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Study on Conformation Change of Thermally Sensitive Linear Grafted Poly(*N*-isopropylacrylamide) Chains by Quartz Crystal Microbalance

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ABSTRACT: The temperature-induced dehydration and hydration of linear thermally sensitive poly(*N*-isopropylacrylamide) (PNIPAM) chains grafted on a gold surface in water were measured in real time by using a quartz crystal microbalance. Our results reveal a gradual dehydration process during the heating from 20 to 35 °C. The dehydration starts at ∼23 °C, much lower than the well-known coil-to-globule transition temperature (∼32 °C) of individual PNIPAM chains free in water, suggesting that dehydration occurs when PNIPAM chains are at the crumpled state. On the other hand, in the cooling process, there exists a hysteresis in the hydration, and such hysteresis only disappears at ∼20 °C, at which water becomes a sufficiently good solvent. This is because some additional hydrogen bonding formed in the collapsed state at higher temperatures could not be completely removed as long as the temperature is not far away from the Θ-temperature (∼30 °C).

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. The only difference is that half a space is not available for such a grafted chain, but all the scaling laws remain the same as in solution. As the grafting density increases, the grafted chains swollen in good solvent are stretching out to form a polymer brush without any overlapping in good solvent due to the effect of exclusion.[1−3] Recently, this coil-to-brush transition has attracted much more interest with various implications,[4−20] such as in colloidal stabilization,[16] self-assembly of polymer chains,[17] and tribology.[18] Theoretically, it has been predicted that as the solvent quality decreases, each stretched chain in a polymer brush will gradually shrink and finally collapse into a globule, which is different from the discontinuous coil-to-globule transition of a linear chain free in solution, because they are constrained on surface.[4−6] Experimentally, some of the past experimental results support such a prediction,[21−26] but the conformation change of grafted linear polymer chains with a decreasing solvent quality still remains an open question.

Poly(*N*-isopropylacrylamide) (PNIPAM) has a lower critical solution temperature (LCST) around ∼32 °C;[27−29] namely, individual PNIAPM chains swell with a random coil conformation at lower temperatures but collapse into a globule when the solution temperature is higher than ∼32 °C. Accordingly, the collapse of PNIPAM chains is conveniently examined by adjusting the solvent quality via temperature. The collapse of PNIPAM chains grafted on surface has been studied before.[23,30−33] Contact angle measurements[30,31] show a sharp solubility transition near the LCST, which is similar to what has been observed on the surface of bulk PNIPAM. Using surface plasmon resonance (SPR), Balamurugan et al.[23] recently showed that the collapse of the chains in a PNIPAM brush was indeed gradual. However, it is found that even linear PNIPAM chains physically adsorbed on the surface of polystyrene nanoparticles[34] or flat gold surface[35] show a coil-to-globule transition smoother than that of free chains due to the surface constraint.

On the other hand, dehydration plays a crucial role in the collapse of biopolymers since hydrophobic interactions have been considered the primary cause for their self-assembly.[36,37] It has been reasonably speculated that the collapse of PNIPAM at high temperatures is due to the dehydration, i.e., water molecules are bound to PNIPAM chains at lower temperatures but detached when the temperature is higher than its LCST. Endo et al.[38] used NMR relaxation times (T_1 and T_2) indirectly studied such a dehydration. To our knowledge, there is no direct evidence so far.

In the present study, we directly grafted linear PNIPAM chains on the flat gold surface of a sensor of quartz crystal microbalance (QCM) and studied the temperature-induced conformation change of the grafted chains. Also, it is expected that if there exist dehydration, we should be able to detect it from the change of the oscillating frequency of the quartz crystal because it is extremely sensitive to a small change of the mass on its surface.[39−46]

Experimental Section

Materials. *N*-Ethyl-*N*′-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDC), *N*-hydroxysuccinimide (NHS), 2-mercaptoaminoethane ($HSCH_2CH_2NH_2$), bromoacetic acid, and isopropylacrylamide (NIPAM) were purchased from Aldrich. 12-Mercaptododecan-1-ol ($HS(CH_2)_{12}OH$) was synthesized according to the procedure of Haussling et al.[47] Linear H_2N-end-captured PNIPAM chains (NH_2-PNIPAM) were synthesized by free radical polymerization with AIBN as initiator and 2-mercaptoaminoethane ($HSCH_2CH_2NH_2$) as chain transfer agent in benzene at 70 °C. The NH_2-PNIPAM aqueous solution was dialyzed twice by using two semipermeable membranes with cutoff molar masses of 7000 and 14 000 g/mol. The apparent molar mass (11 800) and polydispersity index (1.24) of each PNIPAM fraction were determined by size exclusion chromatography (Waters 150C) using monodisperse

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polystyrene as standard and tetrahydrofuran (THF) as eluent with a flow rate of 1.0 mL/min. It is helpful to note that the amine end group was converted to CH_3CONH- with acetic anhydride before the SEC measurement to avoid a possible adsorption on the SEC columns.

Scheme 1 schematically describes the grafting of PNIPAM onto a gold surface. The gold crystal surface was cleaned using Piranha solution composed of one part H_2O_2 and three parts H_2SO_4,[48] then rinsed with Milli-Q water, and finally blown dry with a stream of nitrogen gas. Several wash/dry cycles were performed until concordant frequencies were obtained. The thiol deposition was achieved by immersing the freshly cleaned gold surface with one side protected into a solution of 5 mM $HS(CH_2)_{12}OH$ in ethanol:water (80/20) for 16 h at room temperature. The surfaces were then washed respectively in ethanol and water until concordant frequencies were obtained. The crystals were again immersed in an aqueous solution of 1 M BAA and 2 M NaOH for 3 h at the room temperature and washed and dried. One side of the crystal was covered with a protective casing made of Teflon,[49] and the nonshielded side was then exposed to a solution of 0.2 M EDC and 0.05 M NHS in water for 30 min and followed by the addition of 0.2 M NH_2-PNIPAM aqueous solution. In this way, PNIPAM chains were grafted onto the surface. Rinsing and drying was repeated until stable frequencies were obtained.

Scheme 1

$$\mathrm{Au} + \mathrm{HS(CH_2)_{12}OH} \rightarrow \mathrm{Au{-}S(CH_2)_{12}OH} \xrightarrow{\mathrm{BAA}}$$

$$\mathrm{Au{-}S(CH_2)_{12}OCH_2COO{-}} \xrightarrow{\mathrm{EDC/NHS}}$$

$$\mathrm{Au{-}S(CH_2)_{12}OCH_2COO{-}N(CO)_2(CH_2)_2} \xrightarrow{\mathrm{NH_2\text{-}PNIPAM}}$$

$$\mathrm{Au{-}S(CH_2)_{12}OCH_2CO{-}NH{-}PNIPAM}$$

QCM-D Technique. Quartz crystal microbalance with dissipation monitoring (QCM-D) makes the time-resolved measurements of the changes in both frequency (Δf) and energy dissipation (ΔD) possible.[50] When the crystal is excited to oscillation in the thickness shear mode at its fundamental resonant frequency f_0 by applying a RF voltage across the electrodes near the resonant frequency, a small mass added to the electrodes induces a decrease in resonant frequency (Δf) which is proportional to Δm. If the added mass is evenly distributed and much smaller than the mass of the crystal, the frequency shift is related to the added mass (Δm) and the number overtone of the frequency (n) by the Sauerbrey equation.[51]

$$\Delta m = -\frac{\rho l}{f_0}\frac{\Delta f}{n} \tag{1}$$

where ρ and l are the specific density and thickness of the quartz crystal, respectively, and $n = 1, 2, ...$ The dissipation factor is defined by

$$\Delta D = \frac{E_{\mathrm{dissipated}}}{2\pi E_{\mathrm{stored}}} \tag{2}$$

where $E_{\mathrm{dissipated}}$ is the energy dissipated during one oscillation and E_{stored} is the energy stored in the oscillating system.[50] The measurement of energy dissipation (ΔD) is based on the fact that the voltage over the crystal decays exponentially as a damped sinusoidal when the driving power of a piezoelectric oscillator is switched off. By switching the driving voltage on and off periodically, the series resonant frequency and the dissipation factors are obtained simultaneously.

QCM-D having an AT-cut quartz crystal with a fundamental resonant frequency of 5 MHz and a diameter of 14 mm was from Q-sense AB.[50] The quartz crystal was mounted in a fluid cell with one side exposed to the solution. The constant (C) of the crystal used is 17.8 ng/(cm^2 Hz), and the frequency shift is measurable to within ±1 Hz in aqueous medium. The solution temperature was controlled within ±0.02 °C. In the present study, all the results obtained were from the measurements of frequency changes in the third overtone ($n = 3$). This is because the third overtone shear wave is more sensitive to the surface region than the other overtone shear waves since it senses one layer of liquid over the crystal, while the fundamental tone senses two layers of liquid. For the higher overtones (fifth, seventh) the sensing range is even closer to the surface. Accordingly, the third overtone is not reaching as far from the surface as the fundamental tone. Moreover, the values obtained from the third overtone were found to be more reproducible than those obtained from the fundamental frequency. This is because low harmonics have poor energy trapping and are more often in a mode of oscillation, which is not a pure thickness shear mode. These flexural contributions emit compressional waves which propagate and potentially bounce back to the substrate because they are longitudinal by nature, leading the fundamental tone to be unstable compared to higher overtones.[46]

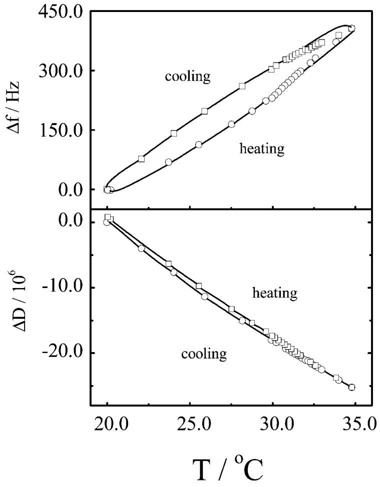

Figure 1. Temperature dependence of changes of frequency (Δf) and dissipation factor (ΔD) of a gold-coated quartz crystal surface prior to the grafting reaction.

The weight of the dry grafted PNIAM layer was determined by QCM in air after it was dried in a vacuum oven at 30 °C for 3 days.

Results and Discussion

It is helpful to note that, before investigating the temperature-dependent changes of frequency (Δf) and dissipation factor (ΔD) of the grafted PNIPAM chains, we first studied the effect of temperature on the gold surface prior to the grafting reaction. As expected, we observed that both Δf and ΔD depend on the temperature, as shown in Figure 1.The increase of Δf as well as the decrease of ΔD can be attributed to the change in viscosity and density of water with an increasing temperature. Kanazwa and Gordon[52] have derived an expression to quantitatively describe the effect.

$$\frac{\Delta f}{f_0} = \frac{-1}{\pi Z_{\mathrm{q}}}\sqrt{\rho \omega \eta} \tag{3}$$

$$\Delta D = \frac{2}{n}\frac{1}{\pi Z_{\mathrm{q}}}\sqrt{\rho \omega \eta} \tag{4}$$

where f_0 is the frequency of the fundamental, Z_{q} is the acoustic impedance of quartz; ρ, η, and ω are the density, viscosity, and radial frequency of the medium, respectively. n is the overtone order. From eqs 3 and 4, it follows $\Delta D/\Delta f = -2/nf_0$. Using $n = 3$ and $f_0 = 5$ MHz, one expects $\Delta D{\cdot}10^6/\Delta f = 0.133$. The data shown in Figure 1 do not agree with this prediction. The deviation

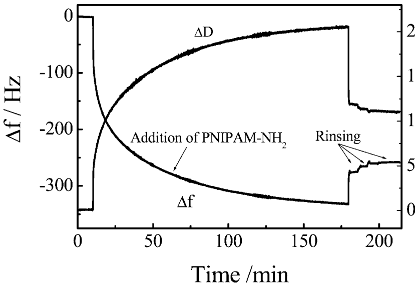

Figure 2. Reaction time dependence of changes of frequency (Δ*f*) and dissipation factor (Δ*D*) during the grafting reaction of PNIPAM onto a gold-coated quartz crystal surface at $T = 20$ °C.

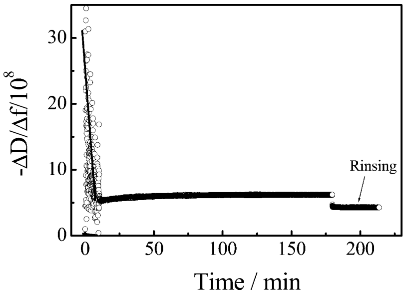

Figure 3. Reaction time dependence of ratio of changes of frequency to dissipation factor ($-\Delta D/\Delta f$) during the grafting reaction of PNIPAM onto a gold-coated quartz crystal surface at $T = 20$ °C.

is easily explained by temperature−frequency coupling since the frequency of a quartz crystal responds to temperature depending on the crystal cut, whereas the dissipation does not. Note that there exists a hysteresis between the heating and cooling processes, especially for the frequency change. A similar behavior was also observed in a recent work.[35] These temperature effects have to be considered (or subtracted) when we study the changes of frequency and dissipation factor of the quartz crystal grafted with linear PNIPAM chains under the same experimental conditions.

Figure 2 shows an in situ measurement of the changes of the resonant frequency (Δ*f*) and dissipation factor (Δ*D*) of QCM immobilized with $-S(CH_2)_{12}OCH_2COO-N(CO)_2(CH_2)_2$ after the addition of linear NH_2-PNIPAM chains. The decrease of Δ*f* as well as the increase of Δ*D* reflects that the grafting reaction is fairly fast in the initial stage and then slows down because the further grafting was hindered by those chains already grafted on the surface. The grafting reaction essentially stops after ∼180 min. The gold surface grafted PNIPAM chains were rinsed three times with Milli-Q water at the room temperature to completely remove the non-grafted PNIPAM chains in the solution. The changes of the resonant frequency (Δ*f*) and dissipation factor (Δ*D*) lead to a new set of data $-\Delta D/\Delta f$, which reflects the internal properties of the layer. The changes of $-\Delta D/\Delta f$ shown in Figure 3 indicate that at least two different kinetic processes during the grafting reaction. In addition, the rinsing has a stronger influence on the dissipation than on the frequency. As discussed below, the rinsed PNIPAM chains physically adsorbed on the layer are more extended and flexible than the chemically grafted ones so that they have a higher dissipative factor. Their removal leads the dissipation to change more compared with the frequency.

Figure 4 shows the temperature dependence of the frequency change ($-\Delta f$) in one heating-and-cooling cycle, where each data point was obtained after Δ*f* approached a constant value. In other words, the grafted PNIPAM chains reached its equilibrium state at each given temperature. As shown in eq 1, the mass change of the sensor (Δ*m*) is proportional to the frequency change (Δ*f*) if the grafted layer is rigid, sufficiently thin in comparison with the thickness of the quartz crystal, and evenly distributed on the surface.[51] In liquid environment, the frequency also responds to the viscosity and density of the contacting solution, which could be calibrated by using the contacting solution as mentioned above. In addition, the effects of the thickness, density, storage modulus, and loss modulus of the layer on the frequency shift and dissipation should be considered.[46] As described below, the layer studied here is very thin, and the density of the layer can change only a little with temperature since the polymer has a density close to water. The density and the storage modulus have probably much smaller effects on the frequency shift and dissipation than the thickness and the loss modulus due to the expelled water. As a simple approximation, we can use the frequency change to estimate the hydrodynamic mass change (Δ*m*) of the grafted layer including anchored PNIPAM chains and those hydrated (bounded) water molecules.[41] Since the PNIPAM chains are anchored on the surface, there should be no change in their masses, reflecting in the fact that both Δ*f* and Δ*D* almost return to their original values at 20 °C after a heating-and-cooling process. The temperature dependence of Δ*f* actually reflects the change of the amount of water molecules hydrated or bounded to the grafted chains. It is helpful to note that the temperature effect on water has been corrected and the frequency change in Figure 1 has been subtracted in Figure 4.

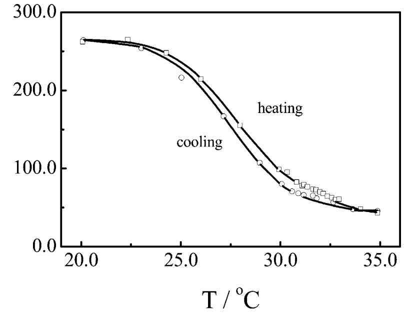

Figure 4. Temperature dependence of frequency change (Δ*f*) of linear PNIPAM chains grafted on gold-coated quartz crystal surface.

Figure 4 also shows the frequency (the decrease of $-\Delta f$) gradually increases in the range 23−35 °C in the heating process. In contrast, previous studies of the coil-to-globule transition of individual PNIPAM chains free in solution showed that the sharp decrease of the overall chain size occurred in a very narrow temperature range 30−32 °C in a similar heating process.[53] The constraint of the surface as well as the interaction between the grafted PNIPAM chains and the surface should be responsible for such gradual collapse in the present study.

On the basis of eq 1, the area per chain occupied is given by

$$S = \frac{1}{\sigma} = \frac{M_n}{\Delta m N_A} = \frac{-M_n}{C\Delta f\, N_A} \tag{5}$$

where σ, M_n, and N_A are the graft density, number-

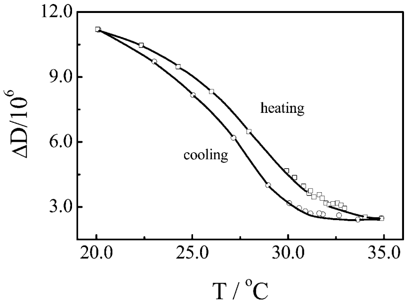

Figure 5. Temperature dependence of change of dissipation factor (ΔD) of linear PNIPAM chains grafted on gold-coated quartz crystal surface.

averaged molecular weight, and Avogadro constant, respectively. The frequency shift (Δf) for the dry grafted PNIPAM layer was determined to be 38 Hz, then the area per chain occupied is calculated to be 8.7 nm^2, and the grafting distance is ~2.9 nm. On the other hand, the thickness (t) of the layer at collapsed state and swollen state can be estimated using eq 6 to be 2.7 and 15.6 nm, respectively.

$$t = \frac{\Delta m}{\rho} = \frac{-C\Delta f}{n\rho} \tag{6}$$

where $\rho \sim 1000$ kg m^{-3} is used as the average density of PNIPAM and water. The results show that the layer is a brush at expanded state but a mushroom at collapsed state. Hu et al.[34] and Plunkett et al.[35] reported that PNIPAM chains physically absorbed on a spherical polystyrene surface or flat gold surface undergo a gradual transition. In the present work, PNIPAM chains are not only grafted to the gold surface with their ends but also physically adsorbed on it with their segments. Because of the interactions between PNIPAM segments and the surface, the equilibrium of physical adsorption shifts with temperature. On the other hand, the restricted PNIPAM chains cannot adjust their conformation as quickly as those chains free in water, leading to a gradual collapse. It is known that the coil-to-globule transition of a polymer chain involve four states, i.e., random coil, crumple coil, molten globule, and fully collapsed globule.[53] The fact that dehydration starts at ~23 °C indicates that the dehydration occurs once the grafted PNIPAM chains begin to crumple.

There exists a hysteresis in the cooling process, implying that the hydration and dehydration involve different energy barriers, presumably due to the formation of additional intrachain hydrogen bonding in the collapsed state.[53] The temperature dependence of the change in the dissipation factor (ΔD), as shown in Figure 5, has a similar trend. However, there is no quantitative theory to link ΔD with the structural information on the thin film on QCM sensor. Qualitatively, many previous studies showed that a dense and compact structure usually had a dissipation factor smaller than a more extended and flexible one.[41,50] This can be, at least partially, attributed to the friction between the layer and solvent. It is possible to correlate the variation of ΔD to the conformation change of the PNIPAM chains.[27−29,53]

A combination of the results in Figures 4 and 5 leads to the temperature dependence of $-\Delta D/\Delta f$ shown in Figure 6. Since $-\Delta f$ is proportional to the mass change of the grafted PNIPAM layer, $-\Delta D/\Delta f$ actually reflects the change of dissipation factor per unit mass. In the past, the change of $-\Delta D/\Delta f$ was used to study the conformation changes of proteins.[41,50] Figure 6 shows that $-\Delta D/\Delta f$ nearly remains a constant in the temperature range 20−30 °C if we consider all the experimental uncertainties associated with both ΔD and Δf in Figures 4 and 5. The increase of $-\Delta D/\Delta f$ in the temperature range of $T > \sim 30$ °C corresponds well to the coil-to-globule transition on individual PNIPAM chains free in water. Since PNIPAM has a structure much simpler than protein chains, the results in Figure 6 clearly shows that we can use the change of $-\Delta D/\Delta f$ to probe the conformation change of polymer chains in the future. Figure 6 further reveals that the heating induced dehydration occurs prior to the collapse of the grafted chains, and the temperature-induced collapse of the PNIPAM chains grafted on the surface is less sharper than that of PNIPAM chains free in dilute solution.

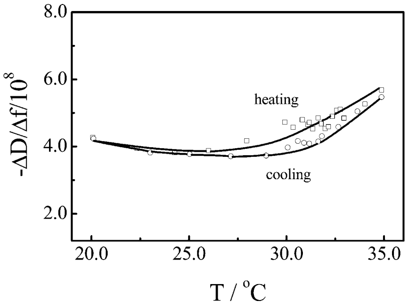

Figure 6. Temperature dependence of ratio of changes of frequency to dissipation factor ($-\Delta D/\Delta f$) of linear PNIPAM chains grafted on gold-coated quartz crystal surface.

As expected, Figure 6 also shows a hysteresis in the heating-and-cooling cycle. As discussed before, it reveals that the hydration in the cooling process is slightly different from the dehydration in the heating process, indicating that they have different energy barriers. A similar hysteresis has been observed before in a laser light scattering study of the temperature-induced coil-to-globule and globule-to-coil transitions of individual PNIPAM chains free in water,[53] which was attributed to the formation of additional hydrogen bonding between different segments within a chain in the collapsed state at higher temperatures. Subsequently, such additional hydrogen bonding cannot be removed in the cooling process when the temperature is near and higher than the LCST because water is still not a good solvent in this temperature range. This could explain the delayed hydration in the cooling process in Figure 4. Eventually, when the temperature is sufficiently low, water becomes such a good solvent that individual PNIPAM globule finally melts into a coil conformation. In the present study, the formation of additional hydrogen bonding between different chains is likely to occur so that the hysteresis is more profound than that in the conformation change of individual PNIPAM chains free in an extremely dilute aqueous solution.

Conclusion

The study of the temperature-induced dehydration and hydration of linear thermally sensitive poly(*N*-isopropylacrylamide) (PNIPAM) chains grafted on a gold surface in water by using a quartz crystal microbalance reveals that the dehydration is gradual during the heating process and the hydration starts at ~23 °C, much lower than the well-known coil-to-globule transition temperature (~32 °C) of individual PNIPAM chains free in water. The present study indicates that the grafted PNIPAM chains undergo a continuous collapse due to the surface constraint. The results also showed that in the cooling process (the swelling of the collapsed chains) there exists a hysteresis in the hydration and such hysteresis only disappears at ~20 °C, at which water becomes a sufficiently good solvent. This indicates the formation of some additional hydrogen bonding formed at higher temperatures in the collapsed state, which could not be completely removed as long as the temperature is not far away from the Θ-temperature (~30 °C).

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