

Collapse and Swelling of Thermosensitive Poly(*N*-isopropylacrylamide) Brushes Monitored by a Quartz Crystal Microbalance

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Thermosensitive poly(*N*-isopropylacrylamide) (PNIPAm) brushes grafted on SiO₂-coated quartz crystal surface were prepared with a surface-immobilized initiator. By using quartz microbalance with dissipation monitoring (QCM-D) technique, we investigated the collapse and swelling of the brushes in water. Both frequency and dissipation of PNIPAm brushes were found to gradually change with a temperature range between 20-40°C, indicating that PNIPAm brushes undergo a continuous transition in contrast with PNIPAm chains in dilute solution exhibiting a sharp coil-to-globule transition. The nonuniformity and stretching of PNIPAm brushes as well as cooperativity between collapse and dehydration are considered to be responsible for the continuity. A hysteresis was observed in the cooling process. This is not only due to the intrachain and interchain interactions formed in the collapsed state, but also to the nonuniform structure and stretching of the high-density brushes.

Key Words: Poly(*N*-isopropylacrylamide), Polymer brushes, Coil-brush transition, Quartz crystal microbalance with dissipation measurement

1. INTRODUCTION

In comparison with free chains in solution, polymer chains grafted on a surface have much richer conformation. For a low grafting density, each chain behaves like a free chain with a random coil conformation, and all the scaling laws remain the same as in solution. As the grafting density increases, the grafted chains swollen in good solvent are stretched out to form a polymer brush without any overlapping due to the effect of exclusion.¹⁻³ Theoretically, it has been predicted that as the solvent quality decreases, each stretched chain in polymer brush gradually shrink and finally collapse into a globule, which is different from the coil-to-globule transition of a linear chain free in solution, because they are constrained on surface.⁴⁻⁶ Some of the experimental results support such prediction,⁷⁻¹² but the conformation change of grafted linear polymer chains with decreasing solvent quality still remains an open to question.

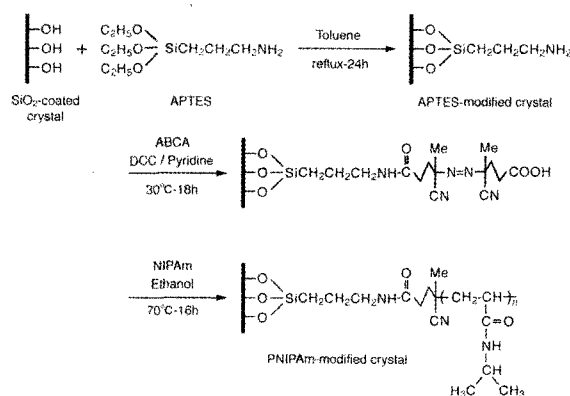
Poly(*N*-isopropylacrylamide) (PNIPAm) has a lower critical solution temperature around 32°C,¹³⁻¹⁶ namely individual PNIPAm chains swell with a random coil conformation at lower temperatures but collapse into globule when the solution temperature is higher than ~32°C. Accordingly, the collapse of PNIPAm chains conveniently examined by adjusting the solvent quality

via temperature. Dehydration is considered to play a crucial role in the collapse of PNIPAm at higher temperatures, i.e., water molecules are bound to PNIPAm chains at lower temperatures but detached when the temperature is higher than its LCST. To our knowledge, there is no direct evidence thus far.

In this study, thermally-induced transition of PNIPAm brushes are investigated by using quartz crystal microbalance with dissipation measurements (QCM-D). QCM probes a combination of the acoustic impedance and thickness. Importantly, the QCM is sensitive to any adsorbed mass, including solvent, associated with the films. In addition, QCM-D technique provides information not only on the behavior of outer layer of the brushes, but on inside the layer, and hence on the viscoelastic properties of brushes.

2. EXPERIMENTAL

Materials. *N*-isopropylacrylamide (NIPAm, Kojin Co.) was recrystallized in toluene/*n*-hexane mixture three times. 4, 4'-Azobis(4-cyanovaleric acid) (ABCA, Acros Organics), 3-(aminopropyl)triethoxysilane (APTES, Shinetsu Chemical), and dicyclohexylcarbodiimide (DCC, Wako Pure Chemical) were used as received. Toluene (Kanto Chemical), *N,N*-dimethylformamide (DMF,



Scheme Preparation of PNIPAm brush.

Kanto Chemical), and ethanol (Kanto Chemical) were distilled over drying agent under dry nitrogen atmosphere prior to use.

Graft Polymerization of NIPAm onto a Crystal Surface. The SiO₂-coated crystal surface was cleaned using H₂O/H₂O₂/NH₄OH (5:1:1 in volume) solution at 80°C for 15 min, and then rinsed with deionized water. The crystal surface was further cleaned with 0.1N HCl, followed by further deionized water rinsing. Several wash/dry cycles were performed until concordant frequencies were obtained. The crystal surface was dried under a stream of N₂ gas. The pre-treated crystal was placed into a 70 mL toluene solution containing 2 mL of APTMS and refluxed under N₂ atmosphere for 24h (Scheme 1). When the silanization was complete, the crystal surface was rinsed successively with toluene, ethanol, and acetone, and finally dried under a stream of N₂ gas. The APTMS modified surface was then exposed to 70 mL solution of DMF containing 0.35 g of ABCA, 3.5 g of DCC, and 87 μL of pyridine as catalyst at 35°C for 24h to introduce the initiator (ABCA) on the SiO₂ surface. For the surface initiated graft polymerization with NIPAm, the initiator modified crystal was immersed in a 70 mL ethanol solution containing 10.5 g of NIPAm with one side covered with a protective casing made of Teflon. After deaeration of the system by bubbling N₂ gas, the graft polymerization was carried out at 70°C for 16h under N₂ atmosphere. The quartz crystal grafted with PNIPAm was rinsed successively with toluene, ethanol and deionized water to remove the PNIPAm chains physically absorbed on the grafting layer. The apparent molecular weight of PNIPAm chains grafted on the SiO₂ surface was determined to be $M_n = 23800$ by gel permeation chromatography for the nonattached PNIPAm chains free in solution. The polydispersity of PNIPAm was evaluated to be $M_w/M_n \approx 1.7$.

Atomic Force Microscopy. The PNIPAm modified crystal surface is characterized by atomic force microscopy (AFM) measurements. The PNIPAm modified crystal surface is characterized by contact-mode

AFM analysis was carried out using SPA 400 scanning probe micro systems (Seiko Instruments Inc.). The images were acquired in solution with silicon nitride tips with spring constant of 0.75 N m⁻¹.

QCM-D. Quartz crystal microbalance (QCM Z-500) having an AT-cut quartz crystal with fundamental resonant frequency of 5 MHz and a diameter of 14 mm is from KSV Instruments, Finland. This instrument allows the simultaneous measurements of changes in resonance frequency f and dissipation energy D . The energy dissipation is measured on the basis of the principle that when the driving power to a piezoelectric oscillator is switched off, the voltage over the crystal decays exponentially and a damped oscillating signal is recorded.^{17, 18} Hence, before disconnection of the driving oscillator, we obtain f , and D is obtained after the disconnection. The dissipation factor is defined as

$$\Delta D = \frac{E_{dissipated}}{2\pi E_{stored}} \quad (1)$$

where $E_{dissipated}$ is the energy dissipated during one oscillation, and E_{stored} is the energy stored in the oscillating system. Any mass Δm , deposited on one or both of the electrodes of a crystal, induces a shift in the frequency Δf that is proportional to the added mass. If the mass is deposited evenly over the electrode(s), and if Δm is much smaller than the mass of the crystal itself, the frequency shift is related to the adsorbed mass by Sauerbery equation¹⁹

$$\Delta m = -\frac{\rho_q t_q \Delta f}{f_0 n} = -\frac{\rho_q v_q \Delta f}{2f_0^2 n} = -\frac{C \Delta f}{n} \quad (2)$$

where ρ_q and v_q are specific density and shear wave velocity in quartz, respectively, t_q is the thickness of the quartz crystal, n is the overtone number, and f_0 is the fundamental resonance frequency ($n=1$). In this study the value of the constant C is 17.7 ng cm⁻² Hz⁻¹. The frequency shift is measurable to within ± 1 Hz in aqueous medium, and the temperature was controlled within a range of ± 0.01 °C. We collected frequency (f) and dissipation (D) values of quartz resonator at the point where frequency attained a constant value at each temperature; i.e., the fluctuation of frequency is within ± 2 Hz. Δf and ΔD values from the fundamental were usually noisy because of insufficient energy trapping and therefore discarded.^{20, 21}

3. RESULT AND DISCUSSION

AFM. To get quantitative and detailed impression of the surface morphology, AFM images of three substrates, (a) SiO₂-coated crystal, (b) APTES-modified crystal, and (c) PNIPAm-modified crystal, were taken. The AFM image of SiO₂-coated crystal shows a relatively smooth surface, and its surface roughness is less than 1 nm. From the AFM image for the APTES-modified crystal surface

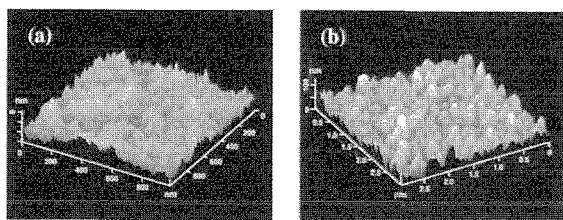


Fig 1. AFM images for (a) APTES-modified crystal, and (b) PNIPAM-modified crystal.

(Fig. 1a), the silane molecules are densely arrayed, and the thickness of APTES monolayer is about 3 nm. The thickness of the PNIPAM-modified layer is about 50 nm (Fig. 1b). It is, however, seen that the surface exhibits, in addition to ordered arrangement of the polymers, a surface corrugation due to the aggregation of PNIPAM chains.

QCM-D. Since the response of the quartz crystal is affected by variation in temperature, viscosity, and the density of the medium above the sensor surface, the inherent crystal effects must be taken into consideration to obtain the true response of the PNIPAM brushes. First Δf and ΔD are measured for SiO₂-coated crystal at different temperatures.

In a Newtonian liquid, the frequency response of a quartz resonator can be quantitatively described by the Kanazawa-Gordon relation²²

$$\Delta f = -n^{1/2} f_0^{3/2} \left(\eta_l \rho_l / \pi \mu_q \rho_q \right)^{1/2} \quad (3)$$

where ρ_q and μ_q are the density and shear modulus of quartz, and ρ_l and η_l are the density and viscosity of the liquid medium, respectively. The dissipation response is given by^{23, 24}

$$\Delta D = 2(f_0/n)^{1/2} \left(\eta_l \rho_l / \pi \mu_q \rho_q \right)^{1/2} \quad (4)$$

The frequency and dissipation response due to the grafting of the polymer chains on the surface of the quartz resonator can be obtained by removing the effects of the viscosity and density of water based on eqs 3 and 4. These values are subtracted from the corresponding Δf and ΔD for PNIPAM-grafted crystal to obtain the corrected Δf and ΔD for the grafted PNIPAM chains. The response curve collected at discrete temperature intervals. The sample was equilibrated at each temperature for 15 min before the data was collected. Frequency attained a constant value at each temperature; i.e., the fluctuation of frequency was within ± 2 Hz in 15 min.

Fig. 2 shows the temperature dependence of frequency shift Δf , and dissipation change ΔD of PNIPAM brushes in one heating-cooling cycle. The frequency shift, Δf , gradually increases with increasing temperature in the heating process over the temperature range 20–40°C. Increase in Δf indicates a decrease in effective mass of the layer attached to the resonator. At lower temperature, water is a good solvent for PNIPAM, therefore PNIPAM chains are in fully hydrated state. As the temperature increases, dehydration occurs and PNIPAM chains

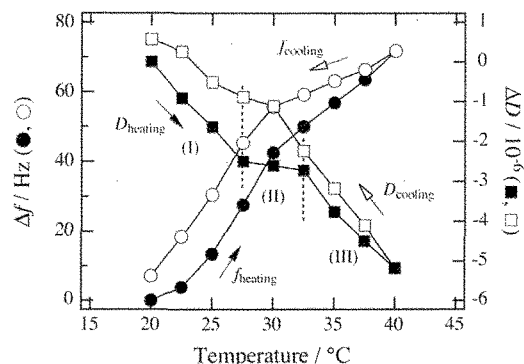


Fig 2. Temperature dependence of frequency shift Δf (●, ○) and dissipation change ΔD (■, □) for PNIPAM brushes at $n = 7$. Closed and open symbols, respectively, indicate heating and cooling processes.

gradually collapse. Since the PNIPAM chains are chemically attached to the crystal, the observed decrease in mass is explained by the loss of hydrated water of PNIPAM chains. On the other hand, gradually decrease in Δf was observed with lowering temperature in the cooling process, which is due to the gradual hydration of PNIPAM chains.

Dissipation of a viscoelastic polymer layer on quartz resonator is strongly influenced by its structure. A dense or rigid layer has small dissipation energy, whereas a looser and more flexible layer has larger dissipation energy. The dissipation decreases with increasing temperature in the heating process, which indicates that PNIPAM brushes gradually collapse into compact conformation. In the cooling process, the dissipation increases with decreasing temperature over a temperature range of from 40 to 20°C, indicating that the collapsed brushes swelled and become more flexible conformation. It is worthy to mention that some characteristic points are observed in the heating and cooling processes. The heating process is characterized by three stages, and there exists a plateau region in ΔD as indicated as stage II (27.5°C < T < 32.5°C) in Fig. 2. ΔD value in the cooling process is larger than that in the heating process, whereas an opposite trend is observed for Δf shown in Fig. 2. This may be related to the characteristics of the outer layer of the PNIPAM brushes. In the heating process, the freely mobile grafted chains, which expected to show the rapid dehydration, make densely packed brushes on the outer layer with increasing temperature. Formation of a dense, surface-anchored outer layer leads to the decrease in ΔD as observed in stage I (T < 27.5°C). Since a dense, collapsed polymer layer impermeable to water is formed in the outer layer, the shrinking of PNIPAM chains is limited by suppressed water permeation from the interior through the dense outer layer, which gives rise to the plateau region in ΔD (stage II). Further heating leads the segments of PNIPAM close to the resonator to be collapse (stage III, 32.5°C < T).

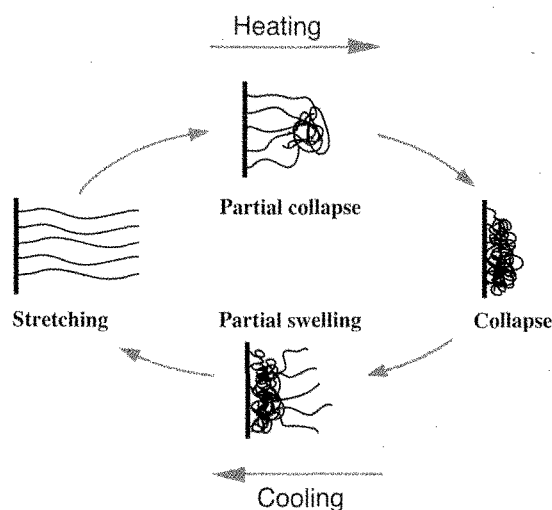


Fig 3. Schematic illustration of collapse and swelling PNIPAM brushes.

In the cooling process, two kinetic steps are identified. In the temperature region from 40°C to 27.5°C, rapid increase in ΔD is observed accompanied by decrease in Δf , suggesting that tails of outer layer of the brushes are hydrated and become flexible. The brushes begin to swell from the outer layer to inner core, which result in some swollen tails behaving as short chains tethered on the inner core. Since the amount of water bound to PNIPAM tails is still limited in this stage, decrease in Δf is small. When $T < 27.5^\circ\text{C}$, the change in ΔD become smaller against the variation of Δf . This is probably because that polymer brushes close to the crystal surface is constrained by knotting and entangling due to the intrachain and interchain interactions formed in the collapsed state. Such interactions hinder the hydration of the collapsed chains in the cooling process. The change in the frequency Δf mainly caused by hydration and dehydration, whereas the change in the dissipation ΔD due to the conformational change. Summarizing above discussion, Fig. 3 schematically illustrates the collapse and swelling of PNIPAM brushes.

4. CONCLUSION

By using quartz crystal microbalance with dissipation monitoring, the phase behavior of PNIPAM brushes in water was observed at various temperatures. PNIPAM brushes exhibit a continuous change in conformation over the temperature range of 20–40°C accompanied with large hysteresis, which reflects the gradual changes in frequency and dissipation. This result is in accordance with theoretical predictions that have suggested that polymer brush structure on planar surface do not exhibit true critical solubility transitions. This continuous change arises from not only intra- and inter-chain interactions formed in the collapsed state, but the high density and nonuniformity of the chains, which leads to broaden the

transition and enlarge the hysteresis.

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