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SHORT COMMUNICATION

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Single polymer molecules adsorbed to mica and the oppositely charged polymer/surfactant complexes formed at the air–water interface visualized by atomic force microscopy

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Abstract In the present study, the structure and morphology of single sodium poly(styrenesulfonate) (PSS) molecules adsorbed to mica surface from the natural aqueous solution is investigated using atomic force microscopy technique. Results show that single PSS molecules are observed which show a morphology of wormlike coils. Meanwhile, single sodium poly(styrenesulfonate) (PSS)/Hexadecyltrimethylammonium bromide (CTAB) complexes deposited on mica from the air–water interface are also observed. However, the PSS/CTA$^+$ complexes show different conformations by appearing in the morphology of circular patches. Experimental data are in fair agreement with the theoretical analysis.

Keywords Structure and morphology · Atomic force microscopy (AFM) · The air–water interface

Introduction

The study of interactions between surfactants and polymers is an interesting field in colloid science owing to a number of commercial applications [1], such as paints, drilling and biological membranes etc. In recent years, various physicochemical methods have been employed to characterize the interactions between polymers and surfactants both in bulk solution properties and at interfaces, such as rheological measurement [2, 3], surface tension method [4–6], fluorescence [7–9] etc. However, these studies have predominately focused on the bulk solution properties, and relatively less is known about the surface properties of such solution [5, 6]. While surface tension has been the main tool for the study of interactions of polymers and surfactants at the air–water interface, a range of experimental technologies, such as X-ray reflectivity [10, 11], neutron reflectivity [12–14], and ellipsometry [15] have been used to characterize the interface properties. On the other hand, so far no direct visualization technique has been employed [11].

Recently, atomic force microscopy (AFM) has been proved to be a powerful tool for the study of polymers and surfactants at interfaces [16–18]. AFM with molecular resolution allow us to investigate interactions on a molecular scale, giving individual results, not only an average result [19]. In this work, we report on the structure and morphology of single PSS molecules and PSS/CTA$^+$ complexes for the first time using AFM.

Experimental section

Materials

Hexadecyltrimethylammonium bromide (CTAB) was of analytical reagent grade (Beijing Xi Zhong Chemical Factory) and was purified by extraction with diethylether followed by three recrystallizations from anhydrous ethanol. After recrystallization, there was no minimum in a plot of surface tension versus concentration. Poly(styrenesulfonate) sodium salt (PSS), obtained form Aldrich Chemical Co, had a molecular weight of 70,000 g mol^{-1} and a M_w/M_n of 1.07. Double-distilled water was used throughout in the study.

π–A isotherms measurement

The surface pressure (π)–surface area (A) isotherm of a spread film was obtained by an LB trough (length 700 mm×width 40 mm, FACE HBM, Japan) equipped with a Wilhelmy plate for monitoring the surface pressure. The entire film balance is trapped in a container to avoid contamination and air currents. The accuracy of the surface pressure was ±0.1 mN/m. Before each experiment, the trough was thoroughly cleaned with acetone and dichloromethane. The surface area was compressed by moving a Teflon barrier at the speed of (20–25 cm^2)/min.

Microscopy

Images were captured with a Nanoscope III AFM (Digital Instrument, Co) using silicon ultralecers in tapping mode. Each mica sample was freshly cleaved just before use. Measurements were performed in the temperature range 20±1°C.

Results and discussion

AFM observation of PSS deposited on mica from aqueous solution

It is accepted that it is hard to attach negatively charged polyelectrolytes on a negatively charged mica surface because of electrostatic repulsive forces. However, under a relatively high polyelectrolytes concentration, the concentration gradient could overwhelm electrostatic repulsive forces and force the polymers onto the mica surface, which allows the imaging of single polymer chains [20]. Here, freshly cleaved mica was immersed in a high PSS concentration solution (0.01 mg/mL) for up to 7 min at ambient conditions to forcibly adsorb PSS, afterward it was rinsed with 1–2 mL H_2O, dried with a stream of nitrogen at the force of 0.5 MPa in the same direction, then was visualized by AFM.

Figure 1a shows a representative AFM image of PSS chains deposited on mica from natural aqueous solution (0.01 mg/mL). The polymer chains are stretched forming wormlike coils due to the electronic repulsion between the charged monomers along the chains. In Fig. 1, a few globular structure can be observed. These globular structures are most likely due to very weakly adsorbed molecules being forced into this conformation as a result of drying of the sample prior to visualizing. The similar results are reported elsewhere [21–24]. Single PSS chains can be visualized on mica. For example, the contrast-enhanced image was obtained by expanding the image in Fig. 1a, as shown in Fig. 1b.

To prove that observed structure represents single PSS molecules, we evaluated an experimental average volume and contour length of the structure based on molecular mass of PSS. The theoretical calculations of single PSS molecules are given by Eq. 1:

$$V_{\mathrm{calc}} = \frac{M}{\rho N_{\mathrm{A}}}, \tag{1}$$

where M is the molecular weight. ρ is the density of PSS, and N_{A} is Avogardro's number. Thus, the single PSS molecular volume is determined: $V_{\mathrm{PSS,\ calc}} = 7{,}000/6.02\times1.1 = 106\ \mathrm{nm}^3$. The average contour length of single PSS molecules is estimated as follows [23]:

$$L = \frac{M}{m_{\mathrm{mon}}} \times 2 \times l \times \sin\left(\frac{\theta}{2}\right), \tag{2}$$

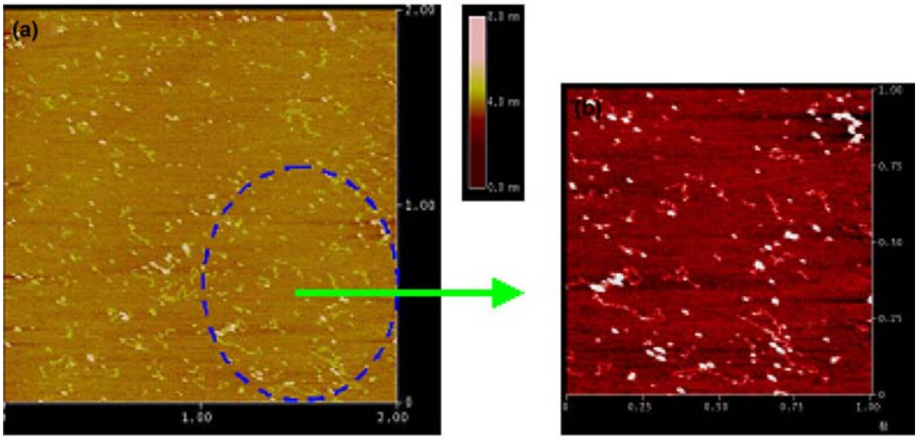

Fig. 1 Representative AFM topography images (2×2 $\mu\mathrm{m}^2$ scan) of PSS deposited on mica (**a**), and enlarged and contrast-enhanced AFM image (**b**)

where $l = 0.154$ nm is the length of the C–C bonds in the backbone, $\theta = 109°$ is the valence angle between C–C bonds in the backbone, and m_{mon} is molecular mass of the monomer unit. So $L_{\mathrm{PSS,\ calc}} = (7{,}000/207) \times 2 \times 0.154 \times 0.814 = 85$ nm.

We also determined the average volume and contour length of single PSS molecules, $V_{\mathrm{PSS,\ exp}}$ and $L_{\mathrm{PSS,\ exp}}$ in AFM experiment by bearing analysis and particle analysis with the standard software of our instrument. After analyzing over 50 isolated PSS molecules in Fig. 1a, the average volume and contour length of single PSS molecules were estimated to be $124.4 \pm 11.9\ \mathrm{nm}^3$, and 72.3 ± 5.22 nm, respectively, which is in good agreement with the calculated values ($106\ \mathrm{nm}^3$ and 85 nm). Thus, it could be clearly demonstrated that single PSS molecules have been observed.

Complex formation of PSS/CTAB at the air–water interface

The CTAB was dissolved in chloroform to make a 1.0 mM solution and then spreaded on the pure water surface by a microsyringe to prepare a monolayer. After allowing 10 min for the evaporation of the solvent, the measurement of surface-area (π–A) isotherms were carried out.

The π–A isotherm of CTAB monolayer is shown in Fig. 2(curve a). From the isotherm, one can observe that the surface pressure of CTAB monolayer is nearly zero during the process of compression, showing a low, straight line. Although CTAB has water-insoluble carbon segments, these CTAB molecules in water surface cannot form a stable monolayer, because the CTAB molecules on the surface easily move into solution under thermodynamic equilibrium. However, when CTAB dissolved chloroform is spread on the PSS solution surface ($C = 0.01$ mg/mL), the π–A isotherm of CTAB monolayer is different from that of CTAB monolayer on the pure water surface, as shown in Fig. 2(curve b). The surface pressure starts to increase gradually at the low-surface-pressure region. With further decrease of surface area, the surface pressure rapidly increases and is broken down until the surface pressure reaches 40 mN/m. Indeed, the monolayer was stable. The phenomena implies coadsorption of PSS and CTAB molecules at the air–water interface and formation of a highly surface-active polymer/surfactant complex because of the strong electrostatic interactions between the charged groups [4, 25].

Figure 3a shows AFM image of PSS/CTA$^+$ complexes transferred to mica surface through a horizontal lifting method at low surface pressure $\pi = 0.5$ mN/m. The PSS/CTA$^+$ complexes deposited on mica surface from the air–water interface show different conformation for the PSS molecules deposited on mica surface from natural PSS aqueous solution, showing the morphology of circular patches. The charged PSS molecules complex with CTA$^+$ ions, and the long-range Coulombic repulsion forces between the charged monomers decrease, thus, an image of the extended wormlike coil-to-circular patch conformational transition of PSS polymer is observed [21, 22]. Cross-section profiles clearly show that the PSS/CTA$^+$ complexes adsorbed to mica formed conelike structure (Fig. 3b, c) as visualized. The average height and diameter of the PSS/CTA$^+$ complex in Fig. 2a was estimated to be 0.746 ± 0.099 nm, 39.7 ± 2.26 nm, respectively. To evaluate the volume of the visualized structure, for simplicity, we used the following formula for the conelike shape [26]:

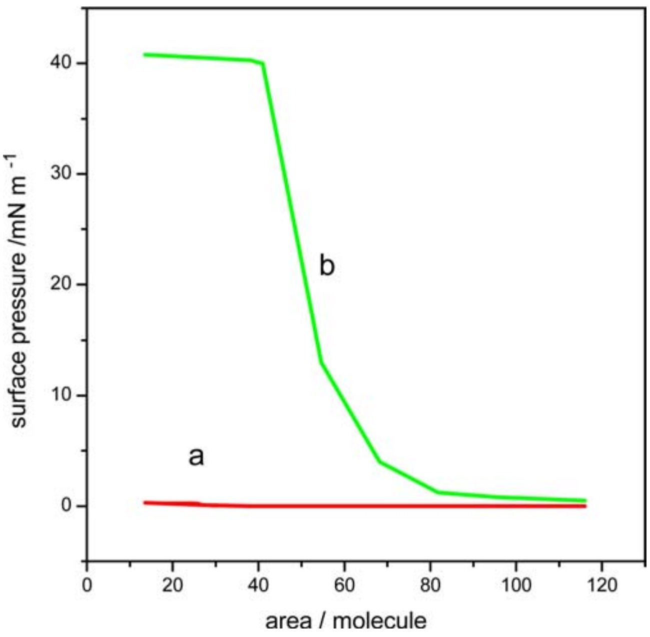

Fig. 2 Isotherm of surface pressure versus mean molecular area

$$V_{\mathrm{cone}} = \frac{1}{3} H\pi (D/2)^2 \tag{3}$$

where, H and D are the height and diameter of structure observed with AFM. So$V_{\mathrm{PSS/CTA^+,exp}} = 1/3 \times 0.746$ $\pi(39.7/2)^2 = 300\,\mathrm{nm}^3$. Single PSS molecules contain about 340 monomers, which means the total charge of 340 per one molecule. It is rational to expect that one PSS molecule can complex with 340 CTAB molecules. Thus, the theoretically calculated volume of the PSS/CTA$^+$ complexes is given by$V_{\mathrm{PSS/CTA^+,calc}} = V_{\mathrm{PSS,\ calc}}$ $+340V_{\mathrm{CTA^+,calc}} = 106 + 340 \times 0.47 = 265\,\mathrm{nm}^3$, which is again corresponds to the experimental value ($300\ \mathrm{nm}^3$). Single PSS/CTA$^+$ complexes deposited on mica form the air–water interface are also visualized directly by AFM.

Figure 4 shows the morphology of PSS/CTA$^+$ complexes deposited on mica from the air–water interface at

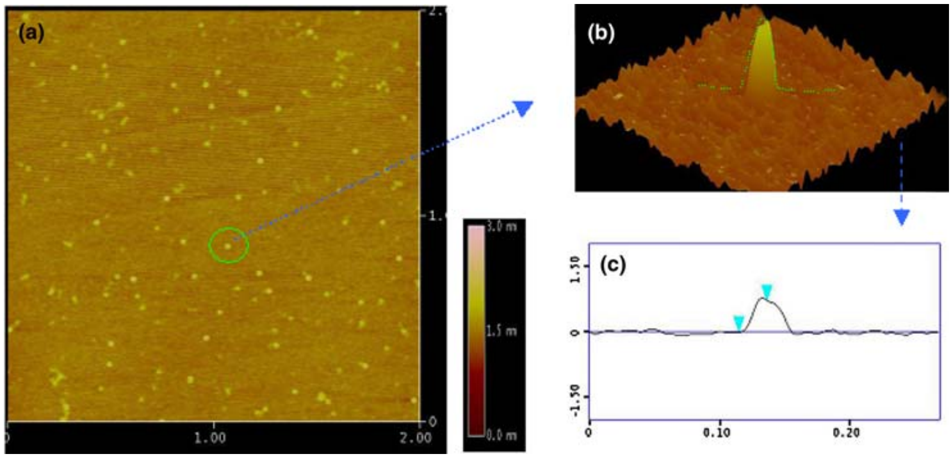

Fig. 3 AFM topographic images (**a**, **b**) and cross-sections of PSS/CTA$^+$ complexes deposited on mica (**c**)

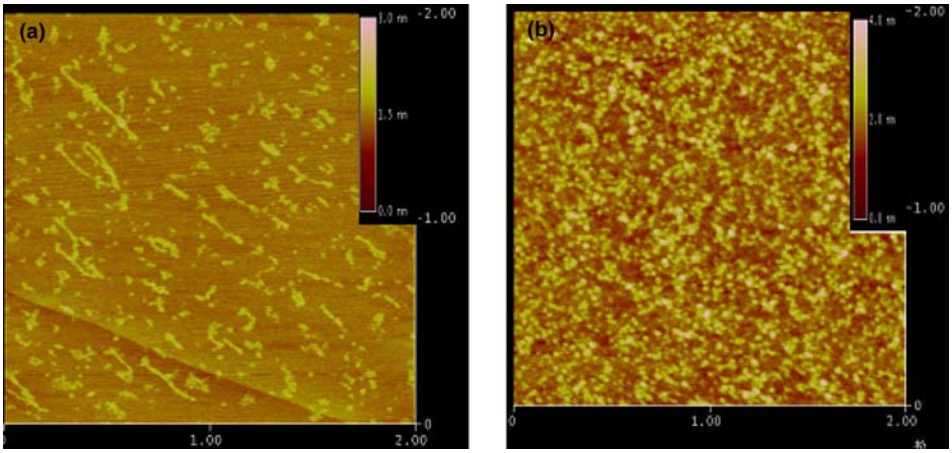

Fig. 4 AFM images (2×2 μm^2 scan) of PSS/CTA$^+$ complexes deposited on mica at surface pressure of **a** 4.5 mN/m, **b** 9 mN/m

surface pressure of 4.5, 9 mN/m, respectively. The number density of the PSS/CTA$^+$ complexes increased with increasing the surface pressure. Two or more individual PSS/CTA$^+$ complexes could aggregate partially or completely (Fig. 4). Densely packed PSS/CTA$^+$ complexes film could be observed at $\pi = 9$ mN/m (Fig. 4b).

Conclusion

Single PSS molecules deposited on mica from aqueous solution were directly observed by AFM, and adsorbed molecules appeared in AFM images as wormlike coils. Meanwhile, single PSS/CTA$^+$ complexes deposited on mica from the air–water interface were also investigated. However, the PSS/CTA$^+$ complexes show different conformation by appearing in the morphology of circular patches. Experimental data are in fair agreement with the theoretical analysis. Furthermore, it gives evidence that the careful AFM is indeed a powerful tool to provide direct images of single macromolecules with a nanometer resolution.

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