Conformational Transition of Poly (Acrylic Acid) Detected by Microcantilever Sensing *

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Poly (acrylic acid) (PAA) chains are grafted on one side of a microcantilever by the self-assembled method and the deflections of the microcantilever are detected as a function of medium pH from 3 to 11. It is found that when the pH varies, the microcantilever deflects because of the changing surface stress. By analysing the electrostatic repulsive effect, the surface stress change is related to the conformation transition of PAA from a collapse state to a swelling state. This method offers the interaction information among the polymer chains during the conformational transition and affords an alternative way to study conformational change of polymers.

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The conformational transition of polymers has been a subject of extensive interest in both theoretical and experimental studies for more than four decades, because it provides a simple model for studying more complicated problems, such as protein folding and DNA packing.[1] When polymer chains are terminally grafted on a solid surface, a novel structure is formed. The polymer chains are stretched away from the surface to form brushes as the result of the balance between segment-segment repulsion and elasticity of the chains.[2] Such polymer chains can change their conformation with the environmental stimulus[3] (such as pH, ions and temperature) and have important applications in the fields of biotechnology, medical analysis and drug delivery systems.[4] Although it is important to study the conformation of these polymer chains, conventional methods can offer little information on the interactions within the polymer chains during the conformation transition. For example, the surface plasmon resonance (SPR) technique[5] affords information on the thickness of the adsorptive polymers, and quartz crystal microbalance (QCM)[6] is sensitive to the mass of the polymers.

In recent years, there has been a proliferation of microcantilever sensors (MCS)[7,8] because this technique provides a versatile approach for measuring forces on a piconewton scale. In most cases, these cantilever sensors are coated on one side with a sensing film or receptor molecules, where analyte binding causes a change of surface stress and leads to measurable cantilever deflections. Recently, our group has successfully applied this method to investigate the conformational change of poly(N-isopropylacrylamide) with temperature.[9] In the present study, we prepare thiol-terminated poly(acrylic acid) (HS-PAA), which is a polyelectrolyte, and investigated its conformational transition with the medium pH changed from 3 to 11.

Figure 1 schematically shows the experimental setup. A diode laser is focused onto the tip of the cantilever. The laser beam reflected off the cantilever is directed into a position-sensitive detector (PSD), and the deflection of the cantilever can be detected. A fluid cell of a 500 μL liquid cavity within which the cantilever is mounted is placed on a temperature controller. The cell temperature is kept at 20°C and controlled within ± 0.01°C. The picture under the microcantilever on the right down shows the geometry of the single surface gold-coated V-shaped silicon nitride cantilever with 200 μm in length, 0.5 μm in thickness and 20 μm width for each leg. The picture on the right (upper) shows a deflected microcantilever, Δz is the cantilever deflection induced by surface stress $\Delta\sigma$, which can be estimated by Stoney's formula[10]

$$\Delta\sigma = \frac{Et^2}{3(1-v)L^2}\Delta z, \tag{1}$$

where E is the elastic modulus of the cantilever material (about 1.8×10^{11} N/m^2 for silicon nitride), ν is its Poisson ratio (about 0.3 for silicon nitride), L and t are the length and thickness of the cantilever, respectively. We define the deflection Δz as positive when the cantilever bending towards the PAA-grafted side, and the deflection Δz as negative when the cantilever bending towards the opposite direction. The

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liquid flow is driven by a peristaltic pump at a constant speed of 0.2 ml/min during the measurement. The deflection signal of the cantilever is recorded in real time during the experiment.

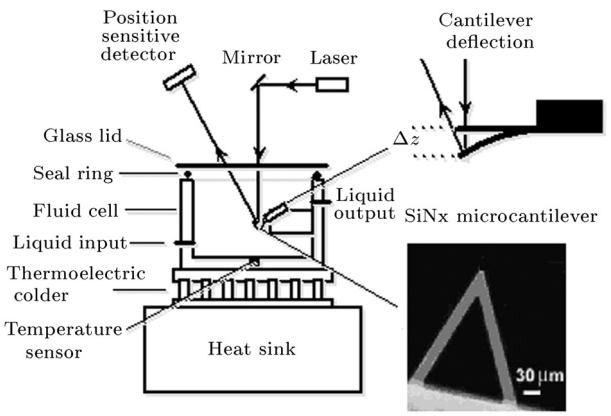


Fig. 1. Schematic diagram of the experimental setup.

To graft polymer chains on the Au coated side of the microcantilever, the cantilever was first immersed in "piranha" (H_2O_2:H_2SO_4= 1:3, 50°C) for 30 min and then rinsed with deionized water. The cleaned cantilever was immediately immersed in the HS-PAA solution for 1 day at room temperature. Because the thiolate group can strongly interact with the gold surface and form a strong Au–S bonding. A polymer brush was formed finally by self-assembly of the HS-PAA chains to the Au surface of the microcantilever.[11] The buffer solutions with pH of 3, 5, 7, 9 and 11 were prepared by addition of 0.1 M NaOH solution to 0.1 M HCl solution. The pH values were measured using a pH meter. The molecular weights (Mw) and the polydispersity indices (Mw/Mn) of HS-PAA sample are 1.3×10^4 g/mol and 1.2, respectively.

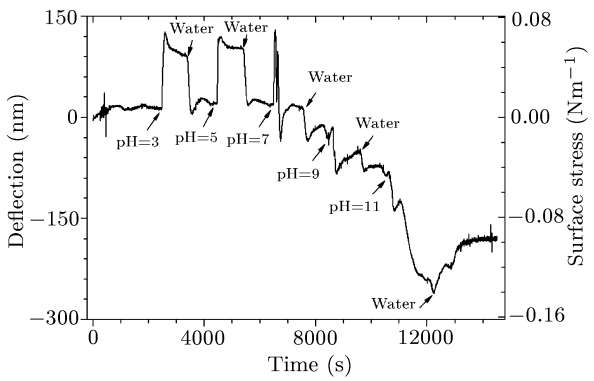


Fig. 2. Deflection of the grafted microcantilever with changing pH.

The deflection of the cantilever with the change of medium pH in real-time is shown in Fig. 2. The surface stress calculated is shown on the right of Fig. 2. A reference cantilever without PAA-grafted was used and the response to pH is shown in Fig. 3. As shown in Fig. 2, a positive deflection of about 120 nm as defined above was observed when the cantilever grafted with PAA was exposed in an acidic solution. With the increasing pH up to 11, the cantilever gave a negative deflection of about 260 nm. A slight deflection of not greater than 50 nm was detected when the reference cantilever was exposed to an acidic solution. Almost no deflection was detected when the pH increased to 11 (Fig. 3). These results indicate that the deflections shown in Fig. 2 are mainly induced by the grafted PAA chains.

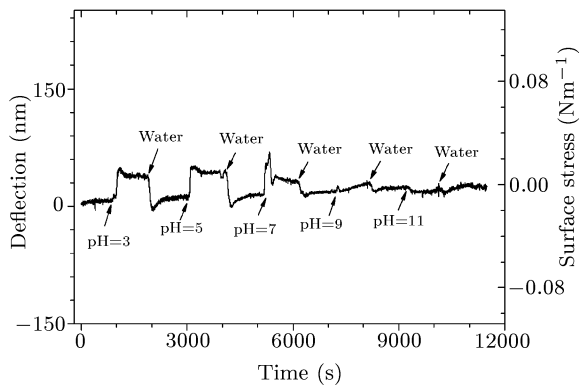


Fig. 3. Deflection of the un-grafted microcantilever with changing pH.

It is well known that the conformation of the polymer chains in the brush is a balance between the segment–segment interactions within the attached chains and the elastic free energy of the chains.[12] PAA is a kind of weak polyelectrolytes. Namely, it could be charged and the local charge density changes with the pH of the medium.[13] Therefore, the electrostatic interaction among the polymer chains plays an important role during the conformational change of the PAA.[14,15] At low pH, the carboxylic groups(-COOH) are protonated and the brush is weakly charged. The polymer chains prefer to adopt a collapse state. As the pH increases, the carboxylic groups begin to ionize. The PAA chains stretch and adopt a swelling state duo to the repulsive electrostatic force among the ionized carboxylic groups(-COO^-). The conformational change of PAA with pH is schematically depicted in Fig. 4.

To understand the results more clearly, the discrete deflections at pH 3, 5, 7, 9 and 11 were extracted and are shown in Fig. 5. The inset diagrams show the possible conformation of the PAA-chains at different pH. When pH < 7, the PAA chains are weakly charged. The chains tend to collapse to make the cantilever bending upwards. When pH > 7, the PAA chains are strongly charged as mentioned above. The repulsive electrostatic interaction favours the surface to expand.

As a result, the cantilever bends downwards as illustrated in Fig. 5.

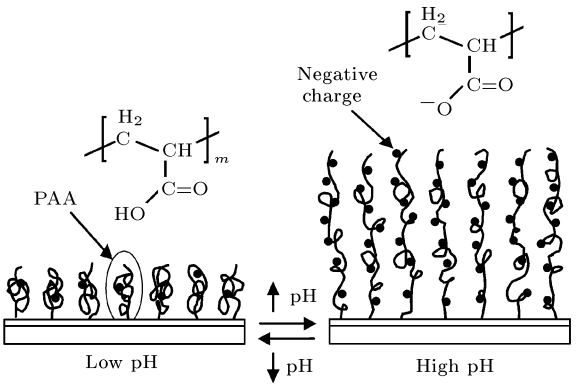


Fig. 4. Schematic diagram of conformational transition of PAA caused by the medium pH.

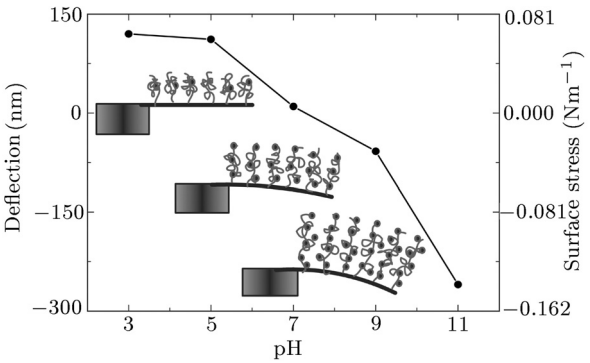


Fig. 5. Schematic illustration of conformation transition with changing pH.

In summary, we have studied the conformational transition of the PAA-chains with pH by microcantilever sensing technology. The deflection of the microcantilever indicates that the surface stress of the microcantilever on the grafted surface changes, which could be attributed to conformational change of the grafted PAA chains due to different charged states. When the aqueous environment is acidic, that is, pH< 7, PAA chains are weakly charged and the chains tend to collapse. The surface stress can make the cantilever bending upwards. When the aqueous environment is switched to alkaline, that is, pH> 7, PAA chains are strongly charged and the electrostatic repulsive interaction favours the polymer chains to stretch. The surface stress causes the cantilever to bend downwards. This method offers the useful interaction information among the polymer chains during the conformational transition and affords an alternative way to study conformational change of polymers, including bio-macromolecule, such as protein and DNA.

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