Spatial and temporal control over adsorption from multicomponent solutions†

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The composition of physisorbed monolayers formed from multicomponent solutions varies with time and selection between two phases is possible by controlled desorption of one phase and the kinetically favored adsorption of another.

Whenever a multicomponent solution is in contact with a surface, there is competition for adsorption sites. The result of this competition is critical in determining important surface properties such as lubrication, adhesion, and reactivity. Competitive adsorption is often examined by quantifying the extent of depletion for different components in contact with an adsorbent although such an approach is time-averaged and does not offer a molecular-level picture of adsorption. An alternative method that has the potential to determine composition as well as the structure of the adsorbed phase is to image model surfaces. Scanning tunneling microscopy (STM) has been employed to determine the self-assembled structures produced by multicomponent systems[1–4] and to compare the kinetic and thermodynamic relationships among different phases.[2,5] STM is the technique of choice for examination of the structure and kinetics of adsorbed molecules due to the high spatial and fast temporal resolution it affords.

Here we report on a dynamic component of competitive adsorption that induces changes in the surface composition. It has previously been observed that upon monolayer formation, a metastable phase may be produced that is ultimately replaced by the more stable phase, whether these are pseudopolymorphs[5] or different compounds.[2] Here we demonstrate that this behavior is not limited to the initial formation of the monolayers, but also arises from other events that induce desorption of the more stable phase, affording a means of selecting between two possible forms with spatial control. Desorption of the most stable phase is, in this case, induced by close proximity of the STM tip. The less stable, but faster-forming, phase then readsorbs and is subsequently replaced by the thermodynamically favored phase. Thus, the second phase can be selected for by desorbing one phase over an area of specified size and position. This offers a powerful means of controlling surface composition for purposes of nanoscale patterning. Also, unlike previous examples of controlled desorption of preformed monolayers followed by the formation of new phases from solution,[6,7] this is a reversible process wherein “switching” of the surface phase occurs.

As part of ongoing investigations into the self-assembly of organic molecules at liquid/solid interfaces,[8,9] the assembly of a diheptadecyl ester of isophthalic acid (**ester**) at the phenyloctane/graphite interface (Fig. 1A) was being explored when a phase (Fig. 1B) was observed that had not appeared in another, well-characterized batch of the compound. This new phase (II) displaced the initially formed one (I) over time. Subsequent analysis revealed that low levels of an impurity were introduced during the synthesis of the ester (by addition of two alcohols to isophthaloyl dichloride). IR and ^{1}H NMR spectroscopies suggested the structure of an anhydride resulting from the bridging

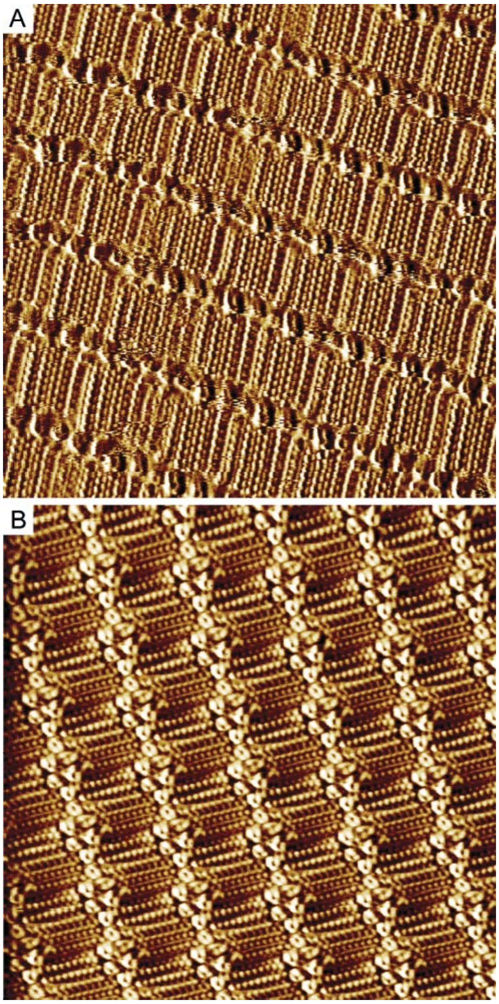

Fig. 1 STM images (20 nm × 20 nm) of (A) **ester** monolayer (phase I) and (B) **anhydride** monolayer (phase II).

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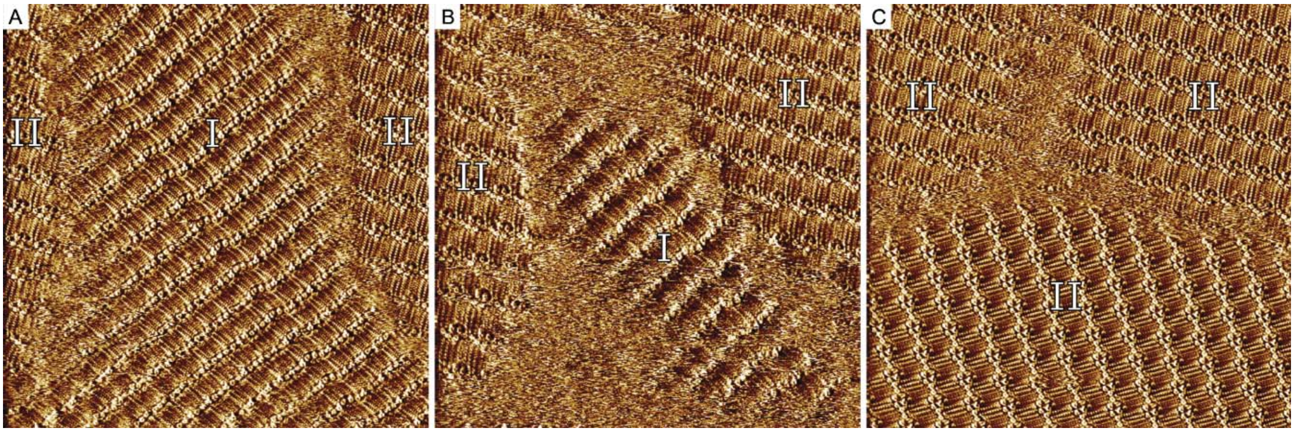

Fig. 2 Sequential STM images (45 nm × 45 nm) of the replacement of an **ester** monolayer (labelled I) by domains of the **anhydride** (labelled II) from a 5.2 : 1 **ester** : **anhydride** molar ratio mixture. (A) Coexisting phase I (center) and phase II (left and right) domains. (B) After 200 s, the phase I domain has shrunk and is surrounded by a featureless area of mobile, unresolved molecules. (C) Finally, phase I was completely displaced (6 min, 47 s total).

of two isophthalic esters, likely the result of partially hydrolyzed starting material. Independent synthesis of diheptadecyl isophthalic anhydride (**anhydride**) confirmed this hypothesis and enabled imaging of the monolayer resulting from the pure **anhydride** solution, phase II, and repetition of the dynamic phenomena in mixed solutions of **anhydride** and **ester** of specified composition.

The **ester** monolayer, phase I, has a simple packing pattern that has been described previously (Fig. 1A)[8] and is characterized by columns of interdigitated molecules. Columns of identical bright benzene rings are separated by the length of one of the alkyl chains, which are oriented at 90° angles to these columns such that the carbon backbones are parallel to the substrate, as indicated by the zig-zag pattern of the hydrogen atoms. The **anhydride** monolayer, phase II, is remarkably complex (Fig. 1B). It consists of columns of benzene rings separated by the length of one alkyl chain, similar to the **ester** monolayer. These columns vary in width in a regular repeating pattern along the column. The columns are one ring wide for two ring heights then two rings wide for two ring heights. The columns are then complementary, where the paired single rings are separated from a pair of double rings by the alkyl chain length. The two phases can be differentiated on a large scale based on the width of the bright lines of benzene rings; the **ester** monolayer has thin lines of constant width whereas the **anhydride** monolayer has lines that vary in width, appearing to have clusters of benzene rings.

Under the conditions examined,‡ the **anhydride** contaminant completely displaces the **ester** monolayer over many minutes (Fig. 2). The displacement of the **ester** by the **anhydride**, even though it is a minority component in solution, indicates that II is the more stable of the two phases. Larger molecules often form more stable monolayers, and this is likely the reason why phase II is more thermodynamically favored than phase I.[1] This is an important caution; even low levels of impurities can completely dominate the observed image in such STM studies because little material is required to coat a low surface area substrate. By using the temporal information in the self-assembly process, major and minor solution components can each be individually imaged in some cases as detailed below.

A particularly unusual dynamic property of the system is that phase (II) displaced the initially formed one (I) over time but could be desorbed from the surface leading to a reproducible formation of I and replacement by II (Fig. 3). When imaging **ester/anhydride**

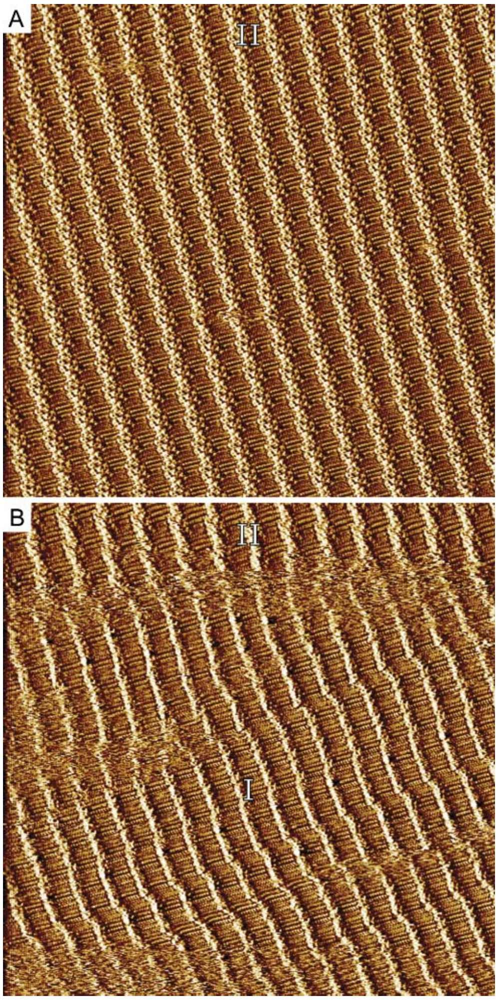

Fig. 3 STM images (50 nm × 50 nm) of (A) an **anhydride** monolayer (labelled II) adsorbed from a 5.2 : 1 **ester** : **anhydride** molar ratio mixture and (B) the **ester** monolayer (labelled I) that results after application of a 3000 pA set current (50 s time difference).

solutions, controllable desorption of the **anhydride** monolayer was achieved by increasing the set current. The scanning parameters usually employed for examination of these alkyl-chain decorated benzene compounds are an applied bias of approximately 800 mV and a set current of 300 pA, because these parameters allow simultaneous high resolution of both the ring and chain functionalities without convolution of substrate features. When the set current is increased to 3000 pA in quasi-constant height mode, scanning continues with the tip much closer to the surface. The contrast is greatly reduced and no monolayer is resolved (see Supplementary Information). No damage to the tip is observed, which would be apparent by a decrease in resolution of the monolayer upon returning to usual scanning parameters. What is observed upon rescanning the area is that part of the monolayer has been disrupted (Fig. 3B).§ Initially, the area where monolayer disruption occurs may appear featureless due to the high mobility of molecules (see Supplementary Information), indicating that the **anhydride** molecules have been forcibly desorbed from the surface, but only in the area to which the increased set current was applied. Following induced desorption, the hole in the **anhydride** monolayer is not necessarily refilled with more **anhydride** molecules, returning to the state the system was in before desorption. Instead, the less strongly adsorbed **ester** molecules commonly fill this gap in the surface, in the same packing motif that is observed from pure **ester** solution (Fig. 3B). This observation indicates that phase I must form faster than phase II at this concentration. The **ester** monolayer formed in the gap is then displaced by the thermodynamically favored **anhydride** in the same process as was observed in Fig. 2. The faster formation of the **ester** monolayer may be due to both the larger concentration in solution and the relative structural simplicity of the **ester** packing compared to that of the **anhydride**. Desorbed **anhydride** molecules were not always observably replaced with **ester** molecules, instead sometimes the **anhydride** monolayer was still observed, but with new domain boundaries. In these cases, desorption and resorption were occurring so quickly that intermediate phases either did not have time to form, or were displaced on a time scale not observable with the STM.

The ability to change surface composition by selective desorption offers a means to influence properties in a local area, thus patterning surfaces with different phases of adsorbed material. Furthermore, rapid and reversible change in the surface composition due to disturbance of the existing phase, by mechanical, electrical, or thermal events, may influence the surface properties in a time dependent fashion. This study highlights an important caveat to consider when studying such thin films. Impurities may completely replace the more abundant material on the surface when they are preferentially adsorbed and adsorption is limited by the available surface area. Essentially identical results were found for an even smaller proportion of the **anhydride** (12.3 : 1 **ester** : **anhydride** molar ratio). Sample purity is therefore essential when studying self-assembly at the solution/solid interface. The ability to select for various phases by purposeful desorption offers a new method for verifying the purity of solutions in adsorption studies and provides a means of analyzing solution impurities *via* their adsorption properties.

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Notes and references

‡ A 1–2 μL drop of solution in phenyloctane was placed on freshly cleaved highly oriented pyrolytic graphite (HOPG) to obtain a self-assembled monolayer. Initial studies used a concentrated solution of diheptadecyl isophthalate and a contaminate identified as diheptadecyl isophthalic anhydride in a 5.2 : 1 **ester** : **anhydride** molar ratio. The experiments were repeated with a 2 μL drop of solution in 1-phenyloctane containing 0.50 mg/mL diheptadecyl isophthalate and 0.050 mg/mL independently synthesized diheptadecyl isophthalic anhydride, resulting in a 12.3 : 1 **ester** : **anhydride** molar ratio. Desorption experiments were performed by increasing the set current to 3000 pA over approximately one third of the scanned area.

§ This stands in contrast to the regular practice of altering the scanning parameters in order to image the underlying HOPG substrate.[10] Visualization of the substrate is achieved without desorption of the monolayer by reduction of the applied bias, and use of an intermediate set current, such as a bias of 200 mV and a set current of 800 pA. Even though the monolayer is no longer observable under these conditions, there is no disruption of the monolayer apparent upon resuming imaging with suitable parameters.

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