Lateral versus Perpendicular Segregation in Mixed Polymer Brushes

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Grafting of incompatible polymers on a substrate prevents macrophase separation and the chains self-assemble laterally. Mixed brushes are exposed to different solvents and the morphology is observed via atomic force and x-ray photoemission microscopy. In a nonselective solvent the different species segregate into parallel cylinders ("ripple structure"). Upon exposure to a selective solvent, we encounter a transition to a "dimple" structure, in which the unfavored component forms clusters. Simultaneously, we observe an enhanced perpendicular segregation. The experimental observations are compared to self-consistent field calculations, where qualitative agreement is found.

Tailoring materials with smart response to external fields is of abiding interest to material science. Modern devices like sensors, switches, or microactuators crucially rely on a response in one or more physical properties (e.g., surface composition and energy, or optical and electrical properties) on external control. These properties may be employed to tune stability [1], wettability [2], adhesion [3], or to regulate interaction with cells and proteins in biomaterials [4], or membranes' permeability [5].

Many polymeric and biopolymeric systems respond to external control by cooperative changes of their conformation (e.g., collapse of the chain structure in a bad solvent or denaturation of proteins). Combination of conformational changes with phase separation can amplify the response, a mechanism which has been recently exploited in the form of two component (mixed) polymer brushes [6] and block-copolymer brushes [7,8].

If such a mixed brush of hydrophilic and hydrophobic homopolymers is exposed to a hydrophilic solvent the hydrophilic component preferentially segregates to the top of the film and the surface becomes hydrophilic. Exposing the same brush to a hydrophobic solvent reversibly switches the surface from hydrophilic to hydrophobic [6]. Such an adoptive behavior is very promising for engineering of smart surfaces for biomedical applications and micro- and/or nanodevices. Although these experiments have demonstrated the usefulness of mixed brushes for constructing surfaces with reversibly tunable wetting properties, the contact angle is sensitive only to the composition on the top of the brush and averages over the lateral structure. The local structure has yet remained unknown.

Grafting two incompatible polymers randomly onto a surface prevents macrophase separation. Two *limiting* types of morphologies can be distinguished: (1) The two species segregate perpendicular to the substrate (layered phase [9]), one species being enriched at the substrate while the other segregates to the top of the brush. The mixed brush remains laterally homogeneous. This homogeneity is advantageous for designing surfaces with reversibly tunable wettability. (2) The two species self-assemble laterally into two-dimensional structures (e.g., the "ripple" phase [9]) with a well-defined lateral length scale, which is of the order of the molecules' extension. Similar to thin films of diblock copolymers these systems might serve as templates for nanostructures.

Understanding and controlling whether lateral or perpendicular segregation dominates is a key to tailor surface properties. In this Letter we study the structure of mixed brushes by self-consistent field (SCF) calculations and experiments. For the first time, we find experimental evidence for lateral phase separation and explore the interplay between lateral and perpendicular segregation. Our SCF calculations indicate that there are two distinct morphologies, one of them ("dimple" structure) has not been predicted previously. Both morphologies are observed in our experiment, and transitions between both morphologies can be induced by the selectivity of the solvent.

Microphase separation of incompressible brushes has been studied analytically in the strong stretching limit by Marko and Witten [9]. The binary brush forms a ripple phase in which the two components segregated laterally into stripes rather than segregating perpendicular to the substrate. Simulations of a mixed brush in a common bad solvent give evidence for more complex lateral structures [10,11]. We have recently developed a general SCF theory for mixed brushes with immobile grafting points in nonselective solvents [12]. The behavior of a mixed brush in a selective solvent, which is most pertinent for practical applications, has yet not been considered. This problem is therefore addressed here.

In our SCF calculations we model the polymers as Gaussian chains. They contain N monomers and are grafted randomly and irreversibly to a surface with a grafting density σ. We assume the two components to have identical chain length N and extension R_e and restrict our calculations to brushes which contain equal amounts of A and B chains. Interactions between the different monomers A and B are modeled by second virial coefficients

v_{AA}, v_{BB}, and v_{AB}. $v = (v_{AA} + v_{BB} + 2v_{AB})/4$ denotes the average excluded volume interaction. The parameters σ, N, and v enter the calculations only in the combination $1/\delta^3 \equiv \frac{3}{2}[vN^2/R_e^3]^2[\sigma R_e^2]^2$ which measures the degree of chain stretching in the brush [13]. We use $\delta = 0.46$ which corresponds to a moderate degree of stretching. $\tilde{\chi} = (2v_{AB} - v_{AA} - v_{BB})/2v$ characterizes the repulsion between the two components and $\zeta = (v_{AA} - v_{BB})/2v$ describes the selectivity of the solvent. The spatial dependence of the composition is expanded in a set of orthonormal functions with the symmetry of the phase under considerations [14]. The free energy of the different morphologies is calculated within mean field approximation and minimized with respect to the length scale of the two-dimensional periodic structure.

In addition to the ripple phase [15] the calculations for mixed brush of symmetrical composition surprisingly find a new dimple phase in which one of the components segregates into clusters which arrange on a hexagonal lattice. The phase diagram as a function of incompatibility $\tilde{\chi}$ and selectivity ζ of the solvent is presented in Fig. 1. Upon increasing the incompatibility in a nonselective solvent $\zeta = 0$, we find a transition from a laterally homogeneous phase (dis) to the ripple phase. As we decrease the solvent quality for the A component $\zeta < 0$ the ripple phase transforms to a "dimple A" structure, where the A component segregates into clusters which arrange on a hexagonal lattice. Likewise, we find a "dimple B" structure with a collapsed B brush when the solvent is poor for the B component ($\zeta > 0$). At higher incompatibility (or poorer solvent quality) only dimple structures are stable. If we increase δ the region of stability of the ripple phase will increase and the transition from the laterally homogeneous phase to the structured phases will occur at lower incompatibility.

In the inset in Fig. 1 we present the laterally averaged composition profiles at $\tilde{\chi} = 2.4$. As we increase the selectivity the B component segregates to the top of the brush, while the relative density of A is higher at the substrate. Contour plots of the composition at small and large solvent selectivity are presented in Fig. 2. Note that the dimple morphology at larger ζ exhibits in addition to the two-dimensional structure a pronounced perpendicular segregation.

In the following we employ two complementary imaging techniques to investigate experimentally the phase segregated structures and surface properties of binary brushes. They have been synthesized on the surface of Si wafers by a "grafting from" approach [15]. For our experiments we have chosen a mixed brush of a random copolymer of styrene and 2,3,4,5,6-pentafluorostyrene (PSF) and polymethylmetacrylate (PMMA). The weight ratio of the random copolymer PSF is styrene: pentafluorostyrene = 0.75:0.25 as evaluated with NMR. Samples have been synthesized by a multistep procedure using radical polymerization initiated with the azoinitiator covalently attached to a Si wafer [6]. We expect this method to minimize the correlation between the grafting points of different species. We find no evidence for lateral segregation on length scales significantly larger than R_e. This indicates that the grafting points are uncorrelated to a good approximation. The molecular weights of the grafted chains were assumed to be the same as for free polymer simultaneously synthesized in the bulk and were measured with gel permeation chromatography. They are 475 kg/mol and 811 kg/mol for the PSF and the PMMA component, respectively. The polydispersity of the brush is larger than in solution [16]. The thickness and refractive indices of the grafted layers were measured with null ellipsometry. The grafting density
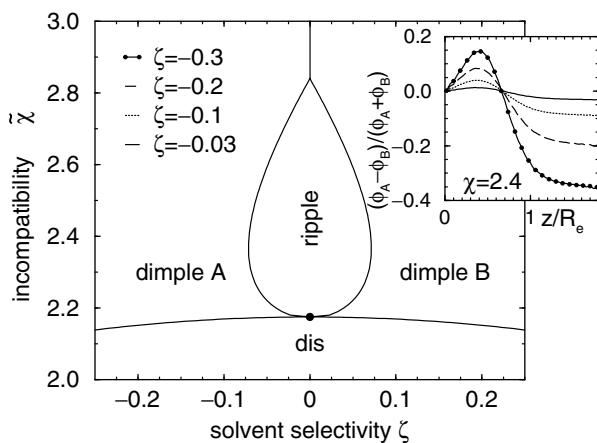
FIG. 1. Phase diagram of a mixed brush as calculated in SCF theory. In addition to a laterally homogeneous phase (dis), the phase diagram comprises a ripple phase and dimples. The inset presents the laterally averaged composition profile at $\tilde{\chi} = 2.4$ and ζ as indicated in the key.
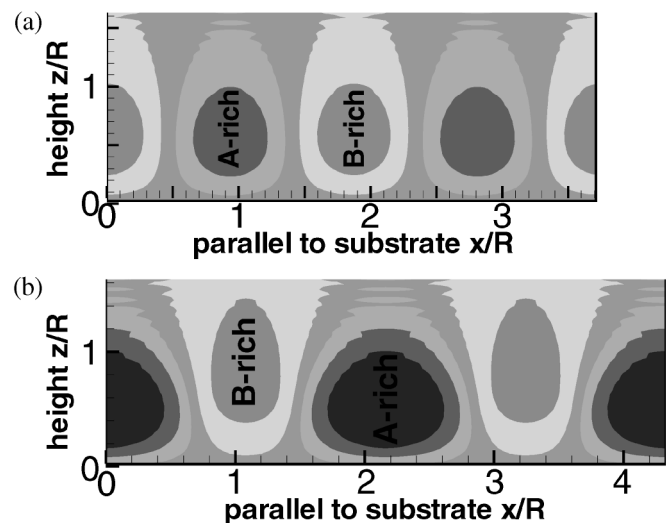
FIG. 2. Contour plot of the composition $(\phi_A - \phi_B)/(\phi_A + \phi_B)$ at $\tilde{\chi} = 2.4$. Each shading corresponds to a composition difference of 0.32. (a) Ripple phase at $\zeta = -0.03$. (b) Dimple A phase at $\zeta = -0.3$.

of PSF is 3×10^{-2} nm^{-2} and that of PMMA is 10% larger. Hence, the typical distance between grafting points $d = 4.5$ nm is about an order of magnitude smaller than the chain extension in the bulk. The morphology of the dry films after exposure to different solvents was studied with atomic force microscopy (AFM). Surface chemical composition with lateral resolution of about 30 nm was studied with x-ray photoemission electron microscopy (XPEEM) at the Advanced Light Source in Ernest Orlando Lawrence Berkeley National Laboratory. In these experiments we make the salient assumption that morphologies which we observe for dry films are also characteristic for the morphology of the swollen films. There is much evidence for that: (1) After exposure to a particular solvent the film was rapidly dried by a flow of nitrogen within a few seconds. The time of solvent evaporation is very much smaller than the characteristic time for transforming one morphology into a different one upon changing the solvent. The latter time scale ranges from several minutes to hours. Hence, rapid solvent evaporation freezes the morphology as it was in the solvent. Under these conditions no effect of the drying rate has been observed. (2) The morphologies after treatment by a particular solvent are reproducible and the morphology reversibly switches upon exposure to another solvent. Therefore, morphologies in our experiment are (close to) equilibrium structures. (3) The morphology after drying does not change in a poor solvent and is stable for a long period of time.

When the mixed brush is exposed to the good nonselective solvent toluene, the (advancing) contact angle of water on the mixed brush is 90° [17]. This value is located between the contact angles 110° and 78° of water on the pure component films PSF and PMMA, respectively. We expect both components to be simultaneously present at the top of the brush. A typical tapping mode image of the PSF-PMMA brush is shown in Fig. 3a. Both species do not mix, but rather segregate into elongated domains with a characteristic lateral length scale. We identify this type of lateral morphology with the ripple phase. In accord with theory, brushes of approximately symmetrical composition form ripple structures when exposed to a good nonselective solvent. Unlike the theoretical prediction, however, no long ranged lamellar order is established in the experiment. Long ranged order might be suppressed by several effects: (1) The radical polymerization mechanism gives rise to a large polydispersity $M_w/M_n > 2$. This implies a considerable variation in the cluster sizes (cf. Fig. 3), which smears out long ranged order. (2) Local fluctuations in the grafting point density might cause variations in the size of the clusters or width of the elongated domains. Slight inhomogeneity in the attachment of the azoinitiator might be an additional source of grafting defects. (3) The transition between the dimple and the ripple structure is reversible and can be repeated many times. The time scale for establishing truly long ranged order, however, might exceed the experimental time scale.
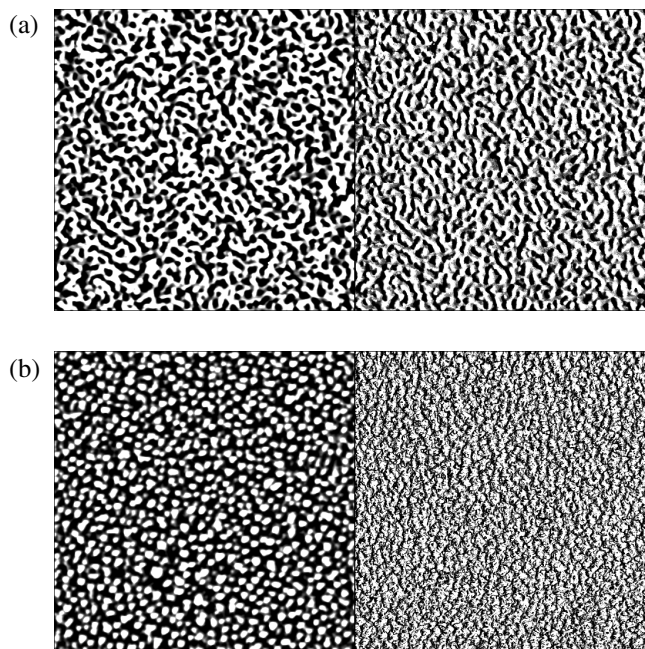

FIG. 3. AFM tapping mode images 5×5 μm of the mixed brush after exposure to (a) the nonselective solvent (toluene) or (b) a good solvent for the B component (acetone). Images on the left-hand side show the topography [z range: 20 nm (a) and 70 nm (b)]. Images on the right-hand side show the phase at 50% set-point ratio in the contact regime.

The lateral phase segregation is corroborated by XPEEM experiments which probe the chemical composition in the top layer (<5 nm) of the brush. The near-edge x-ray absorption of the fine structure spectra exhibit clearly distinguishable C edges for PSF and PMMA at 286.1 and 289.2 eV, respectively. In a nonselective solvent, XPEEM images taken at these energies in Figs. 4a and 4b are inverse one to another and prove the lateral segregation of PSF and PMMA.

After exposure to the selective solvent acetone the morphology changes from the ripple to the dimple structure. A typical AFM image is presented in Fig. 3b. The solvent is bad for PSF and this component forms small clusters. In contrast to the ripple structure the clusters are not interconnected and not elongated. The Fourier transform of the image shows some indication of short ranged hexagonal packing in the dimple phase, but again no long ranged order is established. The radially averaged power spectral density calculated from AFM images yields a length of about 140(30) nm $\approx 2.8(6)R_e$, which is somewhat larger than the periodicity of $2.2R_e$ predicted by the SCF calculations. The quantitative difference might be due to uncertainties and asymmetry in the degree of polymerization or the higher incompatibility and stretching of the experimental system compared to the SCF calculations.

The treatment with a selective solvent greatly reduces the contrast of the phase images in tapping mode AFM (Fig. 3b right) and the XPEEM images (Figs. 4c and 4d) [18], but the height contrast (Fig. 3b left) remains very
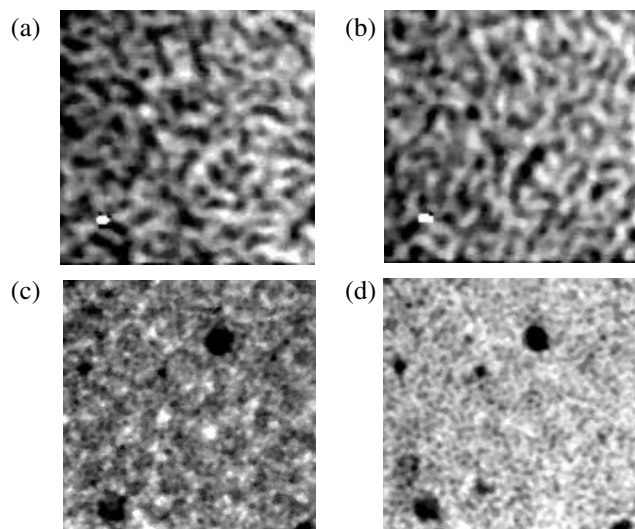
FIG. 4. XPEEM images 3×3 μm after exposure to toluene showing contrast between C edges of both polymers at 286.1 eV (a) and 289.2 eV (b) for PS and PMMA, respectively. (c) and (d) show the corresponding XPEEM images for the selective solvent (acetone).

pronounced. This indicates that the lateral segregation is much reduced *only at the top of the brush*. The contact angle of water on top of the mixed brush is 81°, a value which is close to the value 78° of pure PMMA. The component for which the solvent is good preferentially segregates to the top. A selective solvent suppresses the lateral and enhances the perpendicular segregation. Again, this behavior is in qualitative agreement with the SCF calculations.

In summary, we explored the local structure of binary polymer brushes in selective and nonselective solvents and have observed for the first time lateral phase separation and the interplay between lateral and perpendicular segregation. Experiments and SCF calculations give a mutually consistent picture. Lateral and perpendicular segregation occurs simultaneously. Nonselective solvents enhance the lateral segregation and tend to stabilize the ripple structure. Selective solvents enrich the preferred component at the top of the brush, whereas the unfavorable component forms dimples [19]. We expect our findings to provide guidance for creating materials which respond to variable environments by changing their surface properties or for fine-tuning of wetting properties. The lateral structure might impart distinct features on the adsorption characteristics of molecules, which are of the size of the lateral structure itself.

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[17] Since both constituents are insoluble in water (common bad solvent), the morphology and the contact angle are stable.
[18] The AFM phase contrast (Fig. 3 right) stems from the different viscoelastic properties of the species and is sensitive to the surface composition. Unlike the behavior in nonselective solvents, the XPEEM images in the selective solvent (Figs. 4c and 4d) are *not inverse* to each other. Residual structure is caused by scattering from the topographical structure.
[19] The same interplay between lateral and perpendicular segregation, and the transition from ripple to dimple structures is observed for polystyrene-poly(2-vinylpyridine) and polystyrene-polyacrylic acid mixed brushes.