



## CHAPTER IV RESULTS AND DISCUSSION

The modified surfaces have been synthesized with varying styrene and TEOS concentrations. The amount of AIBN used was 1 mole AIBN to 6 moles of styrene. The morphology of the modified mica surfaces has been investigated both with and without the presence of surfactant to elucidate the impact of surfactant on the polystyrene/silica composite film formation. AFM characterization of the modified mica surfaces is summarized in Table 4.1.

**Table 4.1** Samples of the adsorbed layer of polystyrene/silica composite on mica

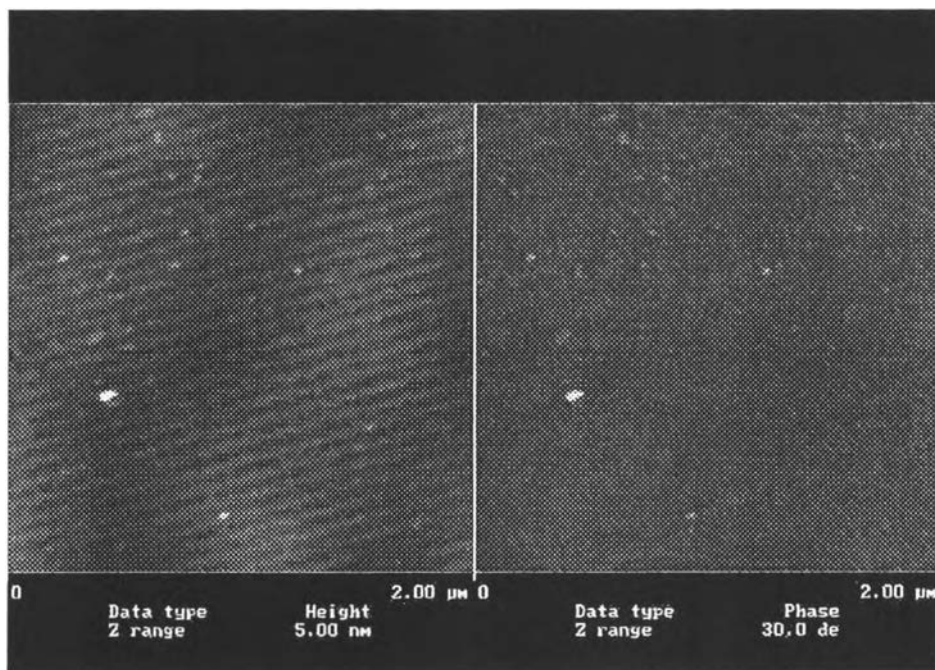
Figure	Without Surfactant		Figure	With Surfactant	
	Styrene ( $\mu\text{M}$ )	TEOS ( $\mu\text{M}$ )		Styrene ( $\mu\text{M}$ )	TEOS ( $\mu\text{M}$ )
4.1	H	-	4.8	H	-
4.2	L	-	4.9	L	-
4.3	-	H	4.10	-	H
4.4	L	L	4.11	L	L
4.5	L	H	4.12	L	H
4.6	H	L	4.13	H	L
4.7	H	H	4.14	H	H

H = Concentration of 3  $\mu\text{M}$

L = Concentration of 0.3  $\mu\text{M}$

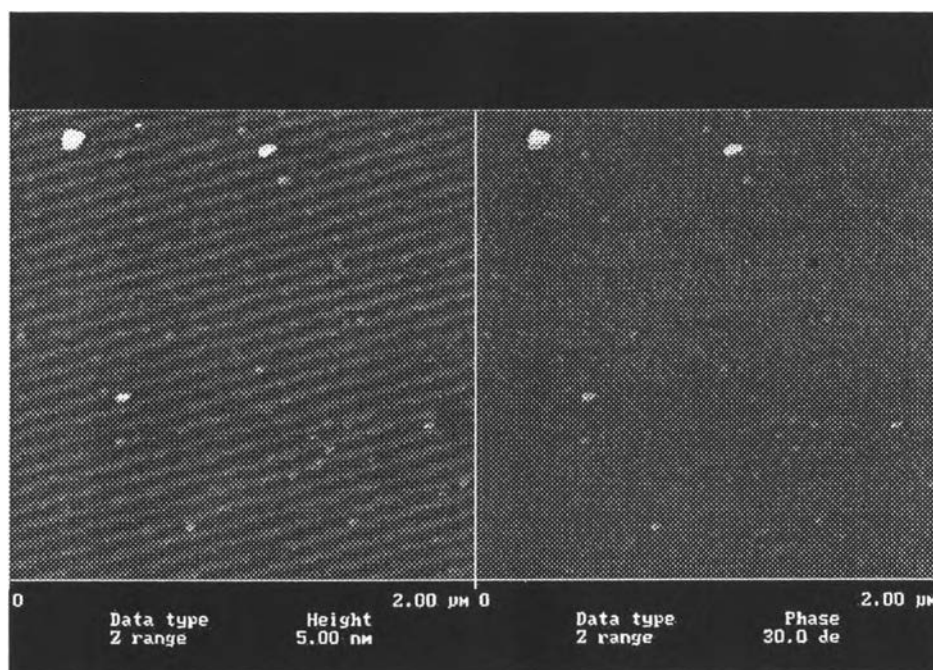
## 4.1 Modified Surface in the Absence of Surfactant Studies

### 4.1.1 Effect of Styrene Loading on the Surface Morphology



**Figure 4.1** Topographic and phase images of formed polystyrene film at a feed concentration of 0.3 μM.

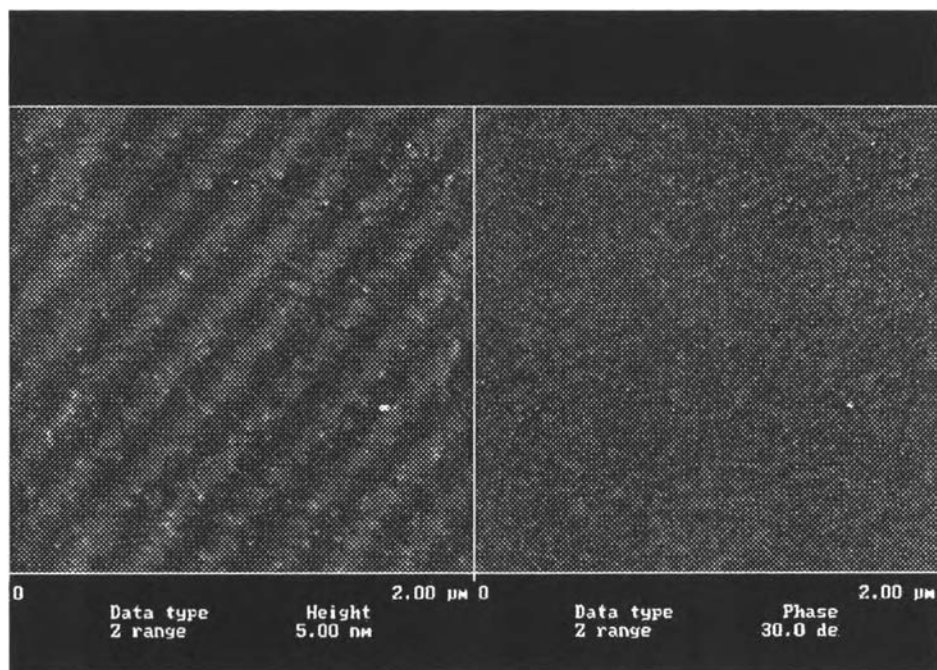
Figures 4.1 and 4.2 show the AFM micrographs of formed polystyrene films on mica at the feed concentration of 0.3 μM and 3 μM on mica, respectively. The images are similar to each other in that the surface morphology lacks clear features and is very flat. There appears to be no significant formation of polystyrene structures on the mica surface in the system modified without added surfactant. Thus, any styrene particles present after polymerization must have formed in the bulk and been deposited onto the sample surface and does not significantly effect the surface morphology.



**Figure 4.2** Topographic and phase images of formed polystyrene film at a bulk concentration of 3 μM.

#### 4.1.2 Effect of TEOS Loading on the Surface Morphology

Figure 4.3 shows the AFM micrograph of the formed silica film on mica at a bulk TEOS concentration of 3 μM. This image clearly shows that the addition of TEOS affects the surface morphology, with AFM images showing silica particles randomly dispersed across the mica surface and having a narrow size distribution.



**Figure 4.3** Topographic and phase images of formed silica film at 3  $\mu\text{M}$  bulk concentration.

The AFM micrographs of modified surfaces (Figures 4.1, 4.2 and 4.3) are employed as references for examining the surface morphology of formed polystyrene/silica composite film on mica as a function of changes in the styrene and TEOS feed concentrations which are shown in Figures 4.4 to 4.7.

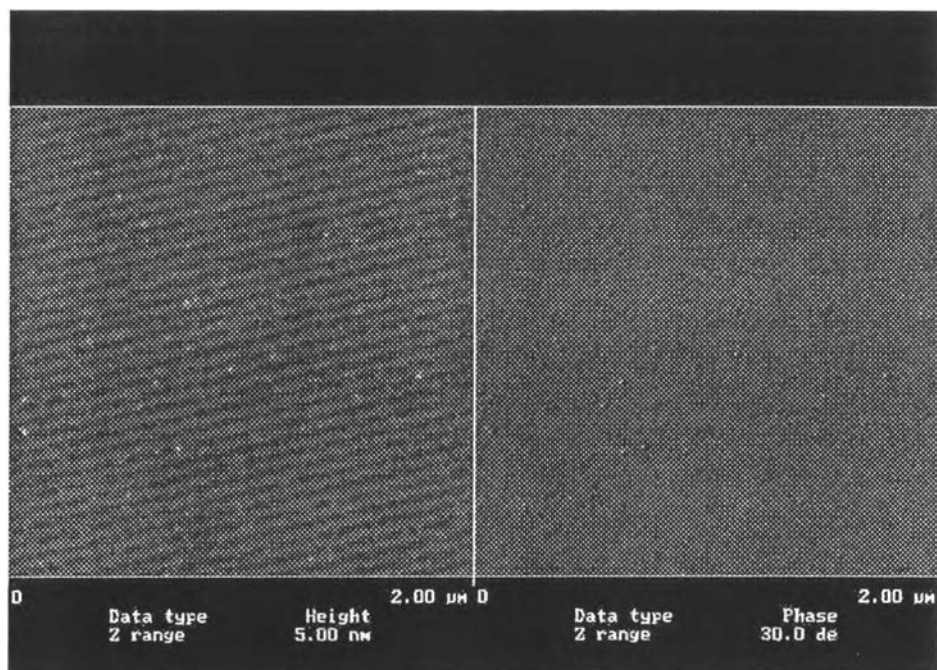


Figure 4.4 Topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS ( $0.3\mu\text{M}$  /  $0.3\mu\text{M}$ ) and  $0.05\mu\text{M}$  initiator.

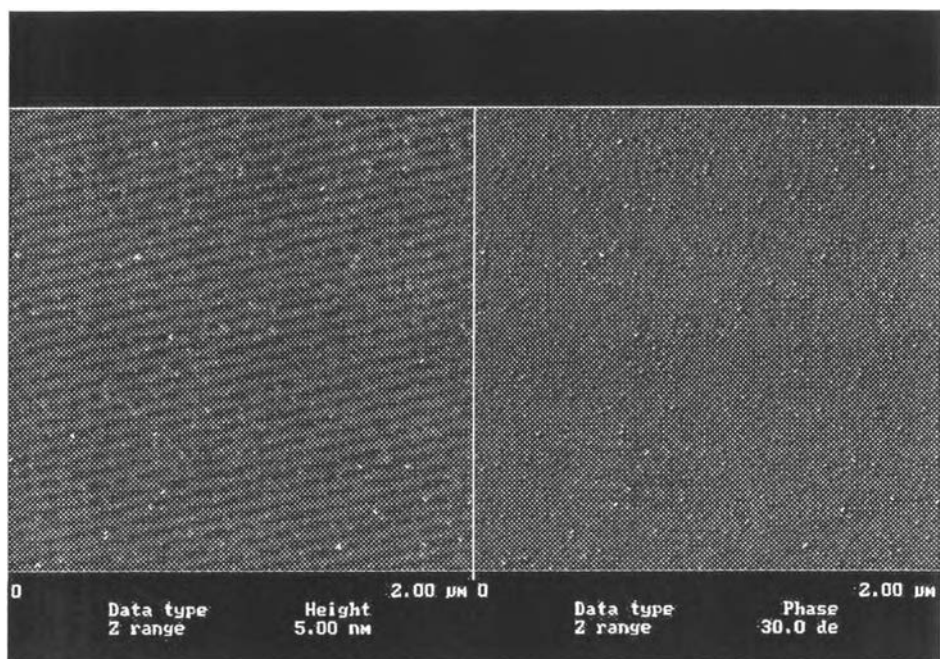


Figure 4.5 Topographic and phase images of formed polystyrene/silica composite film at a 1:10 ratio of styrene to TEOS ( $0.3\mu\text{M}$  /  $3\mu\text{M}$ ) and  $0.05\mu\text{M}$  initiator.

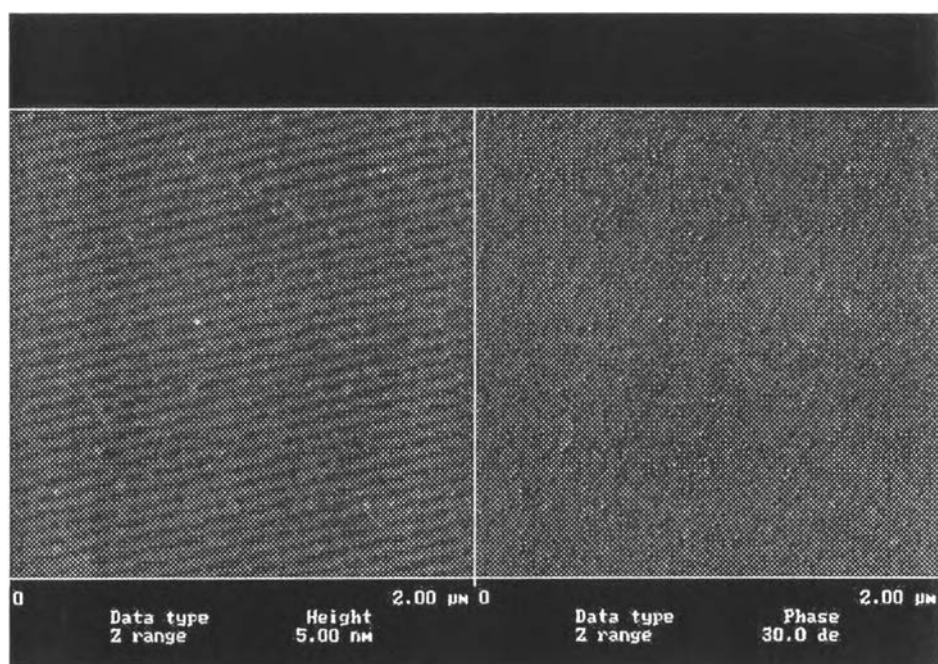


Figure 4.6 Topographic and phase images of formed polystyrene/silica composite film at a 10:1 ratio of styrene to TEOS ( $3\mu\text{M}$  /  $0.3\mu\text{M}$ ) and  $0.5\mu\text{M}$  initiator.

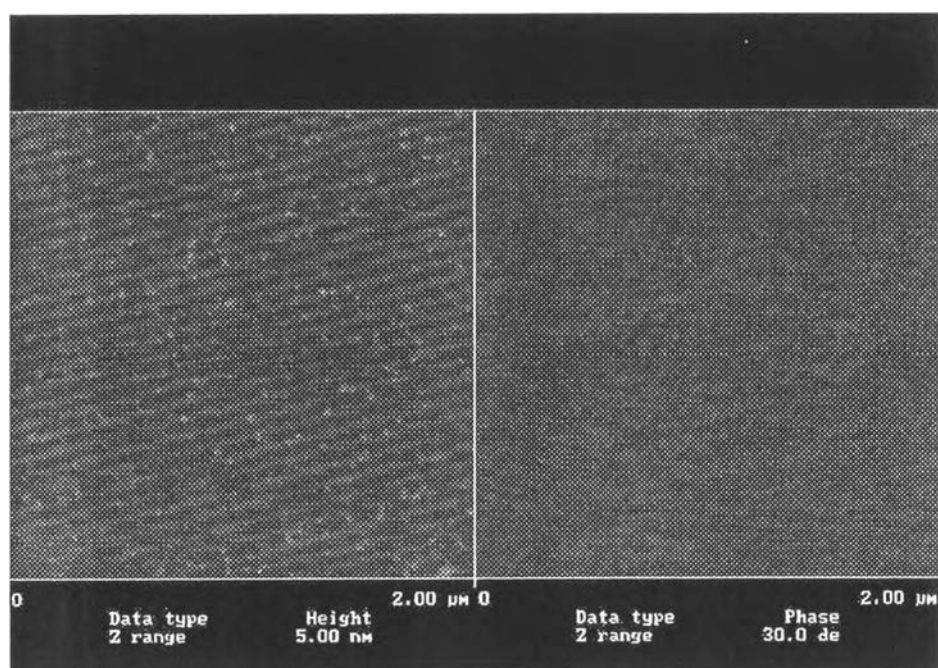


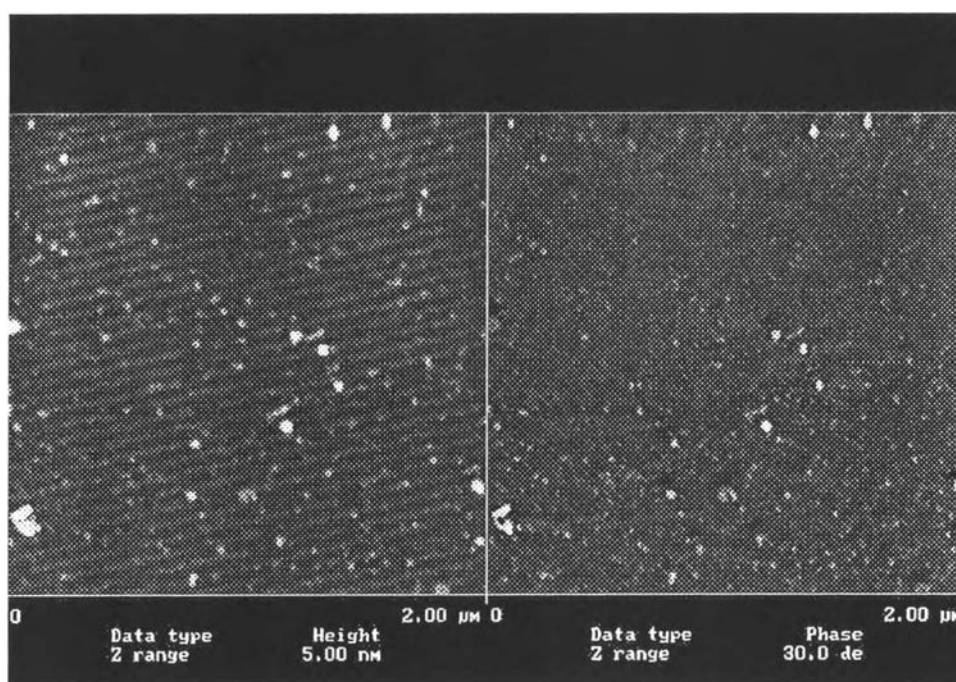
Figure 4.7 Topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS ( $3\mu\text{M}$  /  $3\mu\text{M}$ ) and  $0.5\mu\text{M}$  initiator.

It was clear that the particles found in the samples shown in Figures 4.4 to 4.7 are similar to those found in Figure 4.3, that is, they resemble the formed silica film on the mica. The taller features in the topographic images in Figures 4.4 to 4.7 are individual and/or small clusters of silica particles. AFM measurements after solvent rinsing indicate those silica particles adhere to the mica substrate and are difficult to remove. The silica particles appear to be randomly distributed on the sample surface and the size of formed silica particles is narrow in distribution. The resulting films do not significantly differ from each other in that the surface morphology exhibits scattered particles and multigranular features across the sample surface. Due to the fact that the formed polystyrene reference samples do not have any effect on the mica surface (Figures 4.1 and 4.2), while the formed silica reference sample (Figure 4.3) is similar to the others, it is apparent that the particles shown in Figures 4.4 to 4.7 are governed by the presence of silica and not in the presence of styrene.

## 4.2 Modified Surface in the Presence of Surfactant Studies

The morphology of formed polystyrene/silica composite film on mica has been investigated in the presence of surfactant. A controlled experiment used 0.2 mM Triton X-100<sup>®</sup> which is below the CMC of Triton X-100<sup>®</sup>. The formed polystyrene/silica composite film was examined as a function of changes in styrene and TEOS feed concentrations. AFM was used to image the surface morphology of the formed polystyrene/silica composite film on freshly cleaved mica under ambient conditions.

### 4.2.1 Reference Study



**Figure 4.8** Topographic and phase images of the formed polystyrene film at a bulk concentration of 3 μM and 0.5 μM initiator on mica.



Figure 4.8 shows the AFM micrograph of the formed polystyrene film on mica with 3  $\mu\text{M}$  styrene and 0.5  $\mu\text{M}$  initiator, and 0.2 mM Triton X-100<sup>®</sup> feed. The topographic image shows high contrast which reveals the existence of polystyrene droplets on the mica surface. The features are predominantly discrete polystyrene droplets and/or clusters that appear to have nucleated at many sites. Apparently, the initial styrene monomer concentration is higher than the saturation concentration in the admicelle. Thus, the excess of monomer will phase separate within the admicelle, forming droplet-like aggregates upon polymerization. Either that, or polymerization of styrene in the bulk occurs and the droplets are deposited over the sample surface during washing and drying.

Figure 4.9 represents the AFM micrograph of the formed polystyrene film under the same synthesis conditions as that in Figure 4.8, except the styrene concentration is 0.3  $\mu\text{M}$ . The topographic image revealing a surface that has a characteristic lateral structure with the periodicity of some 100 nm and these periodic structures are exhibited as well-interconnected, tightened and closed-packed completely cover the surface. Comparing the resulting image modified with 0.3  $\mu\text{M}$  and 3  $\mu\text{M}$  styrene reveals that the system of 0.3  $\mu\text{M}$  styrene obviously shows a smooth and homogeneous and that discrete polystyrene droplets and/or clusters are not found on the sample surface. This can be explained by the surfactant aggregates in the system of 0.3  $\mu\text{M}$  styrene have sufficient capacity to adsorb and solubilize all of the styrene without phase separation. Thus, no discrete polystyrene droplets and/or clusters are present on the modified sample surface. Additionally, the phase contrast is smooth, showing no changes in hardness.

Figure 4.10 shows the AFM micrograph of formed silica film on mica obtained at 3  $\mu\text{M}$  TEOS on mica. The surface morphology exhibits the homogeneous globular-shaped features and smooth with highly order and well-connected silica particles thoroughly the sample surface.

With the samples shown in Figures 4.8, 4.9 and 4.10 employed as references, the surface morphology of formed polystyrene/silica composite film on mica as a function of changes in the styrene and TEOS feed concentrations in the presence of surfactant are investigated as discussed in sections 4.2.2-4.2.4.

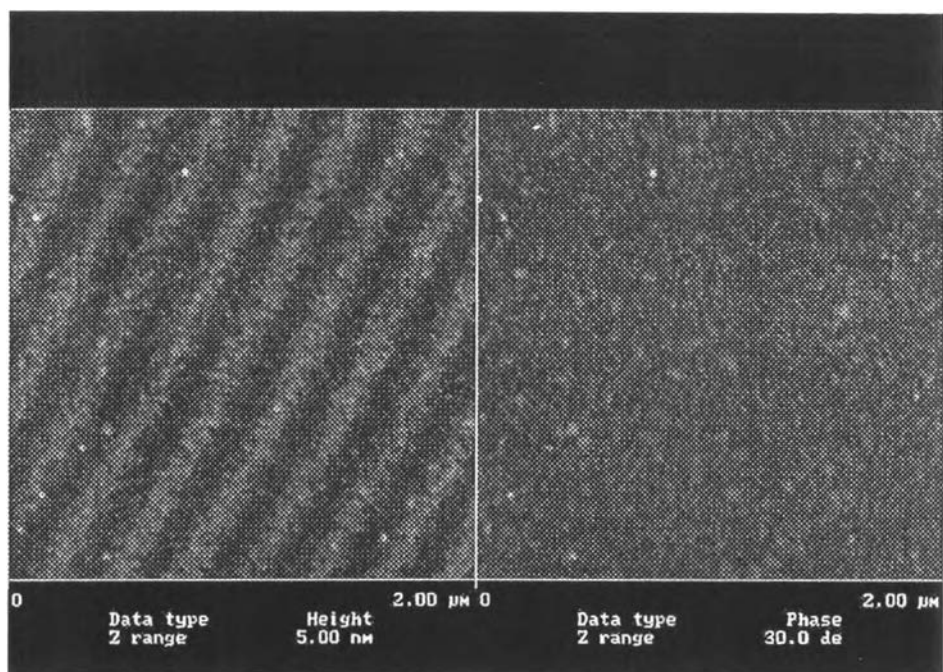


Figure 4.9 Topographic and phase images of formed polystyrene film at a bulk concentration of  $0.3 \mu\text{M}$  on mica.

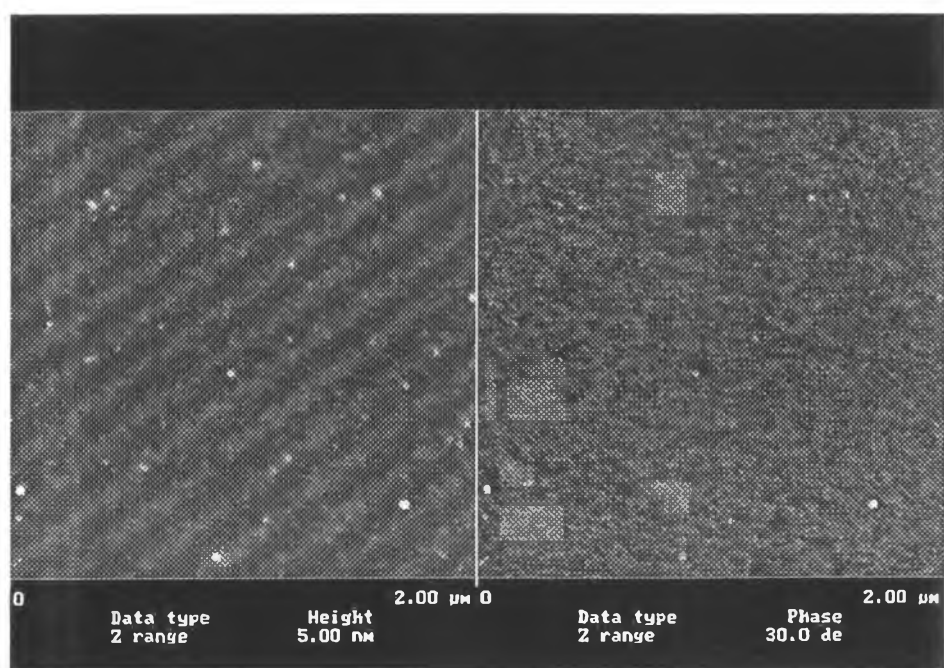
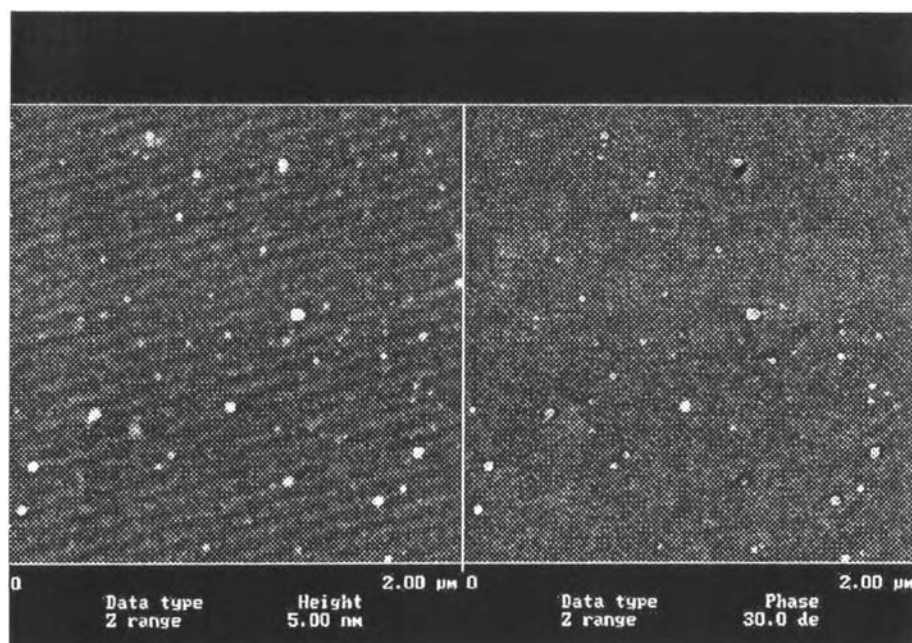


Figure 4.10 Topographic and phase images of formed silica film at a bulk concentration of  $3 \mu\text{M}$  on mica.

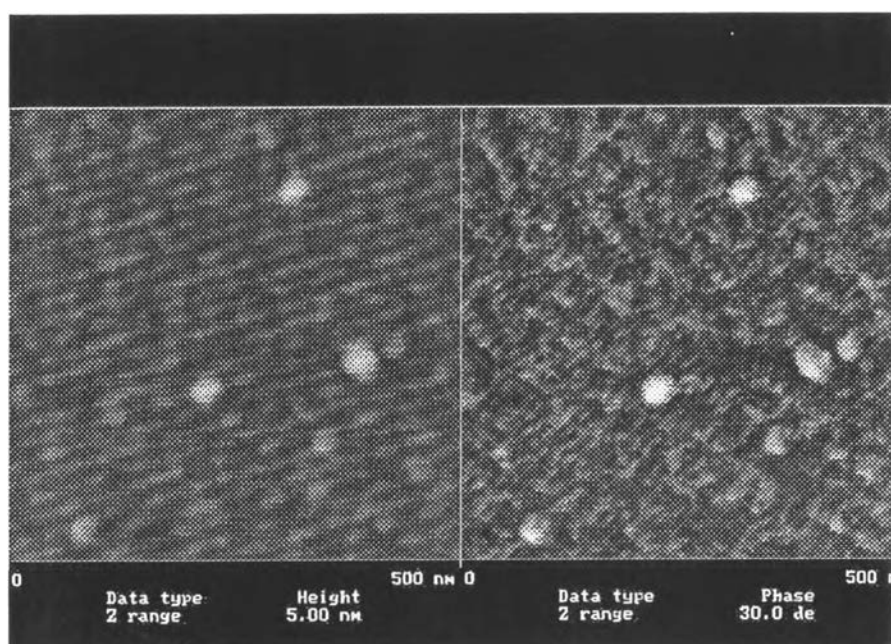
#### 4.2.2 Effect of Styrene Loading on Surface Morphology

The surface morphology of the formed silica film (Figure 4.10) reveals granular features of silica distributed on the mica surface, different from those of the formed polystyrene/silica composite film samples (Figures 4.11 to 4.14). This change in topography is due to the incorporation of styrene into the system and the surface morphology of the composite films is seen to depend on the amount of styrene in feed concentration. AFM images in Figures 4.11 to 4.14 demonstrate that as the styrene concentration ranges from 0.3  $\mu\text{M}$  to 3  $\mu\text{M}$ , the packing of domains (periodic structures or aggregates) become closer and denser ultimately resulting in compact and smooth film with homogeneous surface structure.

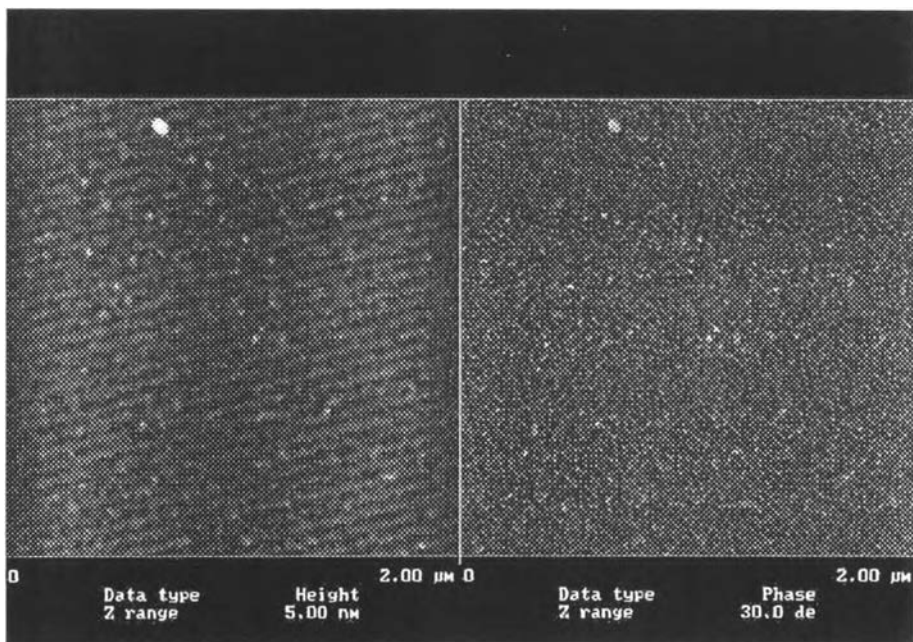
As can be seen, higher concentration of styrene assist the incorporation of TEOS in the polystyrene matrix, inhibits the formation of silica particles on the surface, and fabricates the denser structure with well-connected periodic structure with smooth relief. This interpretation is substantiated by the observation of composite structure in Figures 4.12 and 4.14 which show the formed polystyrene/silica composite film on mica under the same TEOS concentration but different styrene loading. The surface morphology of the lower styrene feed system (Figure 4.12) creates less dense and compact periodical structures showing the silica nodules on the surface. The system at higher feed styrene concentrations shows a denser, closed-pack and homogeneous with a well-connect of periodic structure (Figure 4.14).



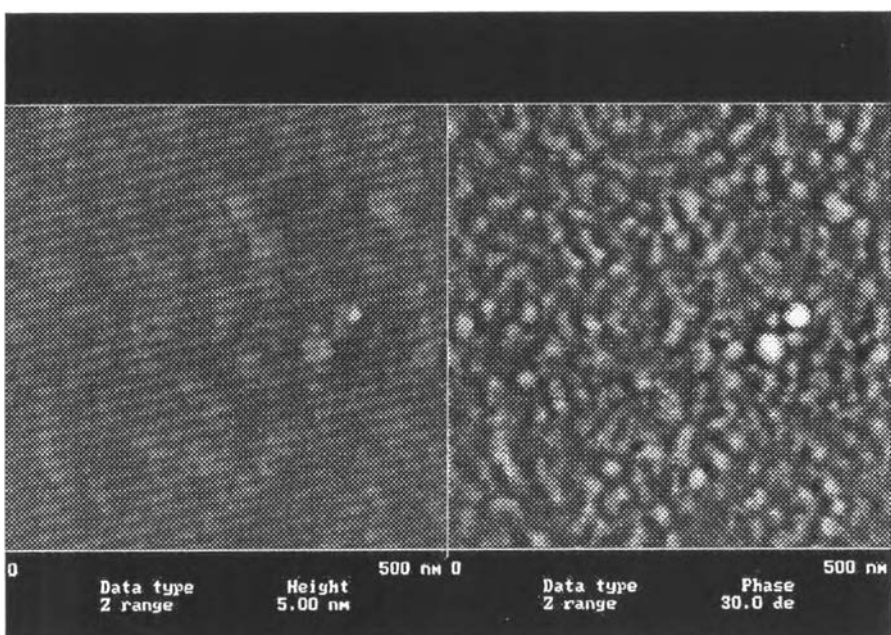
**Figure 4.11a** 2µm x 2µm topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS (0.3µM / 0.3µM) and 0.05 µM initiator.



**Figure 4.11b** 500nm x 500nm topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS (0.3µM / 0.3µM) and 0.05 µM initiator.



**Figure 4.12a** 2 $\mu\text{m}$  x 2 $\mu\text{m}$  topographic and phase images of formed polystyrene/silica composite film at a 1:10 ratio of styrene to TEOS (0.3 $\mu\text{M}$  / 3 $\mu\text{M}$ ) and 0.05 $\mu\text{M}$  initiator.



**Figure 4.12b** 500nm x 500nm topographic and phase images of formed polystyrene/silica composite film at a 1:10 ratio of styrene to TEOS (0.3 $\mu\text{M}$  / 3 $\mu\text{M}$ ) and 0.05 $\mu\text{M}$  initiator.

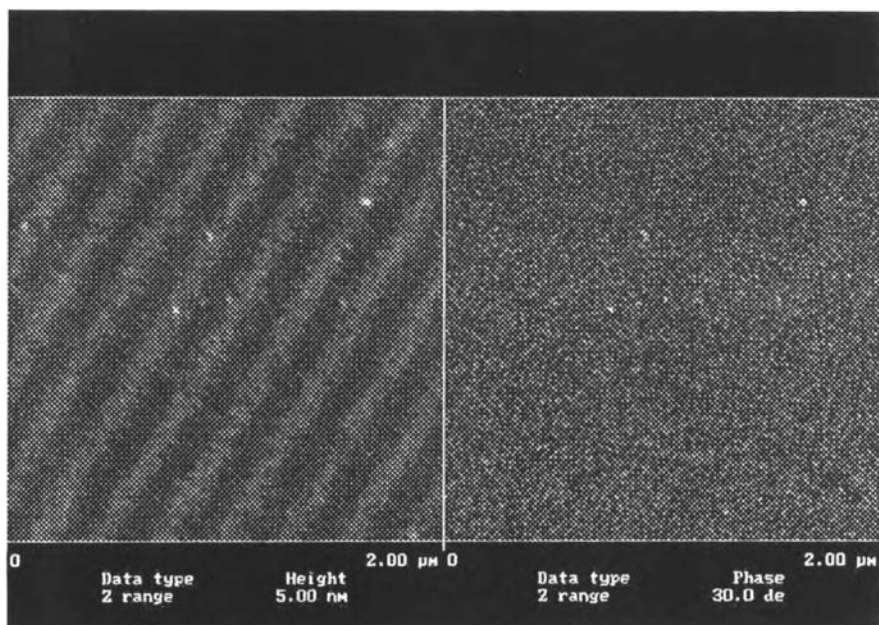


Figure 4.13a 2µm x 2µm topographic and phase images of formed polystyrene/silica composite film at a 10:1 ratio of styrene to TEOS (3µM / 0.3µM) and 0.05µM initiator.

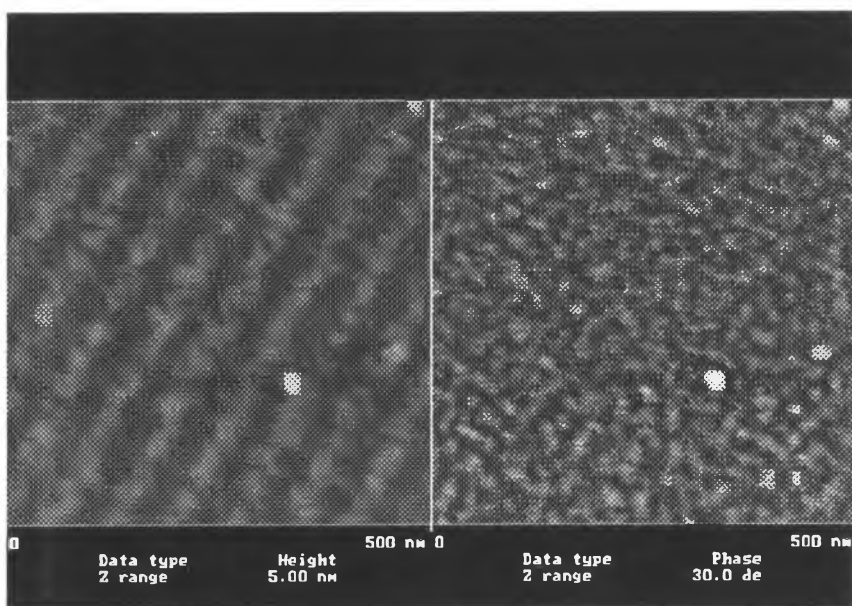
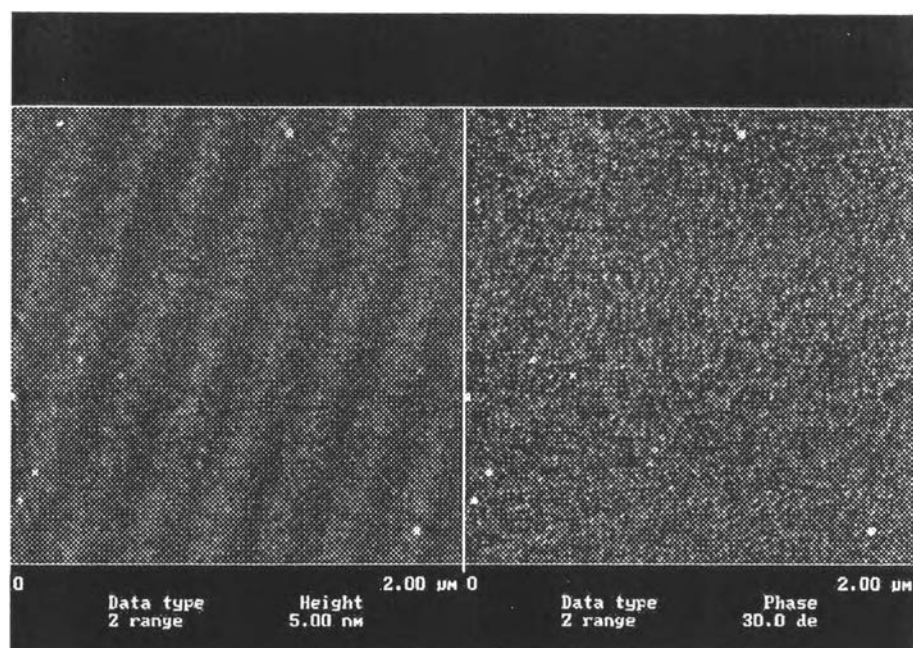
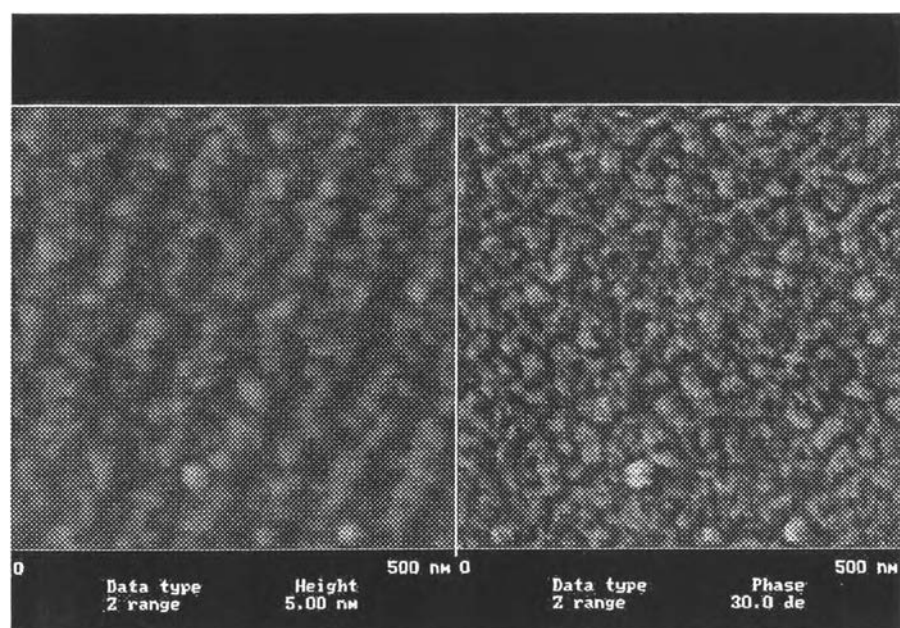


Figure 4.13b 500nm x 500nm topographic and phase images of formed polystyrene/silica composite film at a 10:1 ratio of styrene to TEOS (3µM / 0.3µM) and 0.05µM initiator.



**Figure 4.14a** 2µm x 2µm topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS (3µM / 3µM) and 0.05µM initiator.



**Figure 4.14b** 500nm x 500nm topographic and phase images of formed polystyrene/silica composite film at a 1:1 ratio of styrene to TEOS (3µM / 3µM) and 0.05µM initiator.

#### 4.2.3 Effect of TEOS Loading on Surface Morphology

In this section the formation of polystyrene/silica composite film has been investigated as a function of TEOS feed levels. AFM images in Figures 4.11 to 4.14 show the surface morphology of the modified surfaces with changing TEOS concentration (from 0.3  $\mu\text{M}$  to 3 $\mu\text{M}$ ). Similar results to those observed in section 4.2.2 are seen. That is, at higher concentration of TEOS a dense and highly compact structure is formed while lower concentrations of TEOS produced less dense and compact structures. This interpretation is substantiated by Figures 4.13 and 4.14 which show the formed polystyrene/silica composite film on mica under the same styrene concentration but different in TEOS loading.

The surface morphology of the lower TEOS concentration (Figure 4.13) exhibits deep “valleys” resulting in a less compact structure. Additional TEOS resulted in increased silica dispersion in the polystyrene matrix producing a more homogeneous internal structure and denser structure. This may be because additional TEOS was needed to completely coat the surface.

#### 4.2.4 Effect of Surfactant on Surface Morphology

The morphology of the modified mica surfaces has been investigated both with and without the presence of surfactant to elucidate the impact of surfactant on the polystyrene/silica composite film formation.

The surface morphology of section 4.1 and 4.2 shows the AFM micrographs comparing the formed polystyrene film both with and without the presence of surfactant, respectively. The comparison shows that styrene monomers that are nearly soluble in water will preferentially partition into the admicelle since the admicelle interior is highly hydrophobic. In the admicelle, the bilayer acts as a two-dimensional solvent to concentrate monomer near the surface of the substrate. Consequently, the periodic structures of polystyrene with well-connected, tight and closed-packed entirely cover the sample surface. On the other hand, the formed polystyrene film without the presence of surfactant reveals that the surface morphology lacks clear features and is very flat. This can be indicated that there is not any significant formation of polystyrene film on mica in the absence of surfactant.



Figures 4.3 and 4.10 compare the formed silica film with and without added surfactant, respectively. As expected, the comparison shows that the formed silica film with the presence of surfactant shows the network of uniform and well-connected homogeneous globular structure with a smooth relief. Moreover, these particles are well distributed on the entire surface. Alternatively, the formed silica film on mica in the absence of surfactant exhibits silica particles randomly dispersed and scattered across the sample surface.

From this study it can be seen that the presence of an adsorbed surfactant aggregates dramatically alters the surface morphology of polystyrene/silica composite film on mica. The composite layer in the absence of surfactant shows a rather featureless structure with fine silica clusters adhering to the sample surface. This indicates that no significantly formation of polystyrene/silica composite film on mica can be created in the absence of surfactant. On the other hand, with the presence of surfactant system reveals that the polystyrene/silica composite films are formed on mica surface by reaction within the adsorbed surfactant aggregates. The surface morphology of formed polystyrene/silica composite film creates the periodic structure of composite with well-connected, tightened and closed-packed cover entirely the surface. Multiple scans of the surfaces in many different locations do not detect the presence of multiple layers of material or any surface unevenness. This result confirms that the formed composite films completely and uniformly coat the mica surface.