

Atomic Force Microscopy and Contact Angle Studies of Polymerizable Gemini Surfactant Admicelles on Mica

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ABSTRACT: Atomic force microscopy (AFM) was used to directly observe and characterize a polymer-modified mica surface prepared using a polymerizable gemini surfactant. Normal tapping mode and contact mode AFM were used to image the treated mica surface morphologies in air and liquid environments, respectively. The root mean square (RMS) roughness of mica surfaces before and after surface modification and polymerization was analyzed from these scans. To determine the effect of styrene adsolubilization on the surfactant-modified mica, AFM measurements of the modified mica were made at various styrene concentrations. Contact

angle measurements were also made to further characterize the nature of the surfactant-modified mica surface. The surface morphology and surface hydrophilicity were observed to be different for the modified mica after polymerization. In addition, the polymerized surface maintained its morphology after washing/desorption studies demonstrating the stability of the polymerized surfactant film. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1145–1152, 2010

Key words: polymerizable gemini surfactant; AFM; polymerization; contact angle

INTRODUCTION

Surfactant-modified adsorbents have been extensively investigated for a number of solid surfaces, including alumina,^{1–3} silica,^{4–6} titanium dioxide,⁷ and zeolite.^{8,9} Surfactant adsorption and adsolubilization behavior are important in a number of applications such as surface modification, detergency, lubrication, corrosion inhibition, and mineral flotation.^{10–15}

Adsolubilization results from aggregation of surfactants at the solid–liquid interface which act as a two-dimensional solvent for organic solutes.¹⁶ The inner or core region of the bilayer structure is a nonpolar region that can facilitate the solubilization of nonpolar solute molecules. The intermediate polarity region, or so-called palisade region, is the region between the surfactant head groups and the core region that is characterized by the penetration of

water molecules.² This area has the potential to adsolubilize both polar and nonpolar organic solutes.

Surfactant-modified surfaces face the challenge of substantial losses due to desorption and due to decreases in aqueous surfactant concentration or changes in system pH.¹⁷ A previous study showed the loss of adsorbed sodium dodecyl sulfate (SDS) and pentamethylolyleyl alkyl-1, 3-propane diammonium dichloride (PADD) when the solution pH changed in a column study.⁴ To reduce the amount of surfactant desorbed from the surface, polymerization of the admicelle (adsorbed surfactant aggregate/layer) has been proposed to create a fixed surfactant film.^{18–20}

Gemini surfactants have been reported to be more surface active than conventional surfactants.^{21–24} To minimize surfactant desorption, polymerization of an adsorbed polymerizable gemini surfactant was carried out in this work. The process is similar to the formation of a polymeric thin film by admicellar polymerization which has been used to modify substrate surface properties in other research.^{25,26} Admicellar polymerization is a process whereby *in situ* monomer polymerization takes place inside of adsorbed surfactant bilayers on various substrates.²⁷

Classically, the four steps in admicellar polymerization consist of surfactant adsorption onto solid surfaces, adsolubilization of polymerizable

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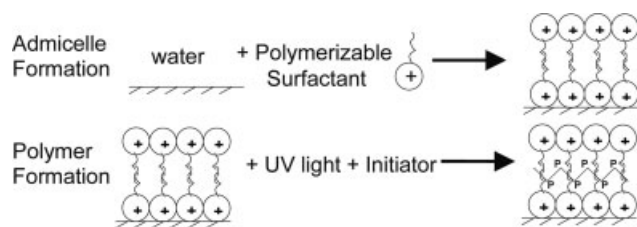


Figure 1 Schematic of the polymerization process for this research.

monomers into admicelles, polymerization of the monomers in the admicelles, and removal of accessible surfactant by washing to expose the polymerized monomer layer.^{28,29} In this work, polymerization was of the surfactant itself rather than an adsolubilized monomer. The schematic of surfactant polymerization is shown in Figure 1. To verify the presence of the polymer thin film, indirect analytical techniques such as FTIR UV-visible spectroscopy have been conducted.^{19–21} More recently, the examination of polymer formation via admicellar polymerization has been studied using atomic force microscopy (AFM) that allows the film to be studied at the nanometer scale.^{29–31} AFM has been used to probe the nature of surfactant-modified mica surface morphologies.^{31–33} The AFM tip can interact with the sample surface at the atomic level. Software is used to interpret the interactions between tip and sample that are sensed as the tip scans across surface to form images of the surface.³⁴ Imaging in aqueous solution has become popular because it has less impact on the samples before imaging and is more representative of surface morphology in an aqueous environment.³⁵ The objectives of this research are to directly observe and characterize the presence of a polymer thin film prepared from polymerizable gemini surfactant using AFM, to evaluate the stability of this film when subjected to desorption (washing) and to examine the effect of adsolubilization on the nature of this film. Along with the AFM examination, contact angle measurements of the admicellar-modified mica surface have been made to help examine these objectives.

EXPERIMENTAL SECTION

Materials

The polymerizable cationic gemini surfactant (PG) used in this study was supplied by the Faculty of Science and Technology and Institute of Colloid and Interface Science from Tokyo University of Science, Japan.²⁵ Table I provides a summary of pertinent surfactant properties for this surfactant. For AFM studies, 9 mm mica discs and 12 mm AFM specimen discs were obtained from Ted Pella Inc. (Reddings,

CA). The electrolyte concentration was controlled using 1 mM sodium bromide (NaBr). Water used in this work was purified with a resistance of 18.2 M Ω cm. All experiments were conducted in ambient air at approximately 25 \pm 1°C.

Atomic force microscopy

The multimode Nanoscope V AFM used was from Veeco/Digital Instruments, Inc. (Santa Barbara, CA). Both contact mode AFM and tapping mode AFM were used to evaluate the samples in this study. In contact mode, topographic and deflection images of liquid samples were captured in a standard fluid cell. The fluid cell was initially cleaned by boiling in an 80/20 volume mixture of deionized water and methanol. Scan rate and set point were changed as needed to prevent applying too much force to the sample surface and thus intrude inside the adsorbed structure.

Silicon nitride tips (0.32 N/m) obtained from Veeco/Digital Instruments, Inc. were used for the liquid imaging. In tapping mode, topography and phase images of dry-modified surfaces were captured using standard 42 N/m silicon probes (Veeco/Digital Instrument, Inc.).

AFM measurement

Force measurements were made by recording the deflection of the free end of the AFM cantilever as the fixed end of the cantilever is extended toward and retracted from the sample. The AFM was set to image the cantilever deflection with a scan rate of 1 μ m/min. The force sensed by the AFM probe is calculated by multiplying the deflection of the cantilever with a spring constant. In this work, the spring constant is 0.0678 N/m. After the tip engaged, the tracking force was adjusted by changing the set point deflection. Force curve analysis allows graphic determination of force exerted by a given deflection set point. Force curve analysis was conducted according to the method of Senden 2001,³⁶ which determines the force versus separation curve based on the force versus distance data.

TABLE I
Polymerizable Surfactant Properties Used in this Research

Surfactant	M_w	% active	CMC (mM)	Molecular structure
Polymerizable cationic gemini surfactant (PG)	690.8	97	0.5	$\begin{array}{c} \text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_{11}\text{N}^+(\text{CH}_3)_2 \end{array} \cdot 2\text{Br}$

TABLE II
Summary of Experimental Set Carried Out in this Research

Mica disc samples	PG (mM)	Percent of surfactant CMC (%)	Styrene (mg/l)	Ratio of styrene feed concentration to surfactant
Experiment set 1				
NP1	0.1	20 CMC	NA	NA
NP2	0.4	80 CMC	NA	NA
Experiment set 2				
P1	0.1	20 CMC	NA	NA
P2	0.4	80 CMC	NA	NA
Experiment set 3				
SI1	0.4	80 CMC	72.5	1 : 0.57
SI2	0.4	80 CMC	109	1 : 0.40
Experiment set 4				
SE1	0.4	80 CMC	72.5	1 : 0.57
SE2	0.4	80 CMC	109	1 : 0.40
Experiment set 5				
NPW1	0.1	20 CMC	NA	NA
NPW2	0.4	80 CMC	NA	NA
Experiment set 6				
PW1	0.1	20 CMC	NA	NA
PW2	0.4	80 CMC	NA	NA

NP, nonpolymerize; P, polymerize; NPW, nonpolymerize with washing; PW, polymerize with washing; SI, styrene addition at initial state; SE, styrene addition at equilibrium state; 1–20% of CMC; 2–80% of CMC; NA, not available.

Contact angle measurement

Contact angles were measured to observe the hydrophobicity/hydrophilicity of the surfactant-modified-mica surfaces using the static sessile drop method with a contact angle goniometer (IT Concepts). A 3 μ L drop of double-distilled water was produced manually by a 1 mL syringe and placed on the freshly cleaved and surfactant-modified mica surfaces to test the initial condition of clean mica and surfactant-modified mica surfaces, respectively. Furthermore, examination of changes in surface hydrophobicity was carried out for specific samples by placing a drop of styrene on the same modified mica surface after measuring water contact angle. All contact angle values are reported as an average of three measurements per sample.

Sample preparation

Characterization of modified-polymerize mica discs
Surfactant solutions were made at 20% (0.1 mM) and 80% of the CMC (0.4 mM) with 1 mM added NaBr in glass vials both without (NP) and with (P) polymerization [experimental sets 1 (NP) and 2 (P), respectively, in Table II]. Mica discs were placed into each surfactant system and allowed to equilibrate for 2 days. Samples were then removed from

the vials for imaging. An initiator (0.05 g of sodium persulfate) was added to the samples in the second set and they were then placed at a distance of 10 cm from a 30 watt UV lamp for 18 h to achieve polymerization.

The mica discs were mounted on 12 mm AFM specimen discs using polymer adhesive with no adhesive exposed on the edges. Contact mode fluid-cell samples were prepared by carefully placing a drop of solution onto freshly cleaved mica. The AFM fluid tip holder was then carefully placed into the fluid cell. Additional solution was gently injected into the fluid cell to achieve a total volume of approximately 0.05 mL. After imaging, the fluid cell and tip were rinsed by methanol followed with deionized water. Dried samples were used for the tapping-mode analysis.

Characterization of styrene adsorbed in PG aggregates adsorbed on modified-polymerize mica discs

Varying amounts of pure styrene were added to the glass vials containing polymerized surfactant-modified mica discs in the presence of 80% CMC of PG solution. Two sets of samples were prepared and analyzed as initial state and equilibrium state corresponding to the time of styrene addition [experimental sets 3 (SI) and 4 (SE), respectively, in Table II]. For the initial state, samples were captured immediately after styrene addition, whereas equilibrium samples were analyzed after 4 days of equilibration.

Determination of surfactant desorption

Both polymerized and unpolymerized samples were washed/desorbed by decanting the surfactant solution and replacing it with (25 mL) deionized water [experimental sets 5 (NPW) and 6 (PW), respectively, in Table II]. This process was repeated five times. The final wash water was allowed to equilibrate for 2 days before the samples were removed for imaging.

RESULT AND DISCUSSION

Unmodified mica

A topography image of an unmodified mica disc is shown in Figure 2(a). The aggregate-free surface had a root mean square (RMS) roughness of 0.068 nm as comparable to the literature,³⁷ which provides a baseline for evaluating morphology changes for subsequent surfactant-modified surfaces. All the RMS values reported in this work are obtained from the average of the different AFM images. They were captured from the different positions on the sample. To determine the hydrophobicity of the surfaces,

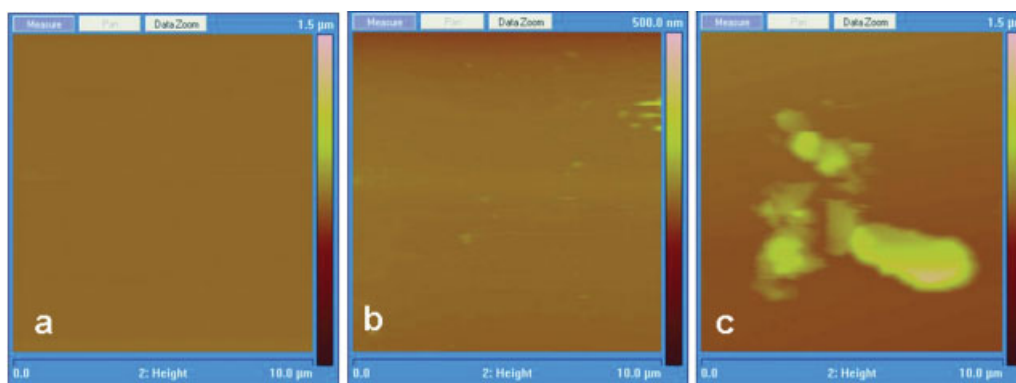


Figure 2 Topography images of mica surfaces for unmodified mica (a), and images of PG adsorbed on mica before polymerization at NP1, 20% CMC (b), NP2, 80% CMC (c) with the presence of 1 mM NaBr electrolyte. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

contact angle measurements were conducted as a measure of surface wettability. The results show that the unmodified mica is hydrophilic (water-wet) with an average initial contact angle of 12° (Table III).

Adsorption of PG on mica

The first set of surfactant-modified mica disc samples investigates the adsorbed structure of nonpolymerized PG. The bulk PG concentrations of 0.1 and 0.4 mM added are approximately 20 and 80% of the CMC value (0.5 mM), respectively. These values are below but approach the CMC to avoid aqueous micelle surface admicelle interaction which would occur above the CMC. Contact mode AFM was used to examine the topographic images for adsorbed surfactant on the mica surface in water. Figure 2(b,c) shows topography images of the adsorbed PG for sample NP1 (20% CMC) and NP2 (80% CMC) (Table II) with the presence of 1 mM NaBr electrolyte, respectively. The results demonstrate that at low surfactant concentrations [Fig. 2(b)] little visible change is observed relative to the mica surface without surfactant [Fig. 2(a)] even though low levels of surfactant adsorption exist in Figure 2(b), while at 80% CMC surfactant loading [Fig. 2(c)], patchy aggregates or “islands” of adsorbed surfactant can be seen on the surface.

As mentioned by Song et al.,³⁸ contact angle measurements can provide useful information on the nature of surfactant aggregates on the surface. Contact angle measurements in Table III indicate that the surface hydrophobicity (contact angle) increases with surfactant adsorption on the mica even at the low surfactant concentration. Increasing of surface contact angles were observed in every condition when compared with the clear blank mica. This agrees with results of Song et al.,³⁸ who reported that contact angles increased with surfactant adsorp-

tion due to organic nature of the adsorbed surfactant bilayer.

Polymerization of PG on mica

The second set of modified mica surfaces was established by applying UV irradiation to polymerize the surfactant-modified surfaces. The average surface roughness of sample P2 (80% CMC) is 249 nm which is much higher than the samples without polymerization (e.g., 70 nm for sample NP2) and for the virgin mica surface (0.068 nm). The huge difference in these values indicates the major change in the surface of the modified mica. The lack of long-range or repeatable structure in the aggregates demonstrates the heterogeneity of the modified surface.

The contact angles for samples P1 and NP1 are quite similar (53 ± 2.2 and 57 ± 3.7 , respectively), whereas the P2 contact angle (47°) is much lower (more hydrophilic) than NP2 (61° , Table III). Thus, a more hydrophilic surface is obtained after polymerization, although still not as hydrophilic as the mica surface. The reason that polymerization creates a more hydrophilic surface at high surfactant loading (80% CMC), while not doing so at lower surfactant concentration (20% CMC), is unclear and should be further evaluated in future research.

Adsolubilization of styrene onto polymerized-surfactant-modified mica surfaces

Experimental sets three and four investigate the impact of styrene addition on the polymerized-surfactant-modified mica surface at the initial state (SI) and at the equilibrium state (SE), respectively. Initial state samples (SI1 and SI2) refer to polymerized surfactant mica surfaces that were imaged immediately after styrene addition. Polymerized samples evaluated 4 days after styrene addition are referred to as the equilibrium state samples (SE1 and SE2). The

TABLE III
Summary of Contact Angle Measurements

Sample condition	Average contact angle (°)			
Effect of concentration	Low feed concentration		High feed concentration	
Clean mica	57 ± 3.7 (NP1)		61 ± 1.5 (NP2)	
12 ^a				
	Before polymerization		After polymerization	
Effect of polymerization				
Low feed concentration (20% CMC)	57 ± 3.7 (NP1)		53 ± 2.2 (P1)	
High feed concentration (80% CMC)	61 ± 1.5 (NP2)		47 ± 4.1 (P2)	
	Before desorption	After desorption (washing)	Before desorption	after desorption (washing)
Effect of desorption				
Low feed concentration (20% CMC)	57 ± 3.7 (NP1)	58 ± 3.1 (NPW1)	53 ± 2.2 (P1)	53 ± 3.1 (PW1)
High Feed Concentration (80% CMC)	61 ± 1.5 (NP2)	48 ± 3.6 (NPW2)	47 ± 4.1 (P2)	41 ± 3.6 (PW2)
	Initial state		Equilibrium state	
Effect of organic solute on admicellar polymerization formation (styrene addition)				
Low feed concentration	52 ± 2.9 (SI1)		53 ± 5.2 (SE1)	
High Feed Concentration	53 ± 1.1 (SI2)		54 ± 2.9 (SE2)	

NP, nonpolymerize; P, polymerize; NPW, nonpolymerize with washing; PW, polymerize with washing; SI, styrene addition at initial state; SE, styrene addition at equilibrium state; 1–20% of CMC; 2–80% of CMC.

^a Value is initial contact angle; at 5 min completely water wet (contact angle = 0)

topographic images of Sample SI2 and SE2 are shown in Figure 3. These results demonstrate that the surface morphology changes after styrene addition and equilibration. At the initial state, few aggre-

gates are observed with the average surface roughness equal to 132 nm (as compared to 252 nm before styrene addition). As equilibrium is approached, the surface roughness increased to 268 nm and the

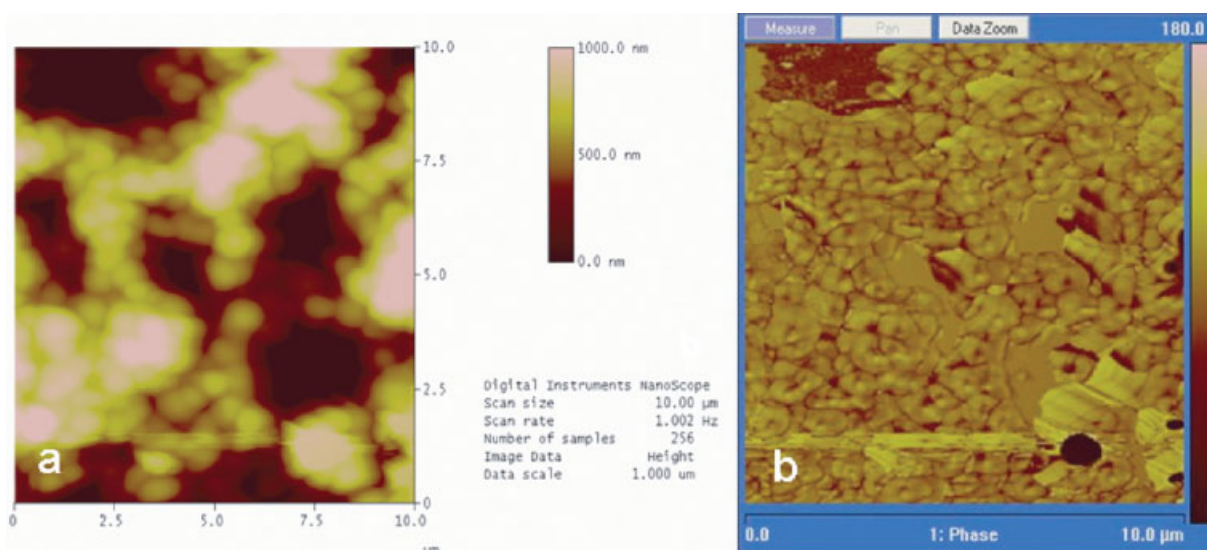


Figure 3 Topography (a) and phase (b) images of styrene adsolubilized into polymerized PG mica surface at the 80% CMC of PG concentration with the presence of 1 mM NaBr electrolyte for equilibrium state, SE2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

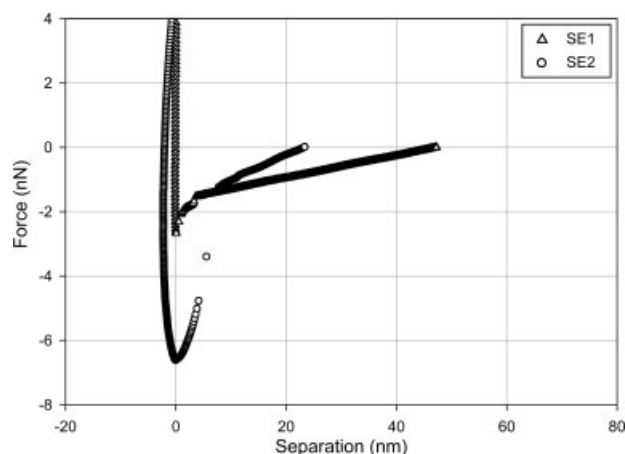


Figure 4 Typical interaction forces between the tip and mica surface as a function of tip-surface separation for sample SE1 and SE2.

aggregates become smaller and more numerous. This is in agreement with the literature,³¹ where changes in surface morphology were observed during the equilibration of the adsorbed aggregates with styrene. The topography images were especially interesting, as they showed the surface going

from a relatively flat layer with droplets of styrene present, to what appears to be a surface aggregate composed of connected emulsion-like droplets with an average diameter of 755 ± 132 nm [Fig. 3(a)]. The phase images in Figure 3(b) emphasize the change to be more discrete, interconnected aggregates. This change was unexpected, and points to future research areas examining the extent of cross-linking/network formation during polymerization and the ability of this polymerized layer to undergo radical phase changes.

The force-separation curve measurements at liquid environment for treated styrene adsorbilize surfaces are shown in Figure 4. The results show that with increasing surfactant admicelles and thus adsolubilization (SE1 versus SE2, respectively), stronger adhesive forces were observed between the tip and the surface. These findings indicate that the tip required more force to get free from the surface while it was retracted with higher surfactant and styrene loading. The nonflat baseline is due to the presence of Coulombic forces encountered near the surface of the aggregate which has adsorbed counterions. This has been observed and also explained by DLVO theory.³⁹ Although these

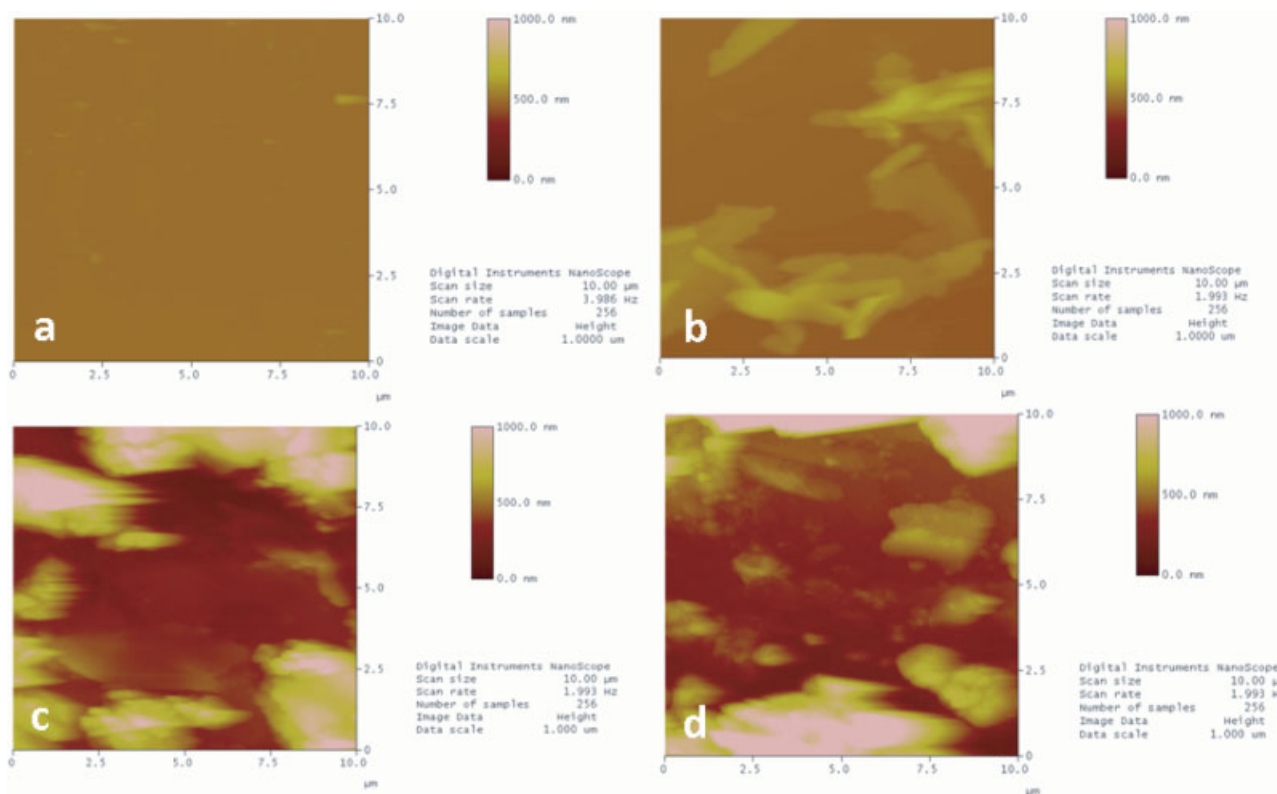


Figure 5 Topographic images comparison of PG adsorbed on mica; (a) NP2, before washing of nonpolymerized surface at 80% CMC, (b) NP2W, after washing of nonpolymerized surface at 80% CMC; polymerized system, (c) P2, before washing of polymerized surface at 80% CMC, and (d) PW2, after washing of polymerized surface at 80% CMC with the presence of 1 mM NaBr electrolyte. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

samples were examined in water, the presence of the surfactant layer, and of a surfactant layer which contains a core which is either very rich in styrene, or nearly pure styrene, allows for capillary forces to occur. This was previously observed during examinations of similar systems.³¹ Although sample SE1 had adhesion forces of 2.7 nN, the SE2 adhesion force is about 6.6 nN which is two times larger than samples with low styrene loading. Thus, the presence of a larger amount of adsolubilized styrene either increased the bilayer viscosity or the presence of a styrene zone in the surfactant layer allowed true capillary forces to increase the adhesive forces between the tip and the bilayer. Collectively, these results demonstrate that adsolubilization does in fact impact the properties of the surfactant-modified surface.

Desorption of PG on mica

Experimental sets five and six examined the impact of washing/desorption of the surfactant from non-polymerized and polymerized surfaces, respectively. Results from surface roughness measurements and visual observation demonstrate increasing surface roughness with increased surfactant loading. Figure 5 shows the topographic images comparison of PG adsorbed on mica before and after washing at different surfactant loading and both with and without polymerization (Sample NP2, NPW2, P2, and PW2). The result from nonpolymerized samples [Fig. 5(a,b)] shows a different morphology of modified-mica surface obtained after washing. Surprisingly, the surface roughness increases and more visible surface aggregates are present when nonpolymerized samples are washed. However, at 80% of CMC-washed surfaces have a lower contact angle with water (48°), indicating a decrease in hydrophobicity, when compared with the unwashed samples (contact angle = 61°). For the polymerized samples, the visual results in Figure 5(c,d) demonstrate that the surface topography is similar after washing (desorption) and before; this is corroborated by contact angle measurements that are statistically the same before and after washing (contact angles of 47 ± 4.1 before washing and 41 ± 3.6 after washing—Table III). These findings demonstrate that the polymerized surfactant film is extremely stable on the mica surface.

CONCLUSIONS

Contact mode and tapping mode AFM were used to examine the presence of a polymer thin film formed from the polymerization of a gemini surfactant on mica. Contact angle measurements were also used to evaluate the hydrophobicity of treated surfaces.

Polymerized PG at a concentration slightly below CMC (80%CMC) show the obvious surface morphology changes over the nonpolymerized surfaces. The surfaces demonstrate decreasing contact angle (increasing hydrophilicity) when modified by the polymerized surfactant. Surface aggregate morphology changes dramatically with the addition of adsolubilized styrene, and the styrene core in the adsorbed layer shows tip-surface adhesion which increased with increasing of styrene loading. The polymerized layers remained essentially unchanged after washing, demonstrating the robust nature of the polymerized layer.

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