

# The Formation of an Irreversibly Adsorbed and Organized Micelle Layer at the Solid–Liquid Interface

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## ABSTRACT

Rod-like aggregates formed from polymerized surfactant systems form organized two-dimensional layers at the solid–liquid interface. These layers are self-organized during the adsorption of the complexes at the solid surface. In common with layers formed from simple surfactants, the adsorbed layer structures show a high degree of ordering at the nanometer to micron length scales. Unlike their simple surfactant analogues, the layers formed using the polymerized surfactant systems are irreversibly adsorbed and are not sensitive to subtle interactions between the substrate and surfactant molecules. This allows for a wide range of processing options for these nanoorganized films.

The self-assembly of colloidal materials at the solid–liquid interface is currently an area of intense scientific activity.<sup>1–3</sup> Organized layers of colloidal objects offer numerous possibilities in the design of new materials. For example, self-organized layers of nanoparticles are expected to have applications as highly resilient coating materials,<sup>4</sup> photonic devices,<sup>5</sup> and templates for nanoporous materials.<sup>4</sup> Recently, surfactants have also been shown to form organized structures at the solid–liquid interface.<sup>6</sup> The range of structures at the interface has been shown to be large, rivaling the rich variations seen in bulk solution.<sup>7–10</sup> The types of structures formed are dependent upon the exact nature of the surfactant and the surface. Common structures include spheres, rods, cylinders, half-cylinders, and bilayers.

Organized layers of surfactant materials provide specific functional advantages when compared to colloidal solids. Typical aggregate structures have at least one dimension of less than 10 nm, making them true nanomaterials. Also, surfactant aggregates can solubilize otherwise insoluble materials within their cores. Such properties have led to the proposal that self-assembled layers of surfactant aggregates be used as templates for surface pattern formation or as potential materials for drug delivery systems.<sup>11,12</sup> However, a significant limitation on such applications is the necessity

for relatively high concentrations of surfactant in the bulk in order for the surface structures to persist.<sup>13</sup> Another disadvantage of these self-assembled surface structures is their sensitivity to changes in all bulk solution properties, i.e., temperature, ionic strength, and pH.

We report here the formation of organized layers of surfactant/polymer aggregates using polymerized surfactant aggregates. Such layers are of interest because they form nanoorganized structures that are permanent, i.e., they are resistant to washing with solvent and they can be removed from solution altogether without degradation. A further appealing property of these materials is that the adsorbed layer structures are not dependent upon the underlying substrate properties. This is in comparison to other systems using surfactants to template polymerization where the structures formed are highly sensitive to the subtle interactions between surfactant and substrate.<sup>14</sup> To our knowledge, these are the first organized layers of small molecule surfactant-like aggregates that can form irreversibly adsorbed organized structures. This permanent characteristic obviously offers important advantages for the use of these layers in subsequent technological applications or in the synthesis of new materials.

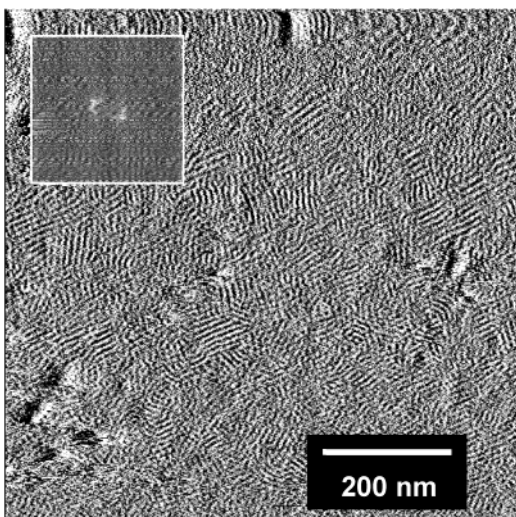
The polymerized surfactant aggregates used here were prepared by the free radical polymerization of the counterion of the cationic surfactant cetyl trimethylammonium vinylbenzoate (CTVB). Prior to polymerization, the monomeric surfactant system produces rod-like aggregates in aqueous

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**Figure 1.** AFM deflection images of an adsorbed layer of poly-(cetyl trimethylammonium vinylbenzoate) [pCTVB] at the mica–water interface. The polymerized surfactant system consists of rigid rod-like aggregates with a characteristic length of 58 nm and a radius of 2–3 nm. The adsorbed aggregates show strong ordering across the surface in local regions of approximately 50 nm × 50 nm. An 800 nm by 800 nm image of the aggregates on the mica surface in equilibrium with a bulk solution at a concentration of 0.01% (w/w).

solution. These aggregate structures were characterized using small angle neutron scattering (SANS)<sup>15</sup> and rheology.<sup>16</sup> The results of these analyses indicated that the aggregates formed a viscoelastic entangled worm-like system at concentrations above 0.1% (w/w).

After polymerization,<sup>17</sup> analysis of the solution indicated the presence of rod-like aggregates with a characteristic length of approximately (46–48) nm and a radius of 2 nm.<sup>15</sup> Conditions during polymerization dictate the length of the resulting aggregates; however, once polymerized, the dimensions of these aggregates are insensitive to changes in concentration, temperature, and ionic strength. This allows for control of aggregate dimensions prior to adsorption at the solid–liquid interface.

Adsorption of the polymerized aggregates at the solid–liquid interface was monitored directly using an atomic force microscope (AFM). The bulk solution concentration was kept dilute at 0.08% (w/w). Images were collected using the soft-contact imaging protocol as described previously.<sup>18</sup> An AFM image of the structure of the adsorbed layer formed at the mica–water interface is shown in Figure 1. The aggregates are seen to form a closely packed layer of relatively rigid tubules. Fourier transform of these data (inset to Figure 1) typically showed an incomplete ring with two bright spots. This representation provides a qualitative characterization of the alignment and length scales of the images. The ring indicates a measure of the characteristic distances between objects in the image, while the two bright spots indicate a preferred orientation of objects in the image. Inspection of the images shows regions of aligned aggregates, an observation reinforced by the bright spots in the Fourier transform. The lateral spacing of the aggregates determined from these images indicated a nearest neighbor distance of  $(9 \pm 0.5)$

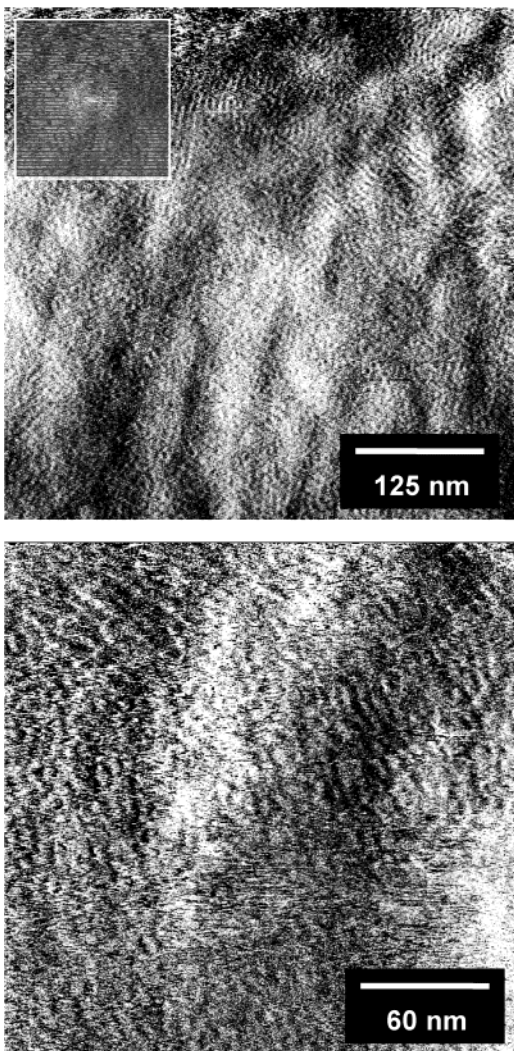
nm. An interesting feature of these data is the strong local alignment of the aggregates in approximately 50 nm × 50 nm regions. Such strong linear alignment has not been reported previously at the mica–water interface for single-tailed surfactants, although similar alignment has been reported for dimeric surfactants at these interfaces.<sup>19</sup>

Confirmation of the polymerized character of these aggregates was obtained from AFM force–distance data.<sup>20</sup> For small molecule surfactant systems, adhesion is maintained until the restoring force of the spring is sufficient to overcome the adhesive interaction. A single jump-out of the tip from the surface is then recorded. In the case of an adsorbed polymer, further attractive interactions at large separation distances are observed as multiple attachments of “loops and tails” are destroyed. Such a complex pull-off pattern was seen for all the polymerized aggregate complexes reported here. This is indicative of their polymeric nature.

Previous research using a range of cationic surfactants has indicated that a more common structure is one of meandering tubules.<sup>6,7</sup> It has also been demonstrated previously that the underlying substrate plays an important role in the structures formed by a given surfactant system.<sup>6</sup> For example, cetyl trimethylammonium bromide (CTAB) has been shown to form spheres on silica, meandering tubules on mica, and rigid half tubules on HOPG. To investigate the effect of substrate, the polymerized surfactant system was adsorbed at the silica–water interface. AFM images of the resultant adsorbed layer are shown in Figure 2. Although not as clear as the mica images, these images indicate an essentially invariant surface morphology in comparison to the mica system. Fourier transform of these data (shown as an inset to Figure 2) indicate a nearest neighbor distance of  $(9 \pm 0.5)$  nm that is also consistent with the mica data. The lack of strong (bright) azimuthal peaks shows that the preferred alignment seen on mica is not as clear on silica. Thus, the adsorbed layer structure is apparently unaffected by the underlying substrate. Instead, the rigid character of the solution aggregate is maintained upon adsorption. This is an important difference when compared to the aggregate structures formed by individual surfactant molecules where the underlying surface is known to play a crucial role in the resulting structures. The interaction of individual surfactants with the surface, and hence the role of their structures, which is normally crucial,<sup>14,21</sup> is irrelevant here. Instead, the only important criterion is that the polymerized aggregate adsorbs to the surface. If this occurs, then the structure of the aggregate in solution is preserved.

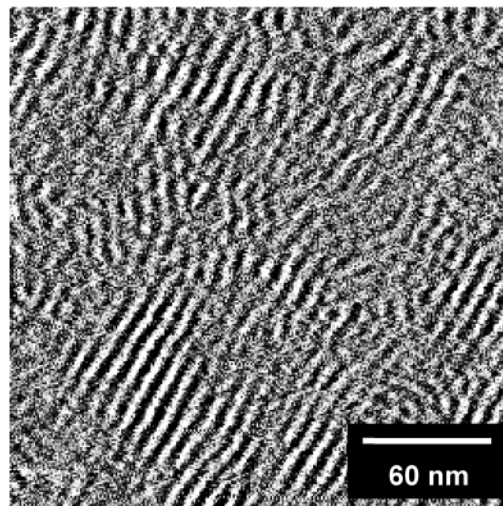
Earlier research has demonstrated the rich variety of surface structures available from adsorbed surfactant aggregates.<sup>7–10</sup> It has been noted frequently that such structures may form the basis of surface templates for nanometer-sized structures.<sup>11</sup> However, a significant limitation is apparent because of the need to maintain a high solution concentration of surfactant in order to maintain these structures at the surface.<sup>13</sup> Thus, any subsequent processing that takes advantage of the surface structures has to be done in the presence of the bulk material. Since the adsorbed aggregates formed here were polymeric in nature, it was hoped that





**Figure 2.** AFM deflection images of an adsorbed layer of poly-(cetyl trimethylammonium vinylbenzoate) [pCTVB] at the silica-water interface: A 500 nm by 500 nm image of the aggregates on the silica surface in equilibrium with a bulk solution at a concentration of 0.01% (w/w), and a 250 nm by 250 nm image of the same surface. The loss of resolution at the lower part of the image is due to difficulties maintaining a stable image force across the total image. A higher image force in this region has resulted in the tip contacting the layer too hard and apparently scraping the adsorbed structures.

solvent exchange could be undertaken without destruction of the surface structures. It is known that polymers will effectively adsorb irreversibly if the polymer molecular weight is large enough.<sup>22</sup> To test the persistence of the adsorbed layer, a layer of polymerized micelles at the mica water interface was rinsed in situ in the AFM with multiple aliquots of pure distilled water. No desorption was observed immediately upon replacement of the bulk polymer aggregate solution with water.<sup>23</sup> The sample was then left to soak in water over a sixteen hour period. An AFM image of the resulting surface structures is shown in Figure 3. Clearly no desorption has occurred during this time period and the original ordering is maintained. Further soaking over a four-day period resulted in no deterioration of the surface structures. In this case, we have a persistent irreversibly adsorbed surface layer. Furthermore, the fact that the surface

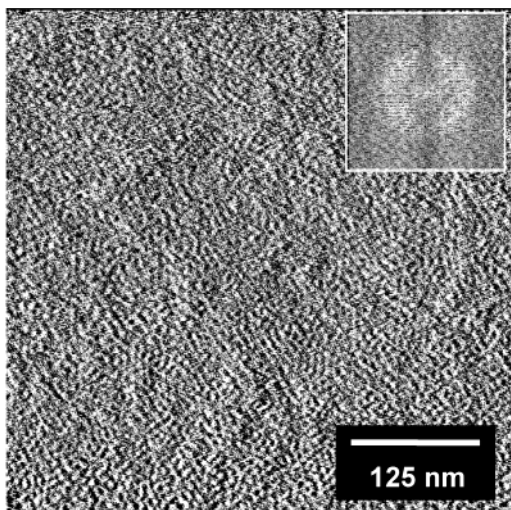


**Figure 3.** A 250 nm by 250 nm AFM deflection image of the pCTVB layer at the mica-water interface after soaking in pure water for 16 h. No desorption can be seen when compared to the original images collected in the presence of polymer in the bulk. The aggregates are effectively irreversibly adsorbed.

persists through washing and soaking stages indicates its potential for further processing. For example an active component that is adsorbed by the micellar cores could be introduced and allowed to adsorb within the structures. This might then itself be further processed. Alternatively, a second layer might be adsorbed to this first adsorbed layer using recently developed layer-by-layer techniques.<sup>24</sup> Whatever the desired application, the complication of bulk material in subsequent processing has now been removed. As a final test of the durability of the adsorbed layer, the substrate was removed and air-dried, then replaced in the AFM and imaged again under water. No gross changes in the structure of the layer were observed.

One of the appealing features of the surface aggregate structures formed from small molecule surfactants is the variety of surface structures possible.<sup>7-10</sup> Typically, variation of aggregate structures, in the bulk, is obtained through changes in factors such as the counterion type and headgroup size,<sup>21</sup> or through the use of mixed surfactant systems.<sup>25</sup> These structure changes in the bulk are frequently mirrored at the solid-liquid interface.<sup>21</sup> In an attempt to alter the adsorbed layer structures seen here, a second polymerized surfactant system was investigated.

This was prepared by polymerization of a mixed monomer system of CTVB and sodium vinyltosylate (NaVT) in a 2:1 molar ratio. Small-angle light scattering indicates that the resulting aggregates are elongated and charged, but conclusive evidence of the detailed structures does not yet exist for this mixed counterion system. An AFM image of the adsorbed layer structure formed from a 0.1% (w/w) solution of the polymerized aggregates is shown in Figure 4. The image reveals a surface covered in closely packed spherical objects. Fourier transforms of these data showed a bright ring that is indicative of amorphous structure of closely packed spheres across the surface. The polymeric nature of the aggregates was again confirmed using force-distance



**Figure 4.** AFM deflection images of an adsorbed layer of poly-(cetyl trimethylammonium vinylbenzoate)-*co*-(sodium vinyltosylate) [p(CTVB-*co*-NaVT)] at the mica–water interface. The polymerized surfactant aggregates are in equilibrium with a bulk solution at a concentration of 0.01% (w/w). The adsorbed layer appears to consist of a system of closely packed spheres with no long range ordering. The Fourier transform of this image shows a ring of bright spots indicating a well-defined nearest neighbor distance but no long-range crystalline symmetry. The polymeric nature of the adsorbates was confirmed using pull-off data from force–distance measurements between the imaging probe and the surface.<sup>20</sup>

measurements with the AFM. Polymeric adsorbates are easily observed from the shape of the pull-off data when the imaging probe is retracted from the surface.<sup>20</sup> These data indicated a distribution of polymer lengths ranging 30 to 70 nm. This implies that numbers of the closely packed spheres at the surface are linked together and are not present as individual objects. Once again, no wash-off of the layer was observed over extended time periods, offering further evidence of the polymeric nature of the adsorbed material. The results presented here are significant. The systems examined form permanently organized two-dimensional layers of micellar aggregates. The ability to rinse these surfaces facilitates subsequent processing of these surfaces. This will significantly improve the possibilities for their application as surface templates or in drug delivery systems.

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