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Field-based Simulations of Directed Self-Assembly in a Mixed Brush System

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ABSTRACT

Self-assembling block copolymer thin films have attracted considerable attention as a promising high resolution lithographic tool due to the 10 nm scale of microdomain ordering and their facility for modulation of size and pattern. However, for block copolymer lithography to be a viable solution for advanced nano-lithographic technologies, several critical requirements need to be satisfied. Our research has focused on developing complementary mixed polymer brush lithography tools satisfying the required criteria, by means of Self-Consistent Field Theory (SCFT) simulations. Specifically, we have concentrated on *graphoepitaxial* techniques that are widely tested and considered a particularly promising method for controlling the microdomain ordering.

Keywords: Mixed brush, Self-Consistent Field Theory (SCFT), graphoepitaxy, grafting density, directed self-assembly

1. INTRODUCTION

Due to the technical and economical limitations associated with optical lithography, there have been numerous efforts to develop novel methodologies and materials that can replace the current technology with higher resolution alternatives. Among various approaches, the self-assembly of block copolymer thin films has attracted considerable attention as a promising high resolution lithographic tool due to its 10 nanometer scale of microdomain ordering and its facility for modulation of size and pattern.[1,2] One widely tested method for controlling the self-assembly of block copolymer thin films is graphoepitaxy which uses a topographically patterned substrate.[3] Many studies have shown that block copolymer systems that are laterally confined by a topographically patterned substrate develop a close-packed microdomain ordering along the walls that can serve to refine long-range in-plane order and can also stabilize desirable nanoscale structures including morphologies that do not occur in the bulk.

While numerous studies on block copolymer lithography have been conducted, mixed brush systems consisting of a mixture of two types of end-grafted polymers, which phase separate in a manner similar to block copolymer thin films, have attracted less attention as a lithographic tool. In part, this is due to the prevalence of defects in such systems and lack of long-range in-plane order. In the present paper, we adapt graphoepitaxial methods to mixed brush systems and investigate the possibility of lateral confinement as a means of inducing long-range, in-plane order in mixed brush systems. Self-Consistent Field Theory (SCFT) simulations are used to predict phase-separated morphologies as a function of the relevant parameters in the system, and to identify promising graphoepitaxial methods for the application of self-assembled mixed polymer brushes in next-generation information storage and electronic devices.[4,5]

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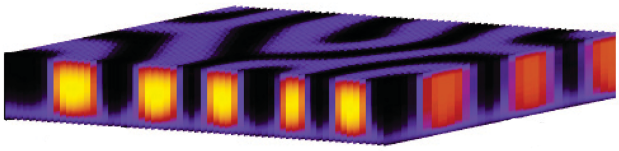

Figure 1. Representative density of A segments in a symmetric mixed brush (f_A= 0.5, $N_A = N_B$) without lateral confinement. Brush height and lateral box size are set to 3 and 30 R_g, respectively.

2. MICROPHASE SEPARATION IN A MIXED POLYMER BRUSH

When two different homopolymers, A and B, are randomly grafted to a substrate, the dissimilar A and B chains prefer to phase separate, but the grafted chain ends limit the phase separation to approximately 10 nm distances. Since mixed brushes microphase separate in different manners depending on the environmental conditions, such as the solvent quality, pH condition, temperature or humidity, one can switch the system from one morphology to another with a different average composition of the uppermost layer of the polymer brush by changing environmental conditions. Due to this special "switching property", mixed brush systems have attracted considerable interest for various applications such as responsive surface coatings, microfluidic devices, etc.[6,7] However, mixed polymer brushes have received less attention as advanced lithographic tools since experimentally observed microphases in mixed brush systems have very short-range order and are often defective, reducing the usefulness of such systems for lithography as compared to block copolymers. In order to improve the usefulness of mixed brushes as a nano-lithographic tool, we have adapted topological confinement methods.

A field theoretic model of mixed brushes is constructed by using the continuous Gaussian-chain model and effective interaction parameters between segments similar to the previous studies for non-tethered block copolymer systems, except that each polymer chain is attached at one end to the surface. We study a melt system with large grafting density and a large polymer/air surface tension leading to a flat top surface. Impenetrable substrate and top surface conditions are implemented through a predetermined "mask" density field, and a pseudo-spectral method with Dirichlet boundary conditions is used to solve the Fokker-Plank partial differential equation (modified diffusion equation) for the chain propagators.[8]

Unlike a block copolymer system, the grafting of the polymers to an impenetrable surface in a mixed brush system produces an initial condition of the chain propagator proportional to a Dirac delta function. To avoid the numerical difficulty caused by spatially resolving the delta function, we assumed that the tethered-end is smeared over a narrow region with the same width as the substrate/polymer interface. To evaluate the partition function and density operator, we followed Müller's approach, in which the partition function is evaluated by integrating the diffusion equation starting at the free chain end, rather than at the grafting point.[5] In this approach, a new complementary propagator is introduced by affecting a summation over the each chains. Under the assumption of high grafting density, the replacement of a summation over chains by a quenched average over the locations of the tethering points is accomplished by introducing an integral over the surface weighted by a grafting probability distribution. By modulating this probability distribution of grafted points, we can thereby simulate systems with spatially varying grafting densities.

Three dimensional SCFT simulations of several mixed brush systems have been conducted and one result is shown in Fig. 1. In this simulation, the top surface of a mixed A/B polymer brush is neutral and A and B polymers of the same lengths are grafted at similar areal densities. We observed lateral microphase separation that is similar to the perpendicular lamellar phase of symmetric block copolymers. In the mixed brush context, this phase is called the "ripple" phase. Similar to the experimentally observed ripple phases in mixed brush systems, it has a very short-range order and is defective.

If the top surface of a mixed A/B polymer brush attracts a specific component, a perpendicular microphase separation is observed, which is called the "dimple" phase.[9] Two dimensional SCFT calculations with various

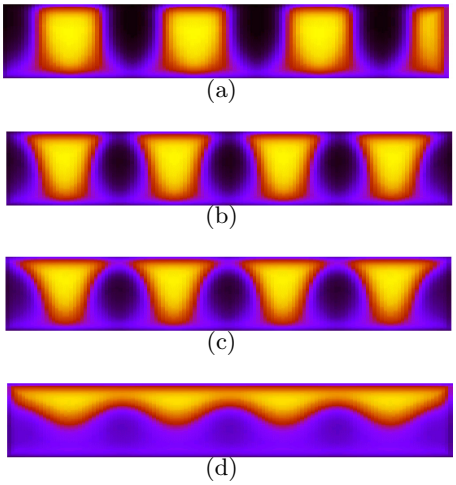

Figure 2. Microphase separation in a symmetric mixed brush where $\chi N_{AB} = 12$ and $N_A = N_B$, with different surface interaction $\chi N_{top,A}$ set to (a) 0, (b) 12, (c) 16 and (d) 20. The interaction between the top surface and B homopolymer is fixed at $\chi N_{top,B} = 0$

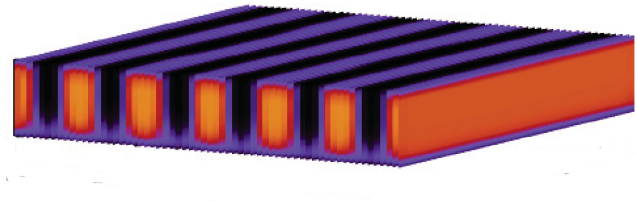

Figure 3. Representative density of A segments in a symmetric mixed brush (f_A= 0.5, $N_A = N_B$) that is laterally confined on two opposing sides. Brush height and lateral box size are set to 3 and 30 R_g, respectively.

surface wetting characteristics are shown in Fig. 2. As the attraction between the top surface with the A polymer increases, it is observed that lateral segregation transforms into perpendicular phase separation.

3. MODULATION OF GRAFTING DENSITY

Graphoepitaxy is adapted to mixed polymer brushes as a possible strategy for addressing the shortcomings of the system as a lithographic tool. Here, however, we explore a different type of confinemnt – a "chemical" (rather than "topological") confinement in which a "pure" polymer brush of either A or B homopolymer is used to laterally confine the mixed A/B brush into a region of prescribed shape. Such confinement masks can be created by a variety of low resolution (micron-scale) soft lithographic methods to pattern orthogonal polymerization initiators that are subsequently elaborated into polymer brushes. SCFT simulation results with lateral confinement indicate that a pure A brush region draws polymer A from the mixed brush to the mask perimeter, thereby reducing the interfacial energy. This in turn creates a polymer B-rich region that follows the contour of the mask and thereby guides phase-separation aligned with the interface between pure and mixed brush regions (Fig. 3).

Inspired by previous studies showing a strong correlation between microdomain ordering and grafting density,[10,11] we conducted systematic studies to better understand the physics of phase-separation processes in mixed brushes under various grafting profiles. When the grafting density ratio between two species A and B varies with a certain spatial frequency, the observed ripple phases in SCFT simulations try to replicate the frequency of grafting density ratio fluctuations even when the amplitude of the fluctuations is small. The Fig. 4 shows the observed "ripple" phase in a mixed A/B polymer brush for a variety of grafting density ratios between the A and

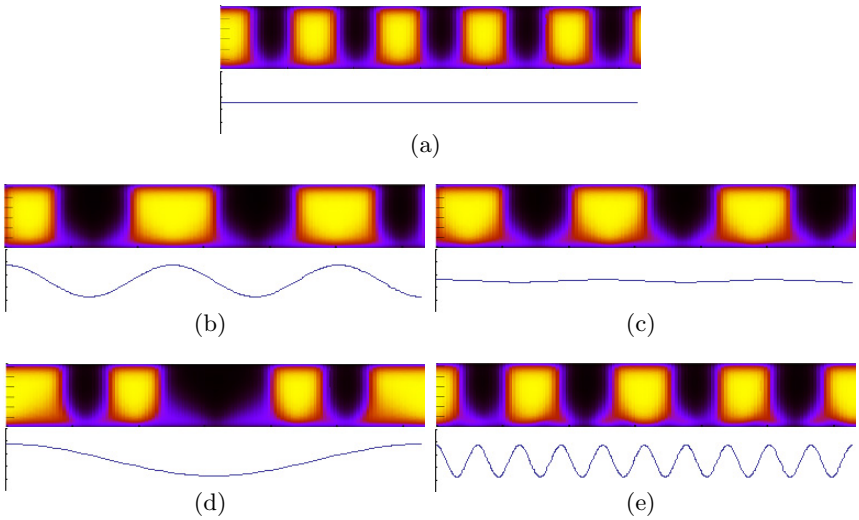

Figure 4. Representative density of "ripple" phase in a mixed A/B polymer brush (top) under a variety of grafting density ratios between the A and B species (bottom). The total grafting density is fixed to be uniform over the domain for a system size of 20 R_g.

B species, where the total grafting density is fixed to be uniform over the domain for a system size of 20 R_g. As the grafting density ratio is varied spatially, we find a strong correlation with the frequency of the self-assembled ripples. While a mixed brush with uniform grafting generates a "ripple" phase with the natural frequency (Fig. 4(a)), varying the grafting density ratio produces composition fluctuations that the microdomain ordering will try to replicate (Fig. 4(b)) even when the amplitude of the fluctuations is extremely small (Fig. 4(c)). In the low frequency limit (Fig. 4(d)), we observe a break-down of the domain into two regions with different domain spacing. In the high frequency limit (Fig. 4(e)), the normal behavior is ultimately restored. This suggests a possibility of forming features with multiple sizes and pitches in different locations on the same layer, which is difficult to realize in block copolymer lithography, since the size of features and the spacing between them is controlled by the molecular weight of the different block components of the copolymers. Thus, by modulating the grafting profile, we expect a new mechanism to control the scale and pitch of self-assembly of mixed brush systems in different regions of the same layer.

4. CONCLUSIONS

Through SCFT simulations, we have investigated the detailed two and three-dimensional configurations of phase-separated morphologies associated with a particular type of mixed brush and confinement conditions. We have shown that long-ranged ordering can be obtained by laterally confining a mixed A/B brush region with a pure polymer brush region of either A or B homopolymer (chemical confinement). Our SCFT results on mixed brushes also demonstrate the possibility of generating patterns with multiple sizes and pitches within a single layer by spatial modulation of the grafting density. We expect this simulation study can help guide the direction of future experimental studies on mixed polymer brushes with an eye to applications in advanced lithography.

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