Polymers on Nanoperiodic, Heterogeneous Surfaces

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Herein we establish a relationship between controlled nanoscale surface interactions and subsequent macromolecular ordering. Striped surfaces of oxide and metal are generated over large areas, where the stripe width is comparable to the size of a polymer molecule. Homopolymers are found to anisotropically dewet such surfaces, while incompatible polymer mixtures phase separate at the substrate/polymer interface on a molecular level. An orientation of lamellar block copolymer microdomains normal to the surface is found, when substrate and polymer length scales are commensurate. [S0031-9007(99)08747-5]

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A homogeneous interfacial interaction places a strong field on thin films which forces an alignment of structures and morphologies parallel to a surface [1–4]. By changing the strength of the interaction, the possibility of locally altering the orientation of the morphology exists [5,6]. Not only is the strength of the interfacial interaction a controlling factor, but also the length scale over which the interaction occurs [7–9]. An equally accessible alternative, therefore, is to use surfaces where the interfacial interaction is laterally heterogeneous, patterned such that the strength of the surface interaction is periodic. Here we report on the influence of commensurability, between the natural length scales of polymeric systems and the periodic pattern on a chemically heterogeneous substrate, on polymer self-organization.

Recognition by a polymer or response of a polymer to lateral heterogeneities requires the proper selection of the length scales [10–15]. Investigation of phase separating homopolymer blends on patterned substrates by Böltau *et al.* revealed that effective replication of a patterned self-assembled monolayer surface by the phase-separated domains occurred only when the period of the surface heterogeneities was commensurate with the coarsened domain sizes. For block copolymers, theory suggests that adsorption to a patterned surface will occur as a self-similar, two-dimensional pattern matching surface film only when similar conditions are met. Halperin finds that for block copolymer adsorption from solution, the stripe width L must satisfy the limits of $D < L \leq L^*$, where D is the correlation length of an adsorbed "blob" of similar chain segments, and $L^* \approx 2N_n\delta^{2/3}a$, where blocks of length N_n segments of size a are adsorbed with a surface energy $-k_BT\delta$ per segment [11]. For melts, Petera and Muthukumar [12] find an abrupt reorientation of the surface pattern induced segregation of a disordered diblock phase, when the condition $L^* = 2\pi R_g/\sqrt{2\sqrt{3}}$ is met, with R_g being the radius of gyration of the diblock in the disordered melt. When $L > L^*$ the anisotropic stretching of chains away from the surface to satisfy connectivity constraints results in a parallel orientation of the morphology. Only at $L = L^*$ is a vertical morphology predicted to develop from the surface. The commensurability constraint from theory is thus predicted to be more rigid for stretched blocks with $L > L^*$ than for the compressed case $L < L^*$. It is clear, however, that commensurability between the size scale of the polymer and the surface pattern must exist in order to induce recognition of the pattern by the polymer as well as accurate replication.

Here the behavior of homopolymers with a characteristic length scale of the radius of gyration R_g, as well as that of mixtures that macroscopically phase separate on the micron scale, and block copolymers having different molecular weights with characteristic lamellar periods in the tens of nanometers regime were investigated on heterogeneous substrates. Striped substrates comprising periodically varying polar (silicon oxide) and nonpolar (gold) interactions have been prepared where the period and stripe width are designed to be comparable to the size of individual polymer chains, and with the period of phase-separated block copolymer lamellae as well.

Nanoscopically grooved surfaces were prepared from Si(113) single crystal wafers miscut by 2.1° or 1.3° towards the (001) crystal plane [16]. The wafers were cleaned by direct-current resistive heating to above 1500 K under UHV, followed by an anneal below 1223 K, resulting in a grooved surface morphology. After the desired annealing time, the samples were quenched by rapidly decreasing the current. The period and amplitude of the grooves on the surface were controlled by the miscut angle of the surface, the annealing temperature, and the duration of the annealing. Typically, the lateral period L of the grooves is tens of nanometers with an amplitude or height h of several nanometers. A 10 s quench was used to generate the samples used for blend and block copolymer films, resulting in a 60 nm groove period with ±10 nm standard deviation.

Metal atoms are subsequently evaporated onto the surface at an incidence angle α, which is less than the apex angle θ of the crystal facets on the surface, as shown schematically in the inset in Fig. 1. This produces a shadowing of the surface features and results in a surface that consists of alternating stripes of silicon (silicon oxide) and the evaporated metal. Here consecutive evaporation of chromium Cr and gold Au were done in a resistive thermal evaporator at vacuum pressures below 4×10^{-6} torr. The initial evaporation of Cr onto the Si surface provided an adhesion layer for the Au. To ensure a collimated beam, the metals were evaporated from a source ~40 cm from the Si substrate through a 6 mm slit aperture. A quartz crystal microbalance was used to regulate film thickness at normal incidence. With $\alpha = 6°$, a shadowing of the surface with 1.5 ± 0.5 nm of Cr (measured *ex situ*) was followed by 2 ± 0.5 nm of Au. A field emission scanning electron microscopy micrograph of a grooved silicon surface after metallization is shown in Fig. 1. From atomic-force microscopy (AFM) measurements it is also evident that the surface is smooth between the Au stripes, indicating that little Au is deposited outside of the desired area. Since Au is an inert, nonpolar material and silicon oxide is polar, Fig. 1 represents a periodic, heterogeneous surface where the chemical heterogeneities are on the tens of nanometers length scale. Because of its simplicity, this technique is highly reproducible.

Previous studies have indicated that polystyrene (PS) preferentially interacts with an Au surface but dewets from a silicon oxide surface [17–19]. A 5 nm thick film of PS (weight average molecular weight $M_W = 9.6 \times 10^4$ with a polydispersity of 1.04) was spin coated from toluene onto a heterogeneous surface having a periodicity of 170 nm and a metallization thickness of 9 ± 1 nm. The film was annealed at 170 °C for 24 hours under vacuum and quenched to room temperature. The AFM image in Fig. 2 shows that the striped topography of the surface is retained. No tendency of the PS film to planarize the surface was evident, rather the PS dewets the oxide stripes and segregates to the Au. The average peak to valley height of the stripes is 25 ± 5 nm, which, in comparison to the original height of 9 ± 1 nm, represents an increase of ~15 nm. Since $\frac{1}{3}$ of the surface is covered with gold stripes, this increase in the peak to valley height is precisely that expected if a lateral segregation of PS to the Au stripes occurred.

Mixtures of narrow molecular weight distribution PS and polymethylmethacrylate (PMMA), 50% by weight, were cast from toluene onto a heterogeneous Au/SiO surface with a 60 nm stripe period, using a small drop of solution that wets the surface entirely. The molecular weight of the two components was comparable and the studies were performed where the molecular weight ranged from 3×10^4 to 1.3×10^5 daltons. The solvent was evaporated over a 20 min period. The substrates were then rinsed with a solvent selective for either PS or PMMA to remove one of the components so as to highlight the phase separated morphology. A 5 min bath in heated cyclohexane removed the PS, while acetic acid (followed by a rapid rinse in deionized water) removed the PMMA.

A morphology consistent with a lateral macroscopic phase separation of PS rich and PMMA rich phases was

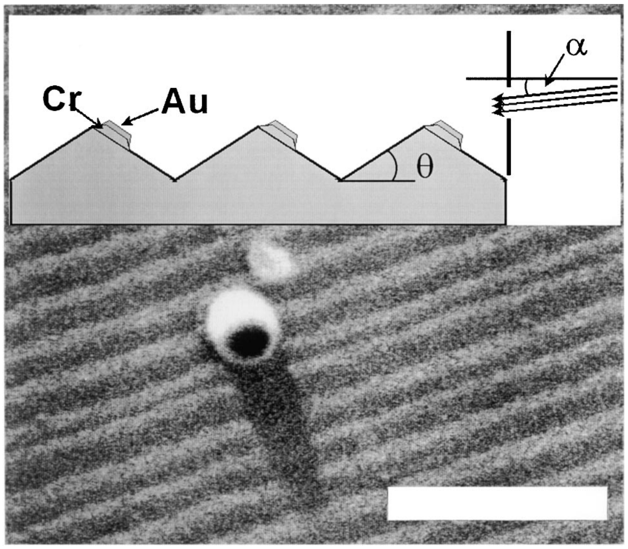

FIG. 1. Field emission scanning electron micrograph of a periodic heterogeneous surface. The surface impurity was included within the micrograph to demonstrate the effects of shadowing. The average stripe period here is 105 nm, with a metallization linewidth averaging 55 nm. The scale bar shown is 0.6 μm. The inset is the schematic diagram of the glancing angle evaporation geometry used. Provided the incidence angle α of the metal atoms is less than the apex angle θ of the facets, shadowing will occur and a heterogeneous surface will be produced.

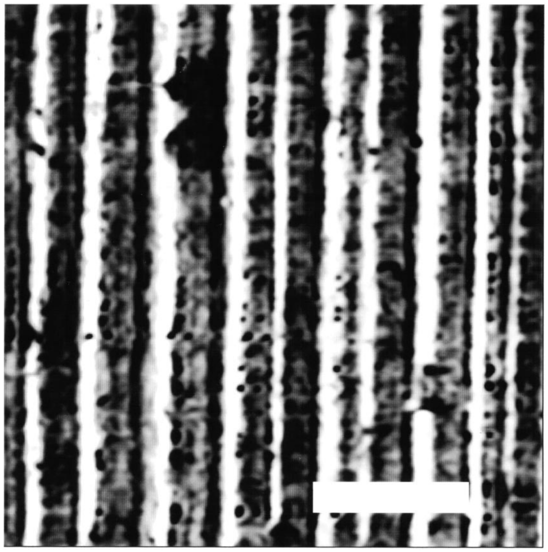

FIG. 2. AFM tapping mode height image of a PS homopolymer on a heterogeneous surface. The PS film was cast from toluene, then annealed. The roughness of this surface is much greater than that of the uncoated heterogeneous surface since the PS preferentially wets the Au. The scale bar shown is 0.5 μm.

evident on a micron size scale after an acetic acid etch. A typical example is shown in Fig. 3(a). Large PS domains from tenths to many microns wide remained, with thicknesses comparable to that of the cast film. On this size scale symmetry in the morphology indicated that neither PS nor PMMA exhibited any affinity for the substrate, and the free surface played no significant role in directing the phase separation of the homopolymers. This morphology was found independent of the molecular weight of the homopolymers. This result is in striking contrast to the morphology of a PS/PMMA mixture prepared on a laterally homogeneous silicon substrate where phase separation produces a uniform layer of PMMA wetting the substrate, and dewetting PS domains on the free surface [14,20]. An acetic acid etch on such a surface would remove the entire film, leaving a bare substrate. Thus, on this size scale, the chemical nature of the substrate has been effectively altered such that the characteristics of the phase-separated morphology are consistent with a chemically neutral, uniform surface. The blend apparently ignores the nanoscopic patterning to which the domain structure cannot adhere and experiences a surface field that is homogeneous.

Images of the same surface on the nanometer scale, however, reveal a very unusual morphology at the substrate. Removal of the PMMA macrophase shows PS remaining on the Au lines in the underlying surface regions, as shown in Fig. 3(b). This is also evidenced by the enhancement of the peak to valley height and the smoothing of the topography along the length of the lines as measured by the AFM. These results show that the interactions of the polymers with the substrate are, in fact, locally specific, and reduce the size scale of phase separation to the nanometer or molecular level at the substrate. Subsequent rinsing of the surface with cyclohexane removes all the PS from the Au lines, and a clean surface with only Au lines remains.

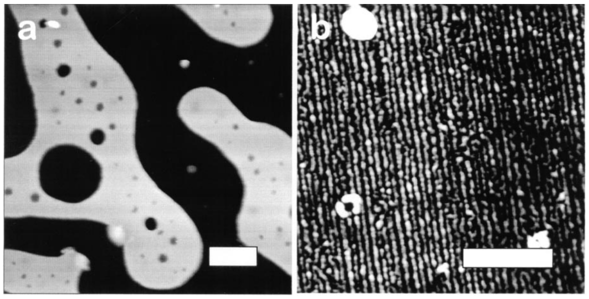

FIG. 3. (a) Micron scale morphology of phase separation. AFM tapping mode height image of a PS/PMMA blend film on a heterogeneous surface after acetic acid etch to remove the PMMA rich phase. PS rich domains indicative of the polymer blend phase remain on the surface. Domains are 40–50 nm in height, comparable to the initial film thickness before etching, and microns in width. The scale bar shown is 0.5 μm. (b) Nanometer scale morphology of phase separation. AFM tapping mode height image of a PS/PMMA blend film on a heterogeneous surface after acetic acid etch to remove the PMMA rich phase. Only PS rich domains remain on the surface, in a pattern indicative of their adsorption onto the gold lines. Line height is roughly 6 nm, with an enhancement of the lengthwise and lateral smoothing of the lines indicating polymer adsorption. The scale bar shown is 0.5 μm.

Selective polystyrene adsorption on the gold lines is present in all molecular weights, though there are slight differences in the morphology of the adsorbed layer. As we increase molecular weight, the quality of the adsorbed layer, defined as how smooth and conformal it appears upon the gold lines, begins to degrade. This is likely due to a change in the nature of the adsorbed layer as a function of molecular weight. In a homogeneous solution, adsorption to a uniform stripe should yield the same average number of surface contacts, independent of molecular weight. The total number of adsorbed chains, however, decreases with molecular weight while still providing an equivalent degree of surface contacts. As solvent quality degrades with evaporation, and coil collapse begins, the lower molecular weight chains will produce a more uniform, but thinner, stripe coverage. Higher molecular weight chains will produce a thicker, yet somewhat discontinuous surface coverage, describing the polymer morphology evident in the AFM data.

Experiments were also performed with symmetric diblock copolymers of PS and PMMA which, in the bulk, microphase separate into an alternating lamellar morphology. A range of molecular weights was examined to study the effect of commensurability between the block copolymer and substrate periods. A 0.1 wt% solution of each copolymer in toluene was cast onto a heterogeneous surface in a manner identical to that used for the mixtures. Figure 4 shows the AFM phase images of the entire series from low to high molecular weight. The degree of commensurability δ is defined as the ratio of block copolymer period in the bulk [21] to the substrate period L of 60 nm.

Distinctly different copolymer morphologies are observed as a function of δ, with a clearly defined commensurate regime, where surface control over lamellar ordering is expressed. The two-dimensional order parameter $f = 2\langle\cos^2\Theta\rangle - 1$, calculated from the Fourier transformed phase image data, are shown in the inset in Fig. 4. Incommensurate cases with too low or too high a copolymer period possess no strong surface direction. The AFM topography and phase images of the low molecular weight samples show no indication of lamellar ordering on these surfaces, while the highest molecular weight sample appears to have developed an unoriented vertical morphology. When commensurate, the lamellae are oriented normal to the substrate surface and are directed by the underlying stripes on the heterogeneous surface. Defects are present which disrupt the long range ordering and are likely due to both the mismatch between the polymer period and the substrate period where $\delta \neq 1$, and the imperfections in the substrate. In the range of $0.75 < \delta < 1$, the individual lamellae vary in thickness, being wider in some regions than others. Buckling along the length of individual lamellae is evident as well, and when the mismatch becomes too great, a merging of lamellar planes is found which is similar to a dislocation. In some cases,

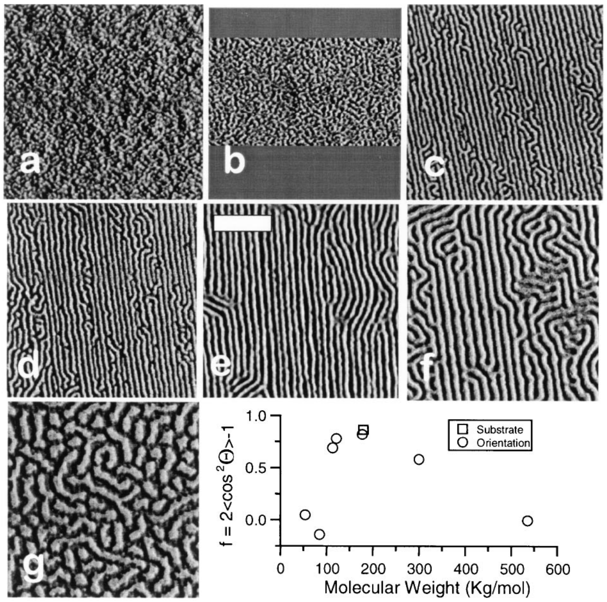

FIG. 4. AFM tapping mode phase images of free surface of PS-b-PMMA films of a range of molecular weights, solution cast on a 60 nm heterogeneous substrate. Molecular weights ($\times 10^3$ g/mol) [degree of commensurability δ], are as follows: (a) 57 [0.48]; (b) 84 [0.61]; (c) 113 [0.74]; (d) 121.3 [0.78]; (e) 177 [0.99], (f) 300 [1.4]; (g) 535 [2.05]. The scale bar shown in (e) is 0.5 μm; same scale applies to all images. Inset is the calculated 2D orientation function for each sample.

a local domain reorientation results. All such defects are due to frustration imparted by the period mismatch. In the range of $1 < \delta < 1.4$, while lamellar orientation and similar defect structures are present, the majority of the polymer remains unoriented. The substrate features serve only as a "guide" in some regions, while in others the surface direction is completely ignored.

Film thickness measured by AFM for all samples was on the order of 30 nm, less than the natural copolymer period. While this may contribute to orientation of the morphology normal to the surface [8,22], it cannot explain the lateral uniformity present, which clearly arises from the heterogeneous substrate. When cast on a homogeneous surface of SiO the block copolymer behavior is distinctly different. For thicker, unconfined films, the lamellar microdomains are oriented parallel to the substrate surface due to strong interactions between the SiO and the PMMA.

These studies have shown that it is possible to prepare laterally periodic, chemically heterogeneous surfaces with nanometer periodicity by use of reconstructed silicon substrates and glancing angle metal evaporation. These unique surfaces can serve as templates to control the dewetting of homopolymers, the lateral phase separation of mixtures, and the orientation and long range ordering of block copolymer lamellae. In the case of blends, two different length scales of interactions are operative. Near the surface, phase separation on a molecular level is evident, whereas slightly removed from the substrate, macroscopic phase separation is seen. For block copolymers, the strength of surface control over lamellar ordering and orientation is found to be strongly dependent on the degree of commensurability between polymer and substrate patterning, where up to a 25% mismatch between complementing length scales still allows strong substrate control. These heterogeneous surfaces represent a unique means of manipulating the size scale and orientation of polymer morphologies over a large range of length scales with a high degree of lateral coherence.

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