

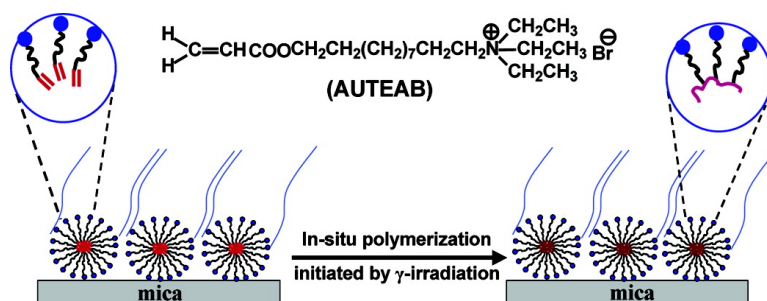
Communication

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*J. Am. Chem. Soc.*, **2004**, 126 (21), 6572-6573 • DOI: 10.1021/ja049431y • Publication Date (Web): 07 May 2004

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## In Situ Gamma Ray-Initiated Polymerization To Stabilize Surface Micelles

Xi Zhang,<sup>\*,†</sup> Mingfeng Wang,<sup>†</sup> Tao Wu,<sup>†</sup> Shichun Jiang,<sup>‡</sup> and Zhiqiang Wang<sup>\*,†</sup>

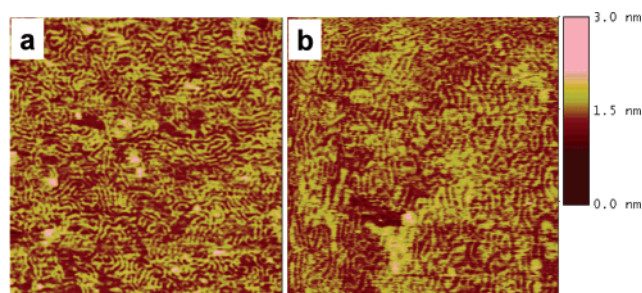
Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 10008, Key Lab for Supramolecular Structure & Materials, Jilin University, Changchun, 130023, P. R. China, and State Key Lab of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130021, P. R. China

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Surfactant molecules containing long hydrophobic alkyl chains and hydrophilic groups can organize into various self-assemblies both in bulk solution and at an interface. Micellar structures of conventional surfactants such as alkytrimethylammonium bromide ( $C_n$ TAB) adsorbed at the solid/liquid interface were directly observed by Manne et al. using atomic force microscopy (AFM).<sup>1</sup> These ordered interfacial aggregates have well-defined sizes and shapes which can be controlled by adding metal halide salts or changing molecular structures,<sup>2</sup> and they have been used as templates to synthesize mesostructured silica films and to mimic biomineralization processes.<sup>3</sup> However, these surfactant assemblies are inherently dynamic and fluid, hence lacking the robustness required for detailed structural characterization and materials application.

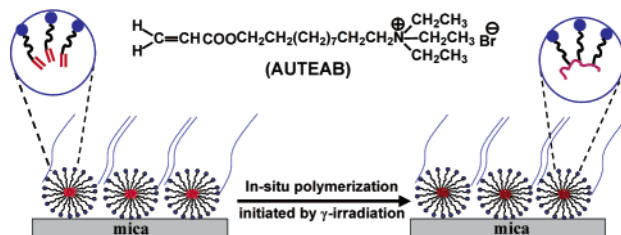
We have been focusing on stabilizing interfacial amphiphile assemblies through a noncovalent approach by introducing mesogenic groups and long spacers into bolaform amphiphiles, which facilitate the  $\pi$ - $\pi$  stacking interaction among building blocks.<sup>5</sup> Herein, we report a unique and simple method of stabilizing surface micelles of a low molecular weight surfactant 11-acryloyloxyundecyltriethylammonium bromide (AUTEAB) through in situ intramicellar polymerization initiated by  $\gamma$ -irradiation on mica surface. Because of the dynamic nature of micelles formed by low molecular weight surfactants, efforts directed at fixing their parent structures in bulk solution by polymerization have met with limited success.<sup>4</sup> To increase the lifetime of the micellar structures that is required for polymerization, we considered two approaches. First, we select surface micelles adsorbed on a solid substrate instead of "free" micelles in bulk solution as polymerization precursors. Second, a cryogenic treatment is used to freeze the surface micellar conformation. We believe that the micelles confined to a two-dimensional surface and kept in a frozen state should have a longer lifetime than the fluid phase in bulk solution. This makes it possible to fix the interfacial organized assemblies by intramicellar polymerization without disruption of their original structures (see Scheme 1).

The polymerizable surfactant AUTEAB was synthesized from the esterification of 11-bromo-1-undecanol with acryloyl chloride in 1,4-dioxane and subsequent quaternization with triethylamine in chloroform (for detailed synthesis and characterization of the monomer, see Supporting Information). The concentration-dependent conductivity of AUTEAB aqueous solution shows a critical micelle concentration (CMC) of  $1.56 \times 10^{-2}$  M. In the solution at a concentration above the CMC, the surfactant can self-organize into micelles both in bulk solution and at a solid/liquid interface. We selected  $4.0 \times 10^{-2}$  M ( $\sim 2.5 \times$  CMC) as the characterized concentration of bulk solution and used in situ AFM (tapping mode in fluid) to observe the micellar structures adsorbed at the mica/



**Figure 1.** AFM height images (300 nm  $\times$  300 nm) of cylindrical surfactant micelles at the mica/water interface before (a) and after (b) the in situ polymerization of AUTEAB on the substrate.

### Scheme 1. Schematic Representation of Stabilizing Confined Surfactant Micelles by In Situ Intramicellar Polymerization at Interface

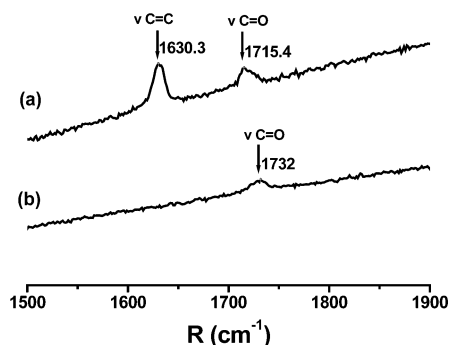


water interface. As shown in Figure 1a, AUTEAB forms cylindrical micelles at the interface after equilibrating in a solution of  $4.0 \times 10^{-2}$  M for at least 1 h. Section analysis shows that the micelles have a uniform spacing of about 6 nm. This value is consistent with the diameter of the micelles, considering the length of the surfactant, which is about 2.0 nm. These interfacial micelles are meandering and show different alignment directions on the substrate.

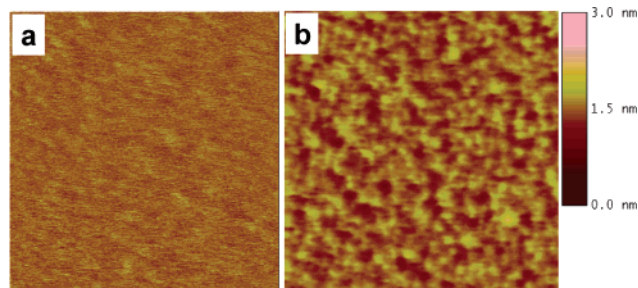
We used  $\gamma$ -irradiation ( $^{60}\text{Co}$  source, dose:  $3.5 \times 10^4$  Gy) to initiate the polymerization of AUTEAB micelles on mica surface. A freshly cleaved mica sheet was first incubated in  $4.0 \times 10^{-2}$  M solution (purged with ultra-purified nitrogen to eliminate oxygen) for 1 h to allow the adsorption and equilibration of the micelles on the substrate. The mica sheet was removed from the solution, immediately transferred to a sealed vial, and kept frozen in liquid nitrogen until the completion of  $\gamma$ -irradiation to avoid the effect of solvent evaporation on the maintenance of surface micelles before the polymerization (for the detailed process of sample preparation, see Supporting Information). After the polymerization, the mica sheet was dried in air and imaged in pure water with in situ AFM at room temperature. As shown in Figure 1b, the preformed micellar structures at the mica/water interface are preserved after polymerization, showing good stability against drying effect in air and the dilution in water.

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**Figure 2.** Confocal Raman spectra of (a) solid powder of AUTEAB monomer and (b) in situ polymerized micelles confirm the adsorption and polymerization of AUTEAB micelles on the mica substrate.



**Figure 3.** In situ AFM height images of (a) adsorbed PAUTEAB layer (400 nm × 400 nm) and (b) AUTEAB aggregates (300 nm × 300 nm) at the mica/water interface. Before recording the images, these aggregates were first adsorbed on mica in  $4.0 \times 10^{-2}$  M solution for about 1 h, then dried in air, and finally equilibrated in pure water for at least 1 h.

To confirm the adsorption and in situ polymerization of the surfactant micelles on the mica substrate, we also used confocal Raman spectroscopy to characterize the polymerized surface micelles. As shown in Figure 2a, the Raman spectrum of AUTEAB monomers shows two bands at 1630 and 1715  $\text{cm}^{-1}$ , corresponding to the stretches of C=C and C=O bonds, respectively. After  $\gamma$ -irradiation, the mica sheet adsorbed with in situ polymerized micelles was directly used for Raman spectroscopy characterization. As shown in Figure 2b, the band of C=C bond at 1630  $\text{cm}^{-1}$  disappears, and the C=O bond stretch shifts from 1715 to 1732  $\text{cm}^{-1}$ . This shift can be rationalized in that before polymerization the C=O bond is in conjugation with C=C and after polymerization is no longer conjugated. This result indicates nearly complete polymerization of the C=C group after  $\gamma$ -irradiation and demonstrates that polymerized micelles are retained on the mica surface.

Under the same  $\gamma$ -irradiation condition with the interfacial in situ polymerization mentioned above, the polymerization of AUTEAB in micellar solution ( $4.0 \times 10^{-2}$  M) led to linear polymeric chains with high molecular weights ( $M_w = 1 \times 10^6 \sim 2 \times 10^6$ ). We explored whether these linear polymeric surfactants that formed in bulk solution could reorganize into cylindrical micellar structures at the mica/water interface similar to AUTEAB monomers by examining the adsorbed structures of polymerized AUTEAB (PAUTEAB) at the mica/water interface. A mica sheet was first incubated in the polymer solution of  $4.0 \times 10^{-2}$  M for 1 h, withdrawn, and dried in air. It was then characterized with in situ AFM in pure water. As shown in Figure 3a, flat surface structures are observed at the mica/water interface. This result supports the conclusion that the micellar structures in Figure 1b are not formed

by post-organization of PAUTEAB at the interface but derived from the in situ polymerization of the preformed interfacial micelles of AUTEAB monomers.

To compare the stability difference of AUTEAB micelles at the interface before and after polymerization, we did a control experiment. Unpolymerized micelles were adsorbed on mica in  $4.0 \times 10^{-2}$  M AUTEAB solution for 1 h, dried in air, and then re-imaged at the mica/water interface with in situ AFM. As shown in Figure 3b, after the mica was soaked in pure water for at least 1 h, the cylindrical micelles disappeared and a film covered with irregular particles was observed at the interface. This result indicates that the unpolymerized cylindrical micelles are labile at the interface, lacking stability against the effect of drying in air and dilution in water. This finding is consistent with the previous results obtained by Ducker et al.<sup>2b</sup> After the in situ intramicellar polymerization, however, the interfacial micelles were robust, and they maintained their structures after the process of drying and dilution (Figure 1b).

In summary, we have developed a unique and feasible method to stabilize surface micelles by in situ intramicellar polymerization initiated by  $\gamma$ -irradiation. In situ AFM provided direct evidence that cylindrical surface micelles can retain their structures with enhanced stability after the polymerization. The robust polymerized surface micelles are important not only for better understanding the self-assembly of surfactant molecules in colloid and interface systems, but also for further applications in templating synthesis of nanomaterials.

**Acknowledgment.** This research is supported by the Major State Basic Research Development Program (G2000078102), National Natural Science Foundation of China (20334010), and “863” project (2003AA302140), P. R. China.

**Supporting Information Available:** Synthesis and characterization of AUTEAB monomer, experimental details for sample preparation before polymerization, in situ AFM characterization, NMR characterization of polymerization in micellar solution, and Raman spectroscopy. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA049431Y