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Exploiting Substrate Stress To Modify Nanoscale SAM Patterns

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Self-assembled monolayers (SAMs) have many applications largely because they can be easily used to engineer surface properties.[1] Mixed SAMs are particularly attractive because their properties can be tailored through small changes in composition[2] and structure.[3] However, there is still incomplete understanding of how to control structure in mixed SAMs. There is evidence that substrate stress can affect adsorption of molecules on surfaces.[4] Recent theoretical studies have further shown that phase-separated patterns formed on unstressed substrates differ from those formed on substrates that are stressed prior to adsorption.[5−7] Here we demonstrate that stress applied *post*adsorption affects diffusion of adsorbed molecules on the surface and can thus be used to modify surface patterns formed by phase separation in adsorbed molecular mixtures. We also show how stress can be used to progress nonequilibrium, kinetically arrested patterns formed on flat substrates toward equilibrium. Specifically, using computer simulations we predict that a kinetically arrested pattern of phase-separated patches formed in a mixed SAM of surfactants on a flat substrate can be progressed to form the equilibrium, striped pattern by stressing the substrate through induction of curvature. We confirm this experimentally by obtaining images of phase separation in mixed SAMs on gold substrates, both pre- and postinduction of curvature in the substrate. The motivation for this work comes from observations that a mixed SAM of surfactants of unequal length and/or bulkiness readily organizes into stripes on highly curved substrates like small nanoparticles[8−11] while patchy domains are usually formed on substrates with a low degree of curvature or no curvature (flat substrates)[2,8,10,12] even when stripes are the equilibrium phase in both cases.[10,13] Highly curved substrates therefore appear to aid in the progression of the metastable patchy phase into the equilibrium striped phase, but no systematic studies have been conducted to test this. Using a simple method, we show that curvature indeed speeds up the separation process substantially.

To study the effect of substrate stress, specifically the effect of substrate curvature, we perform mesoscale dissipative particle dynamics (DPD) simulations[14] of a binary mixture of equal numbers of immiscible surfactants of different lengths initially uniformly mixed on a flat surface. The surfactants are bead−spring chains grafted to a virtual surface. The head groups of the surfactants (i.e., the parts of the molecules that contain the binding moiety) are constrained to move in the $x-y$ plane while the tails are flexible and are free to explore the 3D space in the x, y, and $+z$ directions. A detailed description of DPD simulations of phase separation on flat substrates can be found in refs 10 and 13. The simulation is continued on the flat surface until we obtain a pattern stable over long periods of time. Next, we roll the flat surface into a cylinder and continue the simulation on the cylindrical surface to understand the role of substrate curvature and stress. The head groups of the surfactants are now constrained to move on the cylinder, instead of a flat surface, and the tails spread out radially from the cylinder surface. To roll the flat substrate into a cylinder, we map the positions of the head groups of the surfactants onto a cylinder of radius $R = L_x/(2\pi)$ and length $L = L_y$, where L_x and L_y are the dimensions of the flat substrate in the x and y directions, respectively (Figure 1). The total area occupied by the head groups therefore remains unchanged. The axis of the cylinder is the y-axis, and it extends symmetrically in the $+y$ and $-y$ directions. Periodic boundary conditions are employed in the y direction.

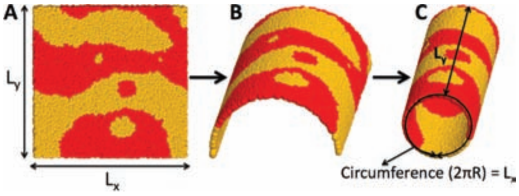

Figure 1. Transfer of an arbitrary pattern from a flat surface onto a cylinder. (A) Starting pattern on flat surface. (B) Intermediate curved surface. (C) Final pattern on cylindrical surface.

Any mixture of two strongly immiscible species (large χ parameter), if given sufficient time, is expected to thermodynamically phase separate as shown for a mixed SAM of immiscible surfactants in Figure 2A. Yet when one surfactant is sufficiently longer/bulkier than the other, stripelike patterns form.[10,13] This is because the longer/bulkier surfactant chains gain free volume and, hence, gain conformational entropy when next to shorter/less bulky surfactants as illustrated in Figure 2B. If the length/bulkiness difference is small and/or χ is so large that the additional entropic contribution is insignificant, mixed SAMs will always show complete phase separation (Figure 2A).

At any given temperature, the length difference and degree of immiscibility are the two main factors that determine the morphology and kinetics of pattern formation. We have shown that moderately immiscible surfactants with small differences in lengths and high surface coverage are likely to get kinetically trapped in nonequilibrium patterns.[13] This is because the high density combined with large intermolecular repulsion reduces the diffusion rate of the chains on the surface and slows down the phase separation process. Consequently, a patchy pattern (Figure 2C) is formed instead of the equilibrium, striped pattern (Figure 2D).

Here we use a mixture of immiscible surfactants of four and seven DPD beads respectively, which forms a slowly evolving patchy pattern on a flat surface.[13] Evolution of the pattern in time

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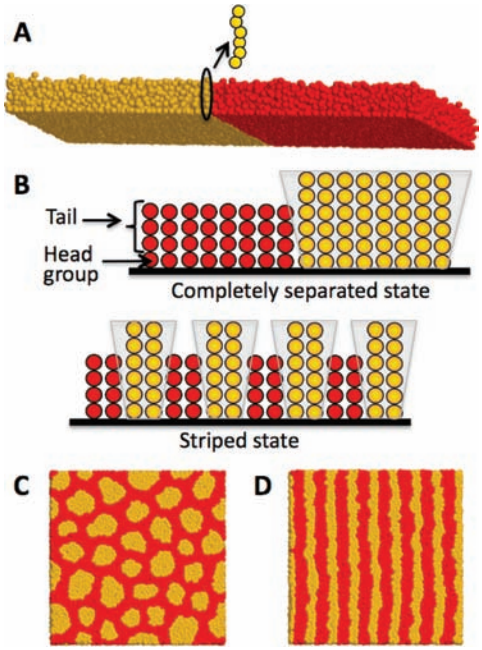

Figure 2. (A) Completely separated configuration for a system of strongly immiscible surfactants with six beads each. (B) Free volume, indicated by shaded gray areas, available to long (yellow, six-bead) surfactants when arranged with short (red, four-bead) chains in 2D completely separated and striped states. The bead in the chain that is constrained to the surface is the head group, and the rest of the chain is the tail of the surfactant. (C) Kinetically arrested patchy pattern obtained from simulation of a mixture of surfactants of lengths four (red) and seven (yellow) beads when starting from a uniformly mixed state. (D) Equilibrated striped pattern for the mixture of surfactants of lengths four (red) and seven (yellow) beads, ascertained by different methods described in ref 13.

starting from a uniformly mixed state is shown in Figure 3A. The resulting patchy pattern is found to be stable for long times (tens of millions of DPD time steps of 0.01 unit each). On induction of cylindrical curvature, this patchy pattern, which had previously arrested, now evolves quickly, with patches merging and elongating to form stripes. Patches that are stable and stay nearly unchanged on flat substrates for millions of time steps start merging to form elongated domains in as few as 50 000 time steps when transferred to the cylindrical surface, and all patches merge into stripelike domains within 5 million time steps. Calculations of the diffusion constant of molecules in the kinetically arrested patchy pattern on the flat surface and in the equilibrium, striped pattern on the cylinder show that they indeed diffuse faster on the cylinder than on the flat surface. Diffusion constants of the head groups on the flat and cylindrical surfaces are $0.0432 \pm (1.9 \times 10^{-5})$ and $0.0535 \pm (5.5 \times 10^{-5})$ bead diameter^2 time^{-1}, respectively. Figure 3A shows the complete process of curvature induction, starting from formation of the arrested patchy pattern, transfer to a cylindrical surface, and subsequent evolution of the pattern on the cylindrical surface. The snapshots taken postcurvature induction are taken by unrolling the cylinder back into a flat surface only for visualization while the simulation progresses on the cylinder. The fast pattern change that we observe serves not only to establish the role of curvature in formation of striped patterns on small nanoparticles but also to demonstrate how surface patterns can be modified postadsorption. In terms of applications, it should be possible to use this method experimentally to modify surface patterns postadsorption as well as to speed up the change from kinetically arrested to equilibrium patterns. The unidirectional curvature of the cylinder aids in the formation of defect-free parallel stripes.

To test the procedure experimentally, we prepared SAMs of octanethiol ($CH_3-(CH_2)_7-SH$) mixed with mercapto-propionic acid ($COOH-(CH_2)_2-SH$) and of octanethiol mixed with methyl benzenethiol ($CH_3-C_6H_4-SH$). The SAMs were prepared by immersing a 1 cm^2 substrate of Au(111) thermally evaporated on freshly cleaved mica (Molecular Imaging) into a 1 mM (total thiol concentration) ethanol solution for two weeks at room temperature.[11] After this incubation time, all of the substrates

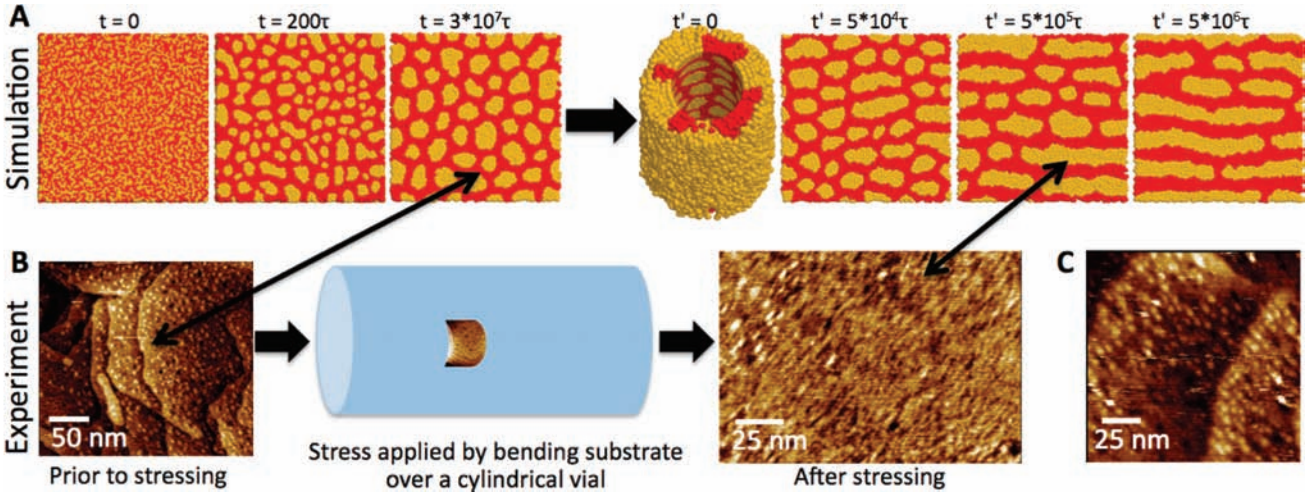

Figure 3. (A and B) Simulational and experimental procedures for applying stress to a substrate after adsorption of surfactants. Simulation pictures, from left to right, show the following: phase separation of two surfactants (red and yellow) on a flat substrate leading to the formation of the patchy pattern which is stable over many time steps (tails removed for clarity); a patch-covered cylinder obtained by rolling the patch-covered flat substrate; the remaining four snapshots show evolution of the patchy pattern on the surface of the cylinder (the cylinder has been unrolled for better visualization of the changing pattern) with the simulation conducted on a cylindrical surface (tails removed for clarity). Red (dark) and yellow (light) beads indicate short and long surfactants respectively. t and t′ indicate time for the simulations on flat and cylindrical substrates respectively. τ is the time step used in both simulations (0.01 unit each). Experimental images, from left to right, show the following : STM image of a patchy pattern on flat substrate formed by octanethiol and mercaptopropionic acid surfactants; cartoon showing application of stress; and alignment and merging of patches after stressing. Dark and light regions indicate short and long surfactants, respectively. Narrow, black arrows link analogous experiment images and simulation snapshots. (C) STM image of aligning and merging patches obtained after stressing another surfactant system: octanethiol and methyl benzenethiol.

were cleaned by rinsing in ethanol first and then acetonitrile and dried through a nitrogen stream. The substrates obtained were imaged using scanning tunneling microscopy (STM).[11,15] An analysis of the images shows a composition of the two surfactants on the surface to be ~1:1. These mixtures of surfactants form patches on flat substrates (Figure 3B); specifically we find that the longer surfactant forms patches in a matrix of the shorter surfactant, as in the simulations. The patchy phase stays unchanged even after a long equilibration time of 2 weeks when it is imaged to obtain the prestressed image. To induce curvature and stress, we take the surfactant-coated substrate and wrap it around a cylindrical vial (radius $\approx$ 1.5 cm) and then incubate the substrate at 60 °C in air for 6 days. This induces a slight curvature and generates a mild stress in the substrate. The substrate is then flattened out and reimaged for comparison with the prestressed image, and the change in pattern is recorded. Figure 3B shows the STM images of the substrate taken before and after induction of curvature. The poststressed image shows the presence of stringlike sequences of patches starting to merge. These sequences are absent in the prestressed image, which only shows separate and unaligned patches. Images of patches aligning and merging were obtained using other surfactant combinations as well (Figure 3C). These stringlike domains resemble an intermediate stage from our DPD simulations, observed before the patches merge to form a stripes-only phase. Narrow, black arrows in Figure 3 mark the analogous experimental and simulation images. The experimental and simulational results are in good agreement.

It is interesting to note that, in our simulation study, patches always merge in the direction of the curvature, i.e. along the circumference, and never along the length of the cylinder. Our results closely resemble the patterns obtained by He and Huang[7] for phase separation on a flat substrate that is stretched preadsorption. Their theoretical results show that the domains formed on stressed substrates are larger, fewer, and more elongated compared to those formed on unstressed substrates. They compare equilibrium patterns formed on unstressed and prestressed substrates, while our starting patchy pattern prior to stressing is nonequilibrium. Although it is not possible to stretch the substrate in our method, we can test whether the patterns formed on prestressed and poststressed substrates are essentially the same. To check this, we have carried out separate simulations starting with randomly distributed surfactants on the cylinder itself (results not shown) rather than first performing the simulation on a flat substrate and subsequently transferring the resulting pattern to the cylinder. We find that, in these simulations also, stripes always form along the circumference of the cylinder rather than along the length. We therefore conclude that patterns formed by applying stress pre- and postadsorption are similar and that the specific direction of the stripes is an outcome of the unidirectional nature of the substrate curvature. A detailed discussion of patterns formed on cylindrical surfaces along with parametric phase diagrams will be presented in a forthcoming publication.

Also worth mentioning is the fact that although both substrate stretching and curvature induction are methods to induce stress in the substrate, and patterns formed by both appear to be similar,[7] the mechanisms for pattern formation are likely different. This is because the free volume available to a surfactant chain in a stretched substrate is different from that on a curved surface. Our method does not allow us to compare the two methods.

In related studies on flat and curved substrates, researchers have shown analytically that in mixtures of immiscible cationic-anionic coassembled amphiphiles stripes are the equilibrium pattern on cylinders while patches are the equilibrium pattern on flat substrates.[5] This is not the case in our SAMs of immiscible, length-mismatched surfactants. In our system stripes are the equilibrium pattern on both cylinders and flat surfaces.

In conclusion, we have demonstrated how stressing a substrate postadsorption can help modify nanoscale patterns formed by phase separation in adsorbed monolayers of immiscible surfactants. This novel method was predicted by simulations and confirmed by experiments, both of which show merging and alignment of the starting patchy pattern into a striped pattern. Curvature was used to overcome the kinetic barrier to formation of stripes on flat substrates and to help progress a kinetically arrested pattern (patches) into the equilibrium one (stripes). This study supports the hypothesis that stress in the form of substrate curvature aids in the formation of stripelike domains in SAMs of immiscible surfactants of unequal lengths on curved surfaces and explains why stripes are imaged readily and frequently in SAMs on gold nanoparticles. This study also presents a reasonable approach toward the achievement of large planar surfaces coated with stripes only a few molecules thick, a structure that leads to many interesting properties when present on the surface of nanoparticles.[16]

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