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Molecular morphology of modified partially hydrolyzed polyacrylamide (MHPAM) on mica substrates and Langmuir–Blodgett films of MHPAM/CTAB complexes as observed by AFM

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Abstract

Direct observation of molecular morphology of modified partially hydrolyzed polyacrylamide (MHPAM) has been studied in this paper by atomic force microscopy (AFM). The MHPAM molecule chains are stretched forming worm-like coils due to the electrostatic repulsion between randomly distributed positive charges along the chain at pH 3. The further data analysis demonstrates single MHPAM molecules are being imaged. In addition, morphology of Langmuir–Blodgett films of MHPAM/CTAB complexes on mica surfaces also investigated as a function of the subphase pH. At pH 6, MHPAM/CTAB molecules covered on mica surfaces adopted the worm-like nanostructures, and at pH 7, conformational transition of polymer complexes appeared, showing the morphology of bump-like to some extent owing to aggregation of intrachains and interchains. Eventually, more compact globule morphology was formed at pH 12.

Keywords: Molecular morphology; Atomic force microscopy (AFM); Langmuir–Blodgett films; Electrostatic repulsion; Polymer complexes

1. Introduction

Polyacrylamide is a kind of water soluble polymers containing both carboxylic and amine groups. Sensitivity of associative properties of aqueous solutions of polyacrylamide to pH, ionic strength, and temperature is high. Introduction of even small fractions of other groups can lead to dramatic changes in polymer solution properties. Over the past three decade, partially hydrolyzed polyacrylamides (HPAM) and theirs derivatives have attracted much interest because of their potential applications in enhanced oil recovery [1–3], wastewater treatment [4], and paper manufacturing [5], et al. Among them, numerous studies in tertiary oil recovery system have come under much greater investigations because their uses can increase sweep efficiency and oil displacement efficiency as viscosity modifiers [6–17]. In a typical

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aqueous polyacrylamide-based petroleum recovery process, the flooding solutions of polyacrylamide are injected into the underground and push the residual oil drops in the porous media pores out. This process should be refer to the study of two interfaces: one is a liquid/liquid (water/oil) interface, the other is a liquid/solid (water/rock) interface. The structural and conformational changes of polymer molecule chains adsorbed onto interfaces are always present responding to change of conditions (ionic strength, pH, solution concentration, charge density), which is the contributory factors to enhanced oil recovery, and the related work have been reported elsewhere at the various interfaces including air/water, water/oil, liquid/solid interface [18–22].

For the past, the surface or interface properties of polyacrylamide solution characterized by conventional methods, such as surface tension [23,24], surface rheology [21,25,26], and neutron scattering [27–29] have been mainly focused on the average results on a macroscopical scale because of the practical and experimental limitations at that time, and relatively less is known about direct structural and morphological observation at interfaces on the nanometre scale. Recently, a few researchers have reported the visualization of different conformations of single polymer molecules on solid surfaces with atomic force microscopy [30–34]. However, as for the adsorption of HPAM on the interface, reports is very scarce in the literature [35–38]. With the further application in many important industry fields, investigations of polyacrylamide at interfaces on the molecular level are still worthwhile for more detailed theoretical and technological studies. In previously paper [37], we reported the morphology of partially hydrolyzed polyacrylamide on mica surfaces in different environment. Herein, a modified partially hydrolyzed polyacrylamide (MHPAM) has been further studied by atomic force microscopy (AFM) at the mica/solution interface. The effects of pH on conformational changes of MHPAM are investigated.

2. Experimental

2.1. Materials

Hexadecyltrimethylammonium bromide (CTAB) was 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 vs concentration. Modified partially hydrated polyacrylamide (MHPAM) with a weight average molecular weight of $0.8 \times 107\ \mathrm{g\ mol^{-1}}$ was obtained from Beijing Hengju Chemical Agent Co., Ltd, and used without further purification. The values of the repeated units (m, n, p) are about 109,825, 15,294 and 7018 and the isoelectric point of this polyacrylamide is about 5.0. The structure of MHPAM is shown in Fig. 1. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were all analytical grade (Beijing Chemical Factory, China). All water used was doubly distilled.

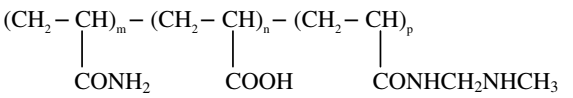

Fig. 1. Structure of MHPAM.

2.2. Atomic force microscopy

A Nanoscope IIIa atomic force microscope (AFM) with the tapping mode (Digital Instruments, Santa Barbara, CA) was used for the images of the adsorbed MHPAM on mica substrates. AFM cantilevers were conductive silicon cantilevers with a typical resonance frequency of 200–300 kHz, spring constant of $35\ \mathrm{N\ m^{-1}}$. The AFM image is shown in the height mode after flattening.

3. Results and discussion

3.1. Structure and morphology of MHPAM adsorbed onto mica surfaces from solution

Solutions were prepared by dissolving the requisite amount of MHPAM to make a concentration of 0.0001 mg/ml, and allowed to equilibrate at room temperature for 12 h. The solution pH was adjusted to 3 by the addition of HCl. The freshly cleaved mica plate was dipped in the aqueous solution of MHPAM for 2 min, and then dried with a stream of nitrogen.

Fig. 2 shows a representative AFM image of MHPAM chains adsorbed on mica from aqueous solution at pH 3. Because organic carboxylic acid has a pK_a value around pH 4.5, and amine group ($-CONHCH_2NHCH_3$) of MHPAM has a pK_b value about pH 10, so the carboxylic acid will not dissociate at pH below 4.5 and the amine group will almost

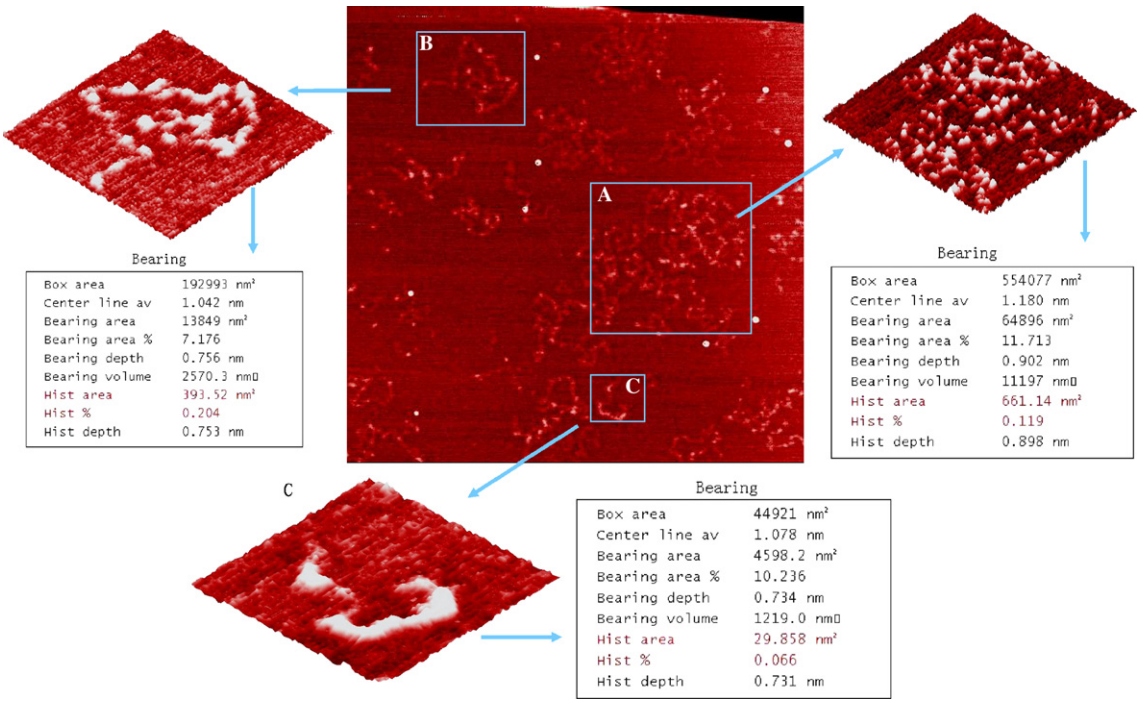

Fig. 2. AFM image (2000×2000 nm^2) of MHPAM chains adsorbed on mica from aqueous solution at pH 3.

fully ionized at our experimental condition, and MHPAM is a strong cationic polyelectrolyte. The MHPAM polymer chains are stretched forming worm-like coils due to the electrostatic repulsion between randomly distributed positive charges along the chain [39,40], as shown in Fig. 2. Individual molecule chains of MHPAM were clearly resolved by AFM. The detailed data analysis of Fig. 2 was characterized using "bearing" function of image analysis software provided by CA company, and the corresponding results were displayed in Fig. 2. Here, "bearing depth" is the average height of MHPAM molecules in the selected domain and "bearing volume" is the corresponding individual molecule chains volume. From Fig. 2, one know that the average height of MHPAM chains in selected domain was 0.734–0.902 nm, which well agreed with that of a single polymer chain reported elsewhere [39], and the volume of individual MHPAM molecules in domain A was about 11,197 nm^3. The theoretical calculations of single MHPAM molecules are given by $V_{calc} = M/\rho N_A$, where M is the molecular weight, ρ is the density of MHPAM, about 1.2 g cm^{-3}, and N_A is Avogadro's number. Thus the single MHPAM molecular volume is determined: $V_{MHPAM,calc} = 8{,}000{,}000/6.02 \times 1.2 = 11{,}074$ nm^3, which was in excellent agreement with that of the single MHPAM molecule in AFM images. From the data analysis described above, It could be clearly demonstrated that single MHPAM molecules have been observed on mica surfaces. Meanwhile, it is noted that what we observed is a folded single MHPAM chain coils because of the difficulty in identifying the ends of the coiled chains. In domain B and C, the experimental volume of single MHPAM molecule was 2075.3, 1219.0 nm^3, respectively. Compared with the values calculated from molecular mass of MHPAM, the different is significant. This discrepancy may be attributed to the high polydispersity of MHPAM polymer.

3.2. Structure and morphology of Langmuir–Blodgett films of MHPAM/CTAB complexes transferred to mica surfaces

Owing to the good solubility in water, CTAB or MHPAM molecules alone cannot form a stable monolayer at the air–water interface. However, the strong electrostatic interactions between the negatively charged $-COO^-$ groups along MHPAM chains and CTA^+ headgroups make MHPAM/CTAB complexes to form stable film at the air–water interface. The MHPAM/CTAB complex films were obtained as follows:

Seven hundred and fifty ml MHPAM aqueous solution ($c = 0.01$ mg/ml) was put into LB trough (FACE HBM, LB Films, JAPAN) as subphase. CTAB was dissolved in chloroform to make a 1.0 mM solution and then spread on the subphase interface. Five minutes was waited for solvent evaporation before compression. After the MHPAM/CTAB complex films were compressed to a perfect surface pressure (18 mN/m) and 5 min was waited for the equilibrium of the films, the MHPAM/CTAB complex films were transferred to mica surface through a horizontal lifting method (HLM), dried in air and imaged with AFM. The subphase pH was adjusted by the addition of either HCl or NaOH.

Fig. 3A shows AFM images of MHPAM/CTAB complex films at pH 6. The carboxylic groups in MHPAM molecules are negatively charged at such pH value, and MHPAM becomes an amphiphilic polyelectrolyte. The negatively charged $-COO^-$ groups along MHPAM chains will complex with CTA^+ ions to form MHPAM/CTAB complexes at the air–solution interfaces. The mica substrates were covered with a nanostructured network and worm-like MHPAM/CTAB complex molecule chains (see Fig. 3B), and it is difficult to distinguish individual MHPAM/CTAB complex molecules because of the mutual entanglement and crossings between themselves. At pH 7, a significant decrease in the degree of ionization of the amine group of MHPAM sets in, and the cationic charge density decreases. One can observe bump-like conformation to some extent owing to the aggregation of MHPAM/CTAB molecules between the intrachain and interchain, as shown in Fig. 3C. At pH 12, the degree of ionization of the amine group of MHPAM is almost zero, and MHPAM/CTAB complex molecule chains are only very weakly

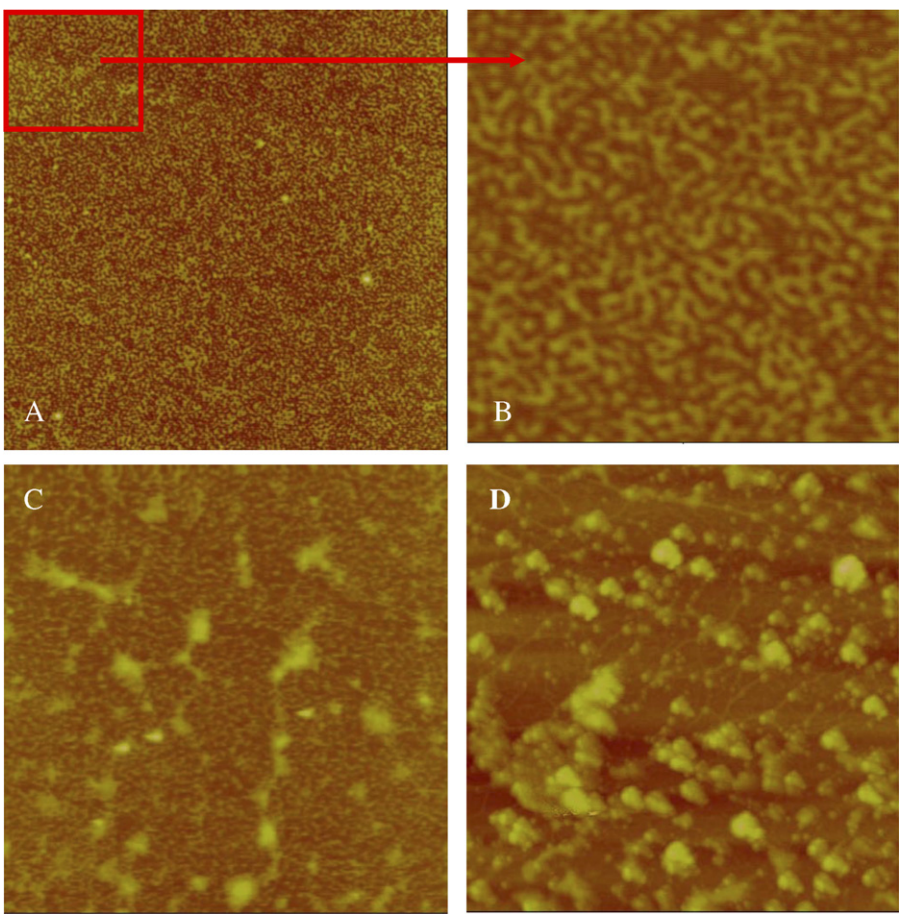

Fig. 3. A series of AFM images (2000×2000 nm^2) of MHPAM/CTAB complex films at the various pH. (A) at pH 6, (B) enlarged image (500×500 nm^2) of Fig. 1a, (C) at pH 7 and (D) at pH 12.

charged, so that molecule chains continuously shrink, curl and collapse to display more compact globule conformation due to attractive short-range Van der Waals. Fig. 3D clearly shows the existence of globular structures. By controlling pH, a series of conformational transition of MHPAM/CTAB complex films on mica surfaces are directly displayed, which is likely related to analogous conformations in solution [33,34].

4. Conclusion

In this paper, we present direct observation of MHPAM chain conformations on mica surfaces, and single MHPAM molecules appear as worm-like coils observed by AFM. Meanwhile, Langmuir–Blodgett films of MHPAM/CTAB complexes on mica substrates transferred from the air–solution interfaces were also investigated, the MHPAM/CTAB molecules undergo conformational transitions from densely packed worm-like nanostructures to bump-like conformation, and to compact globule as the fraction of charged monomers decreases with an increase of pH, and the formation mechanism was briefly explained. This observations would further provide insight into the level of understanding of polymer adsorption at interfaces on the nanometre scale.

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