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An atomic force microscopic investigation of electro-sensitive polymer surface

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Abstract

An electro-sensitive poly(2-acrylamide-2-methylpropane sulfonic acid) (PAMPS) film was fabricated by surface-initiated atom transfer radical polymerization (ATRP) method on silicon substrate. Atomic force microscopy (AFM) experiments in contact mode show that friction force and the adhesion force between the AFM tip and the film may change regularly with the alteration of the applied negative bias voltage between them, indicating that the microscopic wettability of the film can be adjusted by external electric field. On the other hand, the AFM experiments in tapping mode reveal that the film may take corresponding phase change under the electric field. These effects were considered to result from the conformational overturn of the sulfonic groups and the adjacent alkyl chains in the electric field.

Keywords: Electro-sensitive polymer surface; AFM; Adhesion force; Atom transfer radical polymerization

1. Introduction

Stimuli-responsive surfaces [1,2] can react to the external stimuli, and have been realized by various elegant methods [3,4], which play an important role in industrial applications including chemical sensors [5,6], microfluidic devices [7–9], and so on. Among them, the electro-responsive surfaces [10] are of crucial interests because they can be easily modulated by electro-stimulus and integrated into microdivices. Poly(2-acrylamide-2-methylpropane sulfonic acid) [11] is a good electro-sensitive polymer, which can exhibit an extent of volume change under external electric field. In this contribution, we demonstrate that when PAMPS is grafted onto the solid surface, the microscopic wettability can be conveniently triggered by a negatively charged AFM tip. This effect is considered to be the result of the electrical field induced transformational overturn of the polymer chains, which is proved by the corresponding phase change of the film under electric field. It may have potential applications in various domains including microdevices [12–14] and data recording [15–20].

2. Experimental

2.1. Reagents and materials

Silicon wafer (Grinm Semiconductor Materials Co. Ltd., China), acetone, nitric acid, methanol, potassium hydroxide, pyridine, α-bromoisobutyryl bromide (Fluka, Switzerland), *N*,*N*,*N*′,*N*′,*N*′′-pentamethyl-diethylenetriamine (Aldrich, Germany) were used as received. 2-acrylamide-2-methylpropane sulfonic acid (Aldrich, Germany) and CuBr were recrystalized before being used. Toluene, dichloride methane were dried by molecular sieves for 24 h before being used. Double distilled water (>1.82 MΩ cm, MilliQ system) was used.

2.2. Apparatus

AFM experiments in both contact and tapping modes were conducted on SPI 3800N probe station (Seiko instruments

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Inc., Japan). A microfabricated coated-Au silicon cantilever with a bending spring constant of 0.098 N/m and a resonance frequency of 11 kHz was used for all experiments with a 20 μm scanner. And all AFM experiments had been done in air.

2.3. Synthesis of PAMPS thin films on silicon substrates

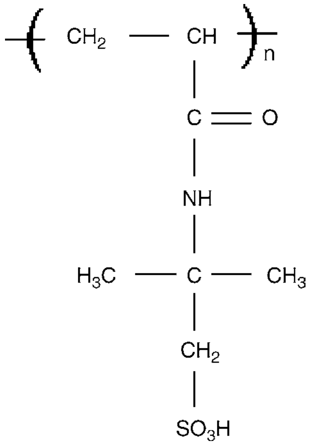
Surface-initiated atom transfer radical polymerization (ATRP) [21,22] was used to fabricate PAMPS thin film on silicon substrate. A clean silicon substrate was immersed in an aqueous NaOH solution (0.1 M) for 2 min and subsequently in HNO_3 (0.1 M) for 10 min to generate surface hydroxyl groups. After the substrate had been washed with an excess of water and dried under a flow of nitrogen, it was heated to reflux in toluene that contained 5 wt.% aminopropyl trimethoxysilane (ATMS) for at least 6 h to obtain chemically bonded $-NH_2$ groups on the surface. The surface was rinsed with toluene and dichloromethane, respectively, to remove remaining ATMS, dried under a flow of nitrogen gas, and immersed in dry dichloromethane that contained pyridine (2%, v/v). The polymerization initiator bromoisobutyryl bromide was added dropwise into the solvent containing the silicon substrate at 0 °C, and the mixture was left for 1 h at this temperature then at room temperature for 12 h. The silicon substrate was cleaned with acetone and toluene, and dried under a nitrogen flow. Then it was immersed in a degassed solution of 2-acrylamide-2-methylpropane sulfonic acid (25 wt.%) in a 1:1 (v/v) mixture of H_2O and MeOH (5 mL), which has been neutralized to pH 7 previously by KOH solution (2 M). After that CuBr (0.032 g, 0.23 mmol) and pentamethyl diethylene triamine (PMDETA; 0.14 mL) were added under stiring. The reaction was performed under temperature of about 60 °C for 100 min.

3. Results and discussion

The structural formula of PAMPS is illustrated in Scheme 1. The X-ray photoelectronic spectrum indicates that the PAMPS film has been successfully grafted onto the silicon substrate. The ellipsometric spectrum results show that the film thickness is about 39.0 ± 1.3 nm.

3.1. AFM investigation of the PAMPS films in contact mode

A conductive Au-coated AFM tip with a negative bias voltage was applied to "write" a small area for four times at first. An electrical field will be generated between the negatively charged AFM tip and the substrate during this process because the polymer film is insulating. Subsequently, the difference between the "written" and the surrounding "unwritten" areas was detected through scanning in a broader area by the same tip without bias voltage. Fig. 1A and B shows the topographic and corresponding friction force microscopy (FFM) images of a PAMPS film containing four small square "written" areas of about 200 nm × 200 nm on which different bias voltages were applied. Although the morphological image only shows relatively very small (height decrease much less than 1 nm, compared to the film thickness of about 40 nm) but irregular change, FFM image exhibits distinct and interesting changes that on the four squares, the friction forces between the polymer film and the AFM tip were obviously smaller than the surrounding area, and decreases regularly with the increase of the bias voltage. However, this effect no longer exists in the control experiments with zero and positive bias voltage indicates that it was not caused by scratching of the AFM tip.



Scheme 1. The structural formula of PAMPS.

In order to confirm this effect, we did further experiments to investigate the adhesion force between the AFM tip (without bias voltage) and the polymer film by the force curves on the negative bias voltage "written" areas and the "unwritten" area. Fig. 1C shows the typical force curve of the Au-coated AFM tip on the "written" area (in this case, the bias voltage is −2.0 V), in comparison with the "unwritten" area. It indicates that the adhesion forces on the "written" areas are much smaller than those on the "unwritten" ones, and the difference between them increases dramatically with the increase of the bias voltage, as shown in Fig. 1D. For the bias voltage of −0.2, −0.8, −1.4, and −2.0 V on the conductive tip, the values are -0.15 ± 0.1, -0.12 ± 0.2, -0.4 ± 0.2, -1.2 ± 0.2 nN, respectively. This is in good accordance with and thus further confirms the FFM observation.

As far as we know, the FFM, together with the adhesion force between the AFM tip and the sample, reflect much useful information, the most important one of which is the microscopic surface wettability [15]. For the conductive AFM tip that applied in this study, which is hydrophilic, the friction force and the adhesion force may decrease with the decrease of the hydrophilicity of the surface. Therefore, it can be reasonably inferred from above results that microscopic wettability on the PAMPS film can be conveniently adjusted by the electric field between the negatively charged AFM tip

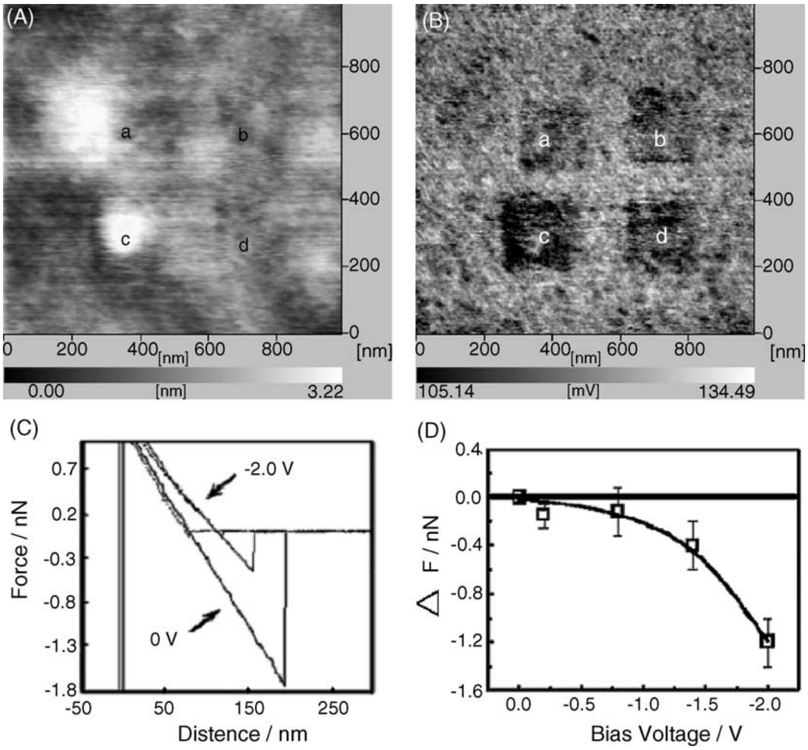


Fig. 1. (A) The topographic image of PAMPS film containing four small areas “written” by different negative bias voltages; (B) corresponding FFM image, (a) −0.2 V, (b) −0.8 V, (c) −1.4 V, (d) −2.0 V; (C) typical force curves for the “written” area (−2.0 V) and the “unwritten” area; (D) the difference between the adhesion force for the “written” and “unwritten” areas in the force curve experiments.

and the substrate, and the larger the negative bias voltage is, the less hydrophilic the surface will be.

3.2. AFM investigation of the PAMPS films in tapping mode

The phase change of the PAMPS film during the process of applying the electric field was also investigated by similar AFM experiments in tapping mode with a bias voltage of −2.0 V. Again, although the topographic image (Fig. 2A) shows no distinct difference, the phase image (Fig. 2B) exhibits remarkable phase angle difference between the “written” and “unwritten” areas [23,24]. No corresponding change can be observed in the experiments of zero or positive bias voltages. These results are well consistent with the observation of contact mode.

From the above results, it can be inferred that the electric field induced microscopic wettability variation is accompanied by the phase change of polymer under corresponding conditions. As indicated by Lahann et al. [7], when the long chain fatty acids that anchored on a solid surface with a relatively low surface concentration are exposed to an electric

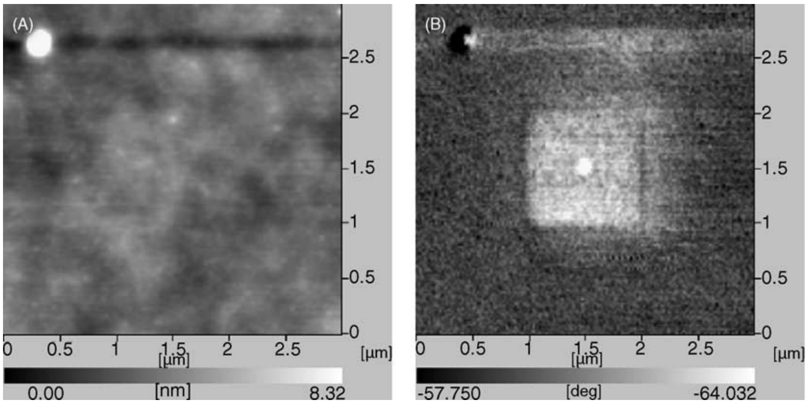


Fig. 2. (A) The topographic image of PAMPS film containing a 1000 nm × 1000 nm area “written” with a bias voltage of −2.0 V; (B) corresponding phase image. The light square is the “written” area.

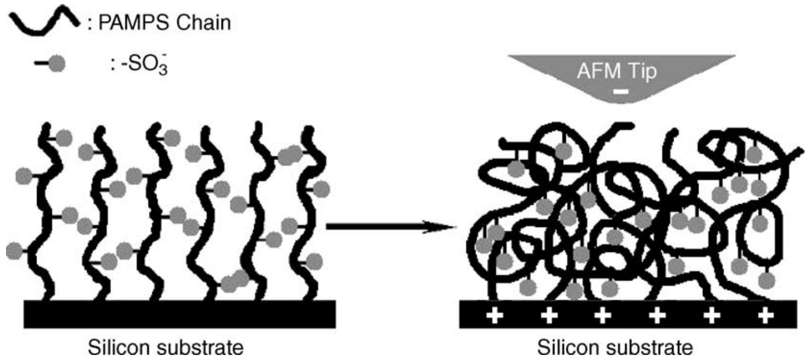


Fig. 3. Proposed principle of constriction of PAMPS film before (left) and after (right) an electrical field was applied.

field, the negatively charged carboxyl groups would bend towards the direction of the positive electrode, and thus the conformational overturn of the fatty acid may occur, which induces the wettability change of the surface. Similarly, there are numerous negatively charged sulfonic groups on the linear PAMPS chains, therefore, when the PAMPS film is scanned by the conductive AFM tip with negative bias voltage, similar conformational overturn (shown as Fig. 3) of the sulfonic groups and the adjacent alkyl chains may also occur as that observed for long chain fatty acids, however, would be confined in a relatively small extent because of the dense package of the polymer chains in the film. On one hand, the conformational change of the sulfonic groups may make it more difficult for them to contact with charged AFM tip, which brings the change of the FFM image and the adhesion force, while on the other hand, it may result in the entanglement and disorder of the polymer chains for a certain extent that causes the variation of the phase image.

In order to verify this explanation, comparison experiments were performed on a non-polyelectrolyte (for example, poly(*N*-isopropylacrylamide), and so on) modified surface. However, no obvious variation was observed for both the FFM and phase images in experiments of the contact and tapping modes, respectively, even when the bias voltage of −2.0 V was applied. It indicates that the numerous charged groups on the polymer chains are essential for the electrosensitivity of PAMPS film.

4. Conclusion

In conclusion, we fabricated electrical-responsive polymer film by in situ ATRP on silicon substrate. AFM experiments in contact mode show that friction force and the adhesion force between the AFM tip and the film may change regularly with the alteration of the applied negative bias voltage between them, indicating that the microscopic wettability of the film can be adjusted by external electric field. On the other hand, the AFM experiments in tapping mode reveal that the film may take corresponding phase change under the electric field. These effects were considered to result from the conformational overturn of the sulfonic groups and the adjacent alkyl chains in the electric field. It may have great applications in the fabrication of smart nanodevice, controlling microfluid, information storage.

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