [23••] were about 2.5 times smaller than theoretically expected. Although this probably represents an inaccuracy in the theory, some of this discrepancy could be attributed to not using the more accurate expression, Equation 1, and the fact that the diblock was significantly asymmetric. More recently, studies have carefully examined the interaction between composition oscillations from opposing surfaces (P Mansky, TP Russell, Y Gallot, personal communication). Interestingly, disordered films avoid destructive interference by phase separating into thicknesses where the oscillations interfere constructively, even in cases where ξ is almost an order of magnitude less than the film thickness!

The quality of a reflectivity experiment is limited by the sophistication used to fit the reflectivity data. Generally, a fit assumes some functional form for the segment profiles with a number of fitting parameters, representing quantities such as the domain and interfacial widths. The danger in this approach lies in the possibility of choosing an inappropriate functional form or one without an adequate set of fitting parameters. Torikai *et al.* [28] attributes some of their poor fits to this problem. A more ideal strategy would use a parameterised functional form to obtain an approximate fit, and then would perform a free-form fit to obtain an accurate and unbiased segment distribution [29]. Certainly, further developments towards improving the numerical algorithms would be welcomed.

Kinetics

Block copolymers offer appropriate systems on which to test and expand our understanding of polymer kinetics. Grim *et al.* [37] have already achieved significant progress by studying the ordering processes in solvent-cast block copolymer films, specifically the development of either islands or holes in the film topography. Their experiments illustrate that the radius, R , of islands/holes formed on the surface grows as $R \propto t^\alpha$, with exponents varying from $\alpha=0.12$ to 0.26. Furthermore, they make a noteworthy effort to theoretically model this behaviour. Assuming no defects other than the islands/holes and that the islands/holes all occur in the same layer, they predict $\alpha=1/3$ for holes; for islands, they suggest the exponent will evolve from 1/4 to 1 to 1/3 with time. For the conditions in their experiment, $\alpha=1$ was expected for the island growth, representing a sizable disagreement with

the measured exponent. They explain the discrepancy in terms of defects and the fact that the islands/holes occur in various layers. Although this study does not provide a convincing explanation for the experimental results, it does stress the complexity involved in block copolymer kinetics. We note that the simple treatment suggested by Joly *et al.* [38] is generally inappropriate because the film thickness does not represent an adequate order parameter.

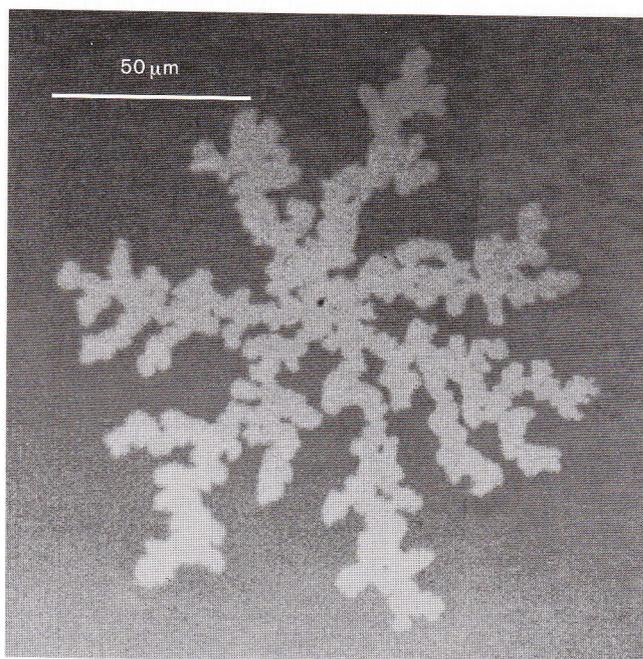
It appears that we must strive to simplify the system. Mansky and Russell [45] have examined conditions under which slightly compressed lamellae order prior to the formation of holes, which would provide a more ideal starting condition. Better yet, the confinement technique in [5] has been used to produce defect-free films of parallel lamellae that can be either highly compressed or expanded. When the top confining layer is stripped off and the film is brought above its glass transition, the kinetics of island/hole formation begins. The ability to start from such a simplified initial condition as opposed to the disordered state treated in [37,38] is a huge advantage in an effort to theoretically model the kinetics. Furthermore, researchers at Minnesota (N Koneripalli *et al.*, personal communication) have formed ultrathin films with a monolayer on the substrate, which is most likely immobile due to strong surface interactions, and a single frustrated (i.e. expanded or compressed) bilayer above. This configuration limits the number of kinetic processes and thus represents an optimal system to study. One of the most striking results to emerge from this work concerns the formation of holes. Under appropriate conditions, a fingering-instability occurs, and rather than growing circular holes, fractal patterns are formed (Figure 4).

It has been demonstrated that the nucleation of islands is far more rapid than that of holes [45,47]. Williams [58] has proposed a simple explanation for this; expanded films can reduce their lamellar period by creating undulations, but an analogous relaxation is not available to compressed films. The ability to create defect-free films in either a compressed or expanded state could provide the means of examining this corrugational instability. Because this instability is highly sensitive to the chain configurations, a more accurate self-consistent field calculation will probably be required in order to obtain quantitative agreement with experiment.

Applications

Monolayer films of block copolymer are certain to become important in the area of surface coatings. By incorporating functional groups into the block copolymer, one of the blocks can be designed to adsorb onto a particular substrate with the exposed block designed to provide the desired surface properties [14]. In addition to forming homogeneous surfaces, there is also the opportunity for creating regular patterns with controllable dimensions [15,59,60].

Figure 4

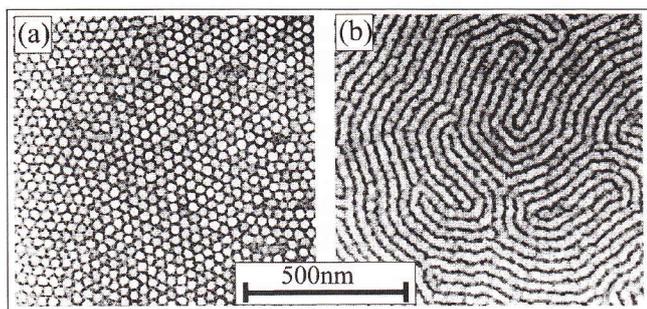


Hole growth in a diblock copolymer film of parallel lamellae producing a pattern with a fractal dimension of 1.66. The film is prepared with 1.5 highly compressed defect-free lamellae, and a dust particle visible as a dark spec in the middle of the pattern initiates the growth. The kinetics involve transport of material from the light region where only a single monolayer of diblock is left covering the substrate. Courtesy of N Koneripalli *et al.*

The lateral structure in block copolymer films is a valuable property that can be used for templates [18,19]. Morkved *et al.* [20] utilized monolayers of hexagonally packed spheres and of perpendicular lamellae to arrange gold particles into well-defined nanoscale arrays. Similarly, Lee *et al.* [21] used block copolymer films to form nanoscale patterns of barium titanate, a dielectric and ferroelectric material used in electronic and electro-optic devices.

Using diblock copolymer films as templates, Park *et al.* [22,63] have recently transferred patterns into silicon nitrate substrates (Figure 5). With sphere-forming diblocks they can etch either hexagonally packed holes or their negative image into the substrate, and with cylinder-forming diblocks they can create fingerprint-like troughs. More recently, these patterns have been successfully transferred onto silicon and germanium substrates (C Harrison, M Park, RM Chaikin, RA Register, DJ Adamson, personal communication). An important advantage of this lithography technique over standard ones is that it can efficiently produce small, highly dense features. This opens up a multitude of potential applications such as X-ray diffraction gratings, magnetic storage, quantum dot arrays, and periodic potentials for two-dimensional electron gases.

Figure 5



Micrographs of nanoscale patterns etched into silicon nitrate using block copolymer templates. The templates for (a) and (b) were formed from monolayer films of sphere- and cylinder-forming diblock molecules, respectively. Adapted with permission from [63].

For some of these applications, it is important to control the domain orientation and to create periodic structures with long-range order. In thin films, defects in the lateral structure cost relatively little energy, thus reducing the natural tendency to form well-ordered domains. Consequently, perpendicular lamellae [33,34,47] and parallel cylinders [9,10,11,21,22] produce fingerprint-like patterns (Figure 5b) rather than a series of parallel domains. Achieving a high degree of lateral periodicity will be a challenge, but one that we should be able to accomplish. Large surface potentials, which tend to pin the block copolymer molecules to the substrate, can be reduced by the methods described earlier, permitting a remarkable improvement in long-range order (C Harrison *et al.*, personal communication). Controlling other substrate properties such as roughness may also lead to higher degrees of order [52]. In bulk samples, shear fields have been exploited to control domain orientation and remove defects; this may also be possible in thin films [35]. Albalak *et al.* [12] have demonstrated that role-casting, followed by a modest amount of thermal annealing, can form nearly single-crystal films. Another approach is to use electric fields, which couple to a difference in the dielectric constants of the two domains [9,10,11,39,61]. With interdigitated electrodes, it is possible to orient large areas of film (Mansky P *et al.*, personal communication).

Block copolymer films also offer the potential of forming membranes with a high density of uniformly sized pores capable of filtering a specific range of particle sizes. Imagine forming a film with hexagonally packed perpendicular cylinders, where the size and spacing is controlled by volume fraction and molecular weight. The minority domains could be etched out to form the desired porous membrane. To strengthen the membrane, the matrix blocks could be cross-linked, or alternatively an epoxy resin could be added to the matrix [16]. Once the epoxy was cured, the block copolymer could be removed, leaving a porous membrane.

Conclusions

Block copolymer thin films are certain to become an increasingly active area of research. Not only are they highly interesting from a purely scientific point of view, they have a great number of potential applications. In order to reap the benefits of these films, we must make an effort to better understand the self-assembly of asymmetric block copolymers [62,63,64]. We must also develop a better understanding of kinetic processes [37,38], since they are likely to lead to a variety of highly metastable states, some that may be useful and others that we will want to avoid. Developing confinement techniques [4,5] and controlling the surface fields [6,7,8] will be instrumental in these studies. We still have much to learn about complex surfaces [8]; for example, what are the effects of roughness or of engraving the surface with a particular pattern [32,65]? Techniques for eliminating defects and controlling domain orientation, such as the application of electric fields [9,10,11] or shear fields [35] will be particularly important in the effort to develop applications. Naturally, the ever increasing variety of block copolymers (chemically and architecturally) will also open up new possibilities. We have yet to explore the effects of blending, such as mixing block copolymers with different bulk morphologies or with large disparities in their natural domain sizes. The study of block copolymer films is in its infancy and only time will tell what will emerge, but undoubtedly it will be a worthy endeavour.

Note added in proof

[65] is a recent paper demonstrating some interesting effects on corrugated surfaces.

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