

Chapter 2

Conformational Change of Grafted Polymer Chains

Abstract Based on the “grafting from” and “grafting to” methods, polymer chains are grafted onto the resonator surfaces. QCM-D is used to investigate the conformational change of grafted chains induced by the variation of external conditions. For the grafted poly(N-isopropylacrylamide) (PNIPAM) chains, the QCM-D studies show that the conformational change of grafted PNIPAM chains induced by the variations of temperature and solvent composition is fundamentally different from that for the free PNIPAM chains in solution and the grafting density plays an important role in the conformational change. For the grafted polyelectrolytes, the chemical oscillation induced periodic collapse and swelling of poly (acrylic acid) brushes and the pH-induced folding of DNA with different grafting densities are discussed in detail with the QCM-D results. The influences of salt concentration and salt type on the conformational change of grafted polyelectrolytes are also discussed in this chapter. The studies demonstrate that QCM-D can provide not only the changes in mass and rigidity of the grafted polymer chains, but also the changes in hydrodynamic thickness, shear viscosity, and shear modulus of the grafted polymer layer, which would give a clear picture on the conformational change of the grafted polymer chains.

Keywords Conformational change • Polymer brushes • Polyelectrolyte • Hydration • Electrostatic interaction • Folding • Counterion condensation • Charge reversal

2.1 Introduction

It is well-known that the interfacial properties are significantly influenced by the conformation of polymer chains grafted at interfaces [1–4]. However, the in situ real-time characterization of the conformational change of grafted chains still remains a challenge [5, 6]. Generally, polymer chains at the solid/liquid interface

would exhibit rich conformations depending on the polymer structure, grafting density, solvent quality, and polymer segment–surface interaction [7–11]. At a low grafting density where the distance between the grafted chains is larger than the size of the chains, the grafted chains usually exhibit a pancake-like conformation when polymer segments attractively interact with the surface [12]. In contrast, if there are no obviously attractive segment–surface interactions, the chains would have a mushroom structure [12]. At a high grafting density where the distance between the grafted chains is less than the chain size, the chains will form brushes [12]. For charged chains, the conformation is also influenced by the electrostatic interactions between the grafted polyelectrolyte chains [13].

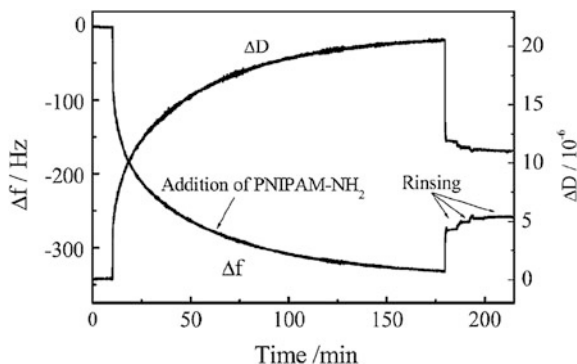
Due to the stimuli-responsive properties of polymers, the conformation of grafted polymer chains will be strongly dependent on the external conditions such as temperature, pH, salt concentration, and salt type [14]. Such stimuli-responsive properties have important implications and applications in the field of smart interfacial materials [15]. In comparison with free chains in solution, polymer chains grafted on a solid surface are expected to exhibit distinct conformational change upon the variation of external environments [16]. In this chapter, we will show that how the QCM-D can be used to investigate the conformational change of grafted neutral and charged polymer chains induced by varying temperature, solvent composition, pH, salt concentration, and salt type [17–24].

2.2 Temperature-induced Conformational Change of Grafted PNIPAM Chains with a Low Grafting Density

Poly (N-isopropylacrylamide) (PNIPAM) is a well-known thermally sensitive polymer and has a lower critical solution temperature (LCST) at ~ 32 °C in water [25]. That is, individual PNIPAM chains adopt a random coil conformation at low temperatures but collapse into a globule when the solution temperature is higher than LCST. In contrast with a linear PNIPAM chain free in solution exhibiting a discontinuous coil-to-globule transition [26], the grafted PNIPAM chains may exhibit different conformational changes due to the constraint of the chains on surface [27]. Some studies demonstrated that grafted PNIPAM chains has a sharp transition near the LCST [28, 29], but other investigations indicated a gradual collapse of the grafted PNIPAM chains over the LCST [30], which agreed with the theoretical prediction [9, 27]. To clarify the question, PNIPAM chains are grafted onto the QCM resonator surface to investigate the collapse and swelling of the grafted chains induced by the variation of temperature.

Actually, PNIPAM chains can be anchored on the solid surface by either “grafting to” or “grafting from” method [31]. The former generally would lead to the grafted polymer chains with a low grafting density, whereas the latter usually results in the grafted polymer chains with a high grafting density [17, 19].

Fig. 2.1 Time dependence of changes in frequency (Δf) and dissipation (ΔD) during the grafting of PNIPAM chains onto the gold-coated resonator surface at T of 20 °C, where the overtone number $n = 3$. Reprinted with the permission from Ref. [17]. Copyright 2004 American Chemical Society



PNIPAM chains are first grafted onto the QCM resonator surface with a low grafting density according to the “grafting to” procedure [17]. Figure 2.1 shows a real-time measurement of Δf and ΔD for the addition of linear NH_2 -PNIPAM to the QCM chamber where the resonator surface is immobilized with the groups of $-\text{S}(\text{CH}_2)_{12}\text{OCH}_2\text{COON}(\text{CO})_2(\text{CH}_2)_2$. The decrease of Δf as well as the increase of ΔD with time indicates the grafting of PNIPAM chains onto the resonator surface. The physically adsorbed chains can be removed by rinsing with water.

Figure 2.2 shows the temperature dependence of $-\Delta f$. The shift in Δf is indicative of the mass change of the grafted polymer layer [32]. $-\Delta f$ gradually decreases with the increase of temperature during the heating process, indicating that the mass of the polymer layer on the resonator surface decreases with temperature. Here, the mass detected by QCM includes the mass of the grafted PNIPAM chains and the coupled water molecules. Since PNIPAM chains are grafted on the surface, the decrease in $-\Delta f$ implies the dehydration of the polymer chains, that is, some bounded water molecules leave the grafted PNIPAM layer. During the cooling process, $-\Delta f$ increases with the decreasing temperature,

Fig. 2.2 Temperature dependence of frequency shift ($-\Delta f$) of linear PNIPAM chains grafted on the gold-coated resonator surface, where the overtone number $n = 3$. Reprinted with the permission from Ref. [17]. Copyright 2004 American Chemical Society

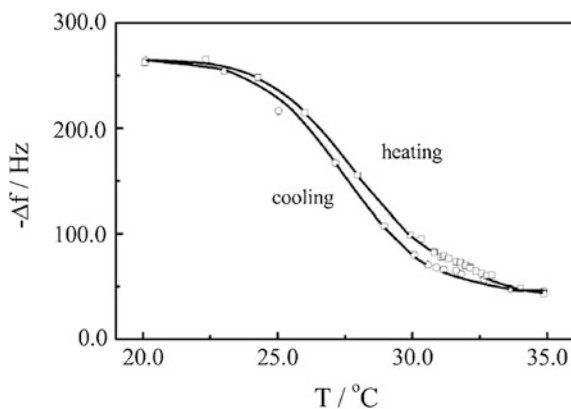
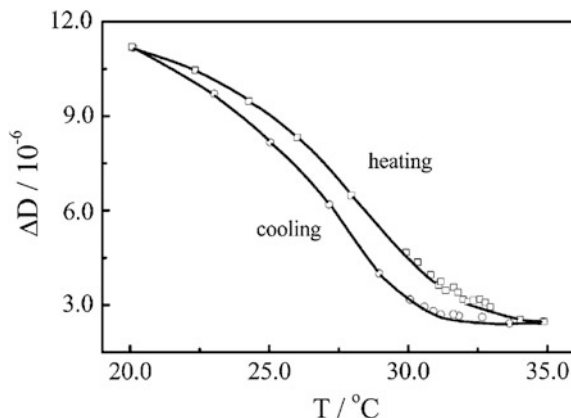


Fig. 2.3 Temperature dependence of dissipation shift ($-\Delta D$) of linear PNIPAM chains grafted on the gold-coated resonator surface, where the overtone number $n = 3$. Reprinted with the permission from Ref. [17]. Copyright 2004 American Chemical Society



indicating that the PNIPAM chains rehydrate again as temperature decreases. Eventually, $-\Delta f$ is back to the original point, suggesting that PNIPAM chains can resume complete hydration at the low temperature.

The temperature dependence of ΔD is shown in Fig. 2.3. It is known that a dense and rigid layer has a small dissipation, whereas a layer with a loose and flexible structure exhibits a large dissipation [33]. It can be seen that ΔD decreases with temperature during the heating process, indicating that PNIPAM chains shrink and collapse into a denser structure. During the cooling process, ΔD increases with the decreasing temperature, indicating the swelling of PNIPAM layer. Additionally, a hysteresis can be observed in the heating-and-cooling cycle in either Fig. 2.2 or 2.3. This is because PNIPAM segments form additional hydrogen bonds at the collapsed state, which cannot be completely removed at the temperature near LCST [34].

On the other hand, the relation of ΔD versus Δf can describe the cooperativity between the conformational change and the hydration of the grafted polymer chains because Δf mainly arises from the hydration/dehydration of polymer chains while ΔD is due to the swelling/collapse of the polymer layer. The fact that ΔD linearly increases with $-\Delta f$ in Fig. 2.4 indicates that the conformational change involves only one kinetic process, which suggests that the dehydration and collapse occur simultaneously in the heating process and the rehydration is concurrent with the swelling in the cooling process. In other words, they have a strong cooperativity during the heating/cooling process.

Fig. 2.4 The relation between ΔD and $-\Delta f$ for the temperature-induced conformational change of the PNIPAM chains grafted on the gold-coated resonator surface, where the overtone number $n = 3$. Reproduced from Ref. [6] by permission of John Wiley & Sons Ltd

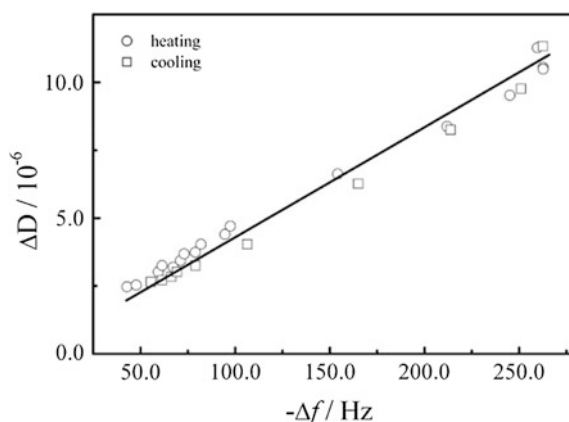
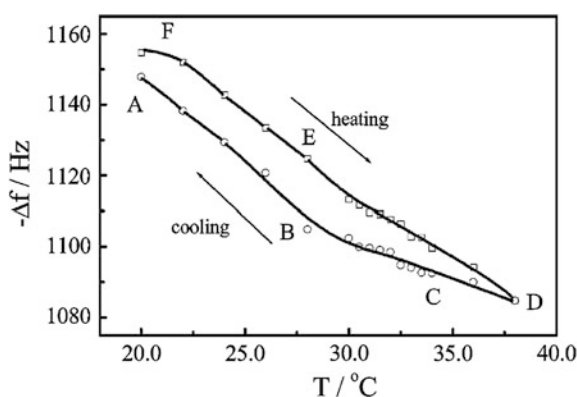


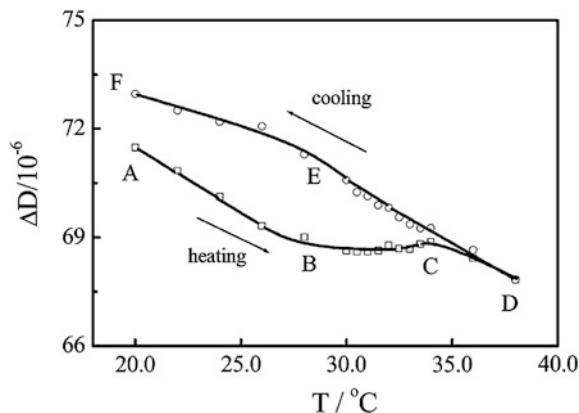
Fig. 2.5 Temperature dependence of frequency shift ($-\Delta f$) of PNIPAM brushes grafted on the SiO_2 -coated resonator surface, where the overtone number $n = 3$. Reprinted with the permission from Ref. [19]. Copyright 2005 American Chemical Society



2.3 Temperature-induced Conformational Change of Grafted PNIPAM Chains with a High Grafting Density

To understand the influence of grafting density on the conformational change of grafted polymer chains, PNIPAM chains are grafted onto a SiO_2 -coated resonator surface via the “grafting from” procedure based on the surface-initiated polymerization method to prepare the PNIPAM brushes with a high grafting density [19]. Figure 2.5 shows the temperature dependence of $-\Delta f$ of PNIPAM brushes in one heating-and-cooling cycle. It can be seen that $-\Delta f$ gradually decreases with the increasing temperature in the heating process over the range of 20–38 °C, which is similar to the observation in Fig. 2.2. At low temperatures, water is a good solvent for PNIPAM, so that PNIPAM chains strongly interact with water molecules. As temperature increases, dehydration occurs and PNIPAM chains gradually collapse, leading to the decrease of $-\Delta f$. In contrast, the collapsed

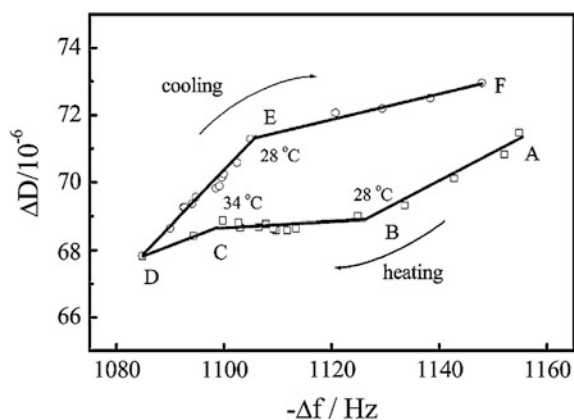
Fig. 2.6 Temperature dependence of dissipation shift (ΔD) of PNIPAM brushes grafted on the SiO_2 -coated resonator surface, where the overtone number $n = 3$. Reprinted with the permission from Ref. [19]. Copyright 2005 American Chemical Society



PNIPAM brushes become swollen and rehydrate again with the decreasing temperature in the cooling process, as indicated by the increase of $-\Delta f$. Obviously, the continuous change of frequency in both heating and cooling processes is markedly different from the discontinuous coil-to-globule transition of individual PNIPAM chains free in water [26].

Figure 2.6 shows the temperature dependence of ΔD in one heating and cooling cycle. ΔD decreases with the increasing temperature in the heating process, indicating that PNIPAM brushes gradually collapse into a more compact structure. In the cooling process, ΔD increases with the decreasing temperature, indicating that the collapsed brushes become more swollen and flexible. Also, ΔD in the cooling process is larger than that in the heating process at the same temperature, whereas an opposite trend is observed for $-\Delta f$ in Fig. 2.5. This phenomenon should arise from the formation of tails on the outer layer of the brushes, which have significant effects on the dissipation. Specifically, the brushes begin to swell from their outer layer to inner core in the cooling process, resulting in some

Fig. 2.7 The relation between ΔD and $-\Delta f$ for the PNIPAM brushes grafted on the SiO_2 -coated resonator surface during the temperature induced conformational change, where the overtone number $n = 3$. Reprinted with the permission from Ref. [19]. Copyright 2005 American Chemical Society



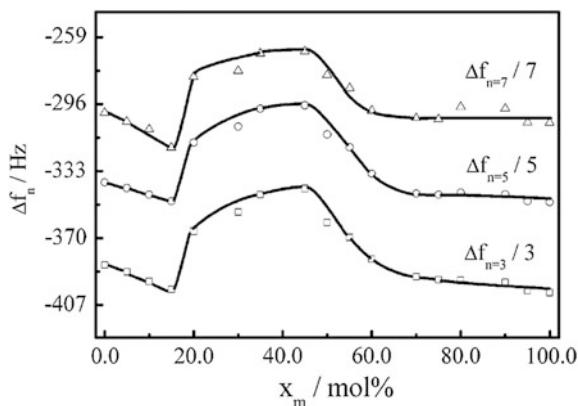
random and flexible tails on the layer surface, thereby giving rise to a larger ΔD than that in the heating process. The collapsed PNIPAM brushes cannot be completely back to the initial swollen state during the experimental time scale, as indicated by the fact that both ΔD and $-\Delta f$ are not back to their original values at 20 °C, which is different from that for the grafted PNIPAM chains with a low grafting density (Figs. 2.2 and 2.3).

In the relation between ΔD and $-\Delta f$ (Fig. 2.7), three kinetic processes can be observed in the heating process. When $T < 28$ °C (A to B), ΔD decreases with the decrease of $-\Delta f$, implying the concurrent shrinking and dehydration of grafted PNIPAM chains. In the range 28 °C $< T < 34$ °C (B to C), ΔD slightly changes as $-\Delta f$ decreases. Here, PNIPAM brushes are partially collapsed in this range of temperature. The conformational change of the partially collapsed brushes is limited due to the steric barrier, so that ΔD slightly changes. On the other hand, not all the detached water molecules during shrinking at $T < 28$ °C can leave PNIPAM brushes immediately, some of them are trapped in the dense brushes. As temperature increases, the trapped water molecules gradually diffuse out of the brushes, leading to an obvious decrease of $-\Delta f$. Obviously, the cooperativity between the collapse and the dehydration is weak due to the retarded dehydration, which is also responsible for the continuous collapse transition. Further heating would overcome the steric barrier, leading to more collapse and dehydration, as reflected by the decreases in ΔD and $-\Delta f$ at $T > 34$ °C (C to D). In the cooling process, when the temperature is higher than 28 °C (D to E), ΔD rapidly increases with the increasing $-\Delta f$, suggesting that the flexible tails are formed on the outer layer of PNIPAM brushes during the rehydration. When $T < 28$ °C (E to F), ΔD slows down its increase because the hydrated chains in the outer layer tend to stretch and pack more densely. For the same $-\Delta f$, the value of ΔD in the cooling process is always higher than that in the heating process, further indicating that the flexible tails have a pronounced effect on the dissipation. The hysteresis observed in the heating and cooling cycle is attributed to the additional hydrogen bonds formed in the collapsed state. Besides, the nonuniformity and the stretching of the brushes are thought to further enlarge the hysteresis. In fact, the poly (N-isopropylacrylamide-co-sodium acrylate) copolymer brushes also exhibit a similar conformational change when temperature is varied [20].

2.4 Solvency-induced Conformational Change of PNIPAM Brushes

PNIPAM not only has the thermosensitive property, but also exhibits a reentrant behavior or cononsolvency in response to the composition of a mixed solvent consisting of water and a water-miscible organic solvent [35]. That is, PNIPAM is soluble in either water or organic solvent but precipitant in their mixture with a certain composition. Several models have been proposed to explain the reentrant

Fig. 2.8 Methanol molar fraction (x_m) dependence of frequency shift (Δf_n) of the PNIPAM brushes at different overtones ($n = 3, 5, 7$). Reprinted with the permission from Ref. [18]. Copyright 2005 American Chemical Society



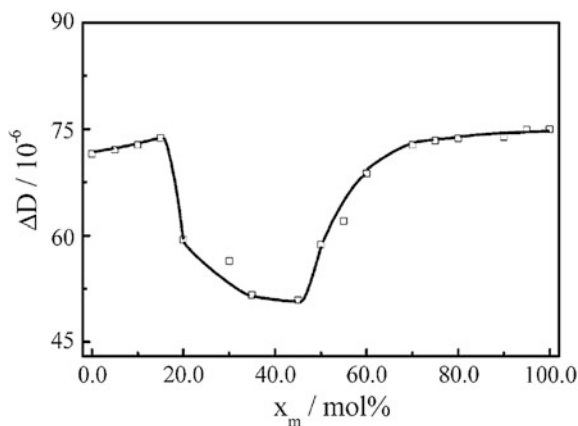
behavior, including the perturbation of the water–methanol interaction parameter (χ) by PNIPAM chains [36], the formation of complexes between water and methanol [37], and the formation of competitive hydrogen bonds between PNIPAM chains and solvent molecules [38]. To have a better understanding of the reentrant behavior, QCM-D is employed to investigate the conformational change of PNIPAM brushes on a SiO_2 -coated resonator surface induced by varying the solvent composition of water–methanol mixtures [18].

Figure 2.8 shows the methanol molar fraction (x_m) dependence of frequency shift (Δf_n) of PNIPAM brushes at different overtones. For the sake of comparison, the frequency shift measured at each overtone is divided by n . The overtone dependent Δf_n indicates that PNIPAM brushes have a viscoelastic nature. The Δf_n in response to the composition of the water–methanol mixtures at different overtones exhibits the same trend. At $x_m \sim 17\%$, Δf_n sharply increases, indicating the sharp decrease of the number of solvent molecules bound to PNIPAM chains. The gradual increase of Δf_n in the range of x_m between 20 and 45 % reveals a continuous desolvation of the grafted PNIPAM chains. Further increase of the methanol content leads to the resolution of the grafted PNIPAM chains, as indicated by the sharp decrease of Δf_n at $x_m \sim 50\%$ and the following slow decrease at $x_m > 60\%$. Obviously, when the x_m is in the range of 17–50 %, the water–methanol mixtures are poor solvents for PNIPAM. The solvation-to-desolvation-to-resolution transition reflects the swelling-to-collapse-to-swelling of the grafted PNIPAM layer.

Figure 2.9 shows x_m dependence of ΔD of the PNIPAM brushes. In contrast to Δf , there is a sharp decrease of ΔD at $x_m \sim 17\%$, indicating the collapse of the PNIPAM brushes. The gradual decrease of ΔD in the range of x_m between 20 and 45 % indicates a further collapse of the PNIPAM brushes. The sharp increase at $x_m \sim 50\%$ reflects that the collapsed PNIPAM brushes re-swell into a looser layer.

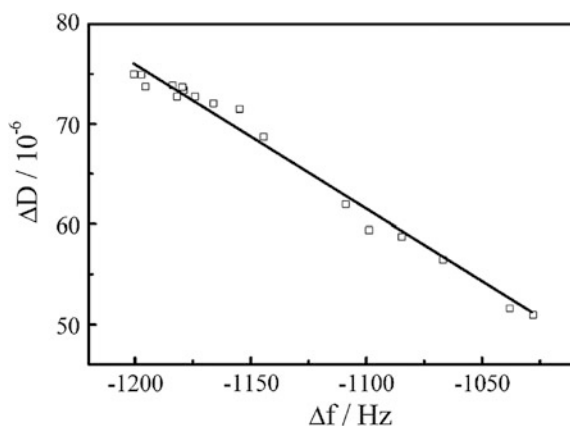
The cooperativity between the collapse/swelling and the desolvation/solvation of the PNIPAM brushes can be viewed by the relation of ΔD versus Δf . Figure 2.10 shows that ΔD linearly decreases as Δf increases, suggesting that the

Fig. 2.9 Methanol molar fraction (x_m) dependence of dissipation shift (ΔD) of the PNIPAM brushes, where the overtone number $n = 3$. Reprinted with the permission from Ref. [18]. Copyright 2005 American Chemical Society



reentrant transition involves only one kinetic process. This fact reveals that the desolvation and collapse occur simultaneously and the solvation is concurrent with the swelling. Namely, the cooperativity is strong in the present system. This fact also indicates that no preferential solvation occurs here, which is quite different from the case of polymer brushes in a mixture of good and poor solvents [39]. The reentrant transition of the PNIPAM brushes in the mixture of water and methanol is probably due to the formation of water/methanol complexes or clusters consisting of a certain number of water and methanol molecules, which is very sensitive to the solvent composition. Such a complexation leads the water–methanol mixture to change suddenly from a good solvent to a poor one for PNIPAM at $x_m \sim 17\%$, and develops into a good solvent again at $x_m \sim 50\%$. In such a solvent mixture, either PNIPAM brushes or individual PNIPAM chains are expected to undergo a sharp reentrant transition.

Fig. 2.10 The relation between ΔD and Δf for the solvency induced conformational change of the PNIPAM brushes, where the overtone number $n = 3$. Reprinted with the permission from Ref. [18]. Copyright 2005 American Chemical Society



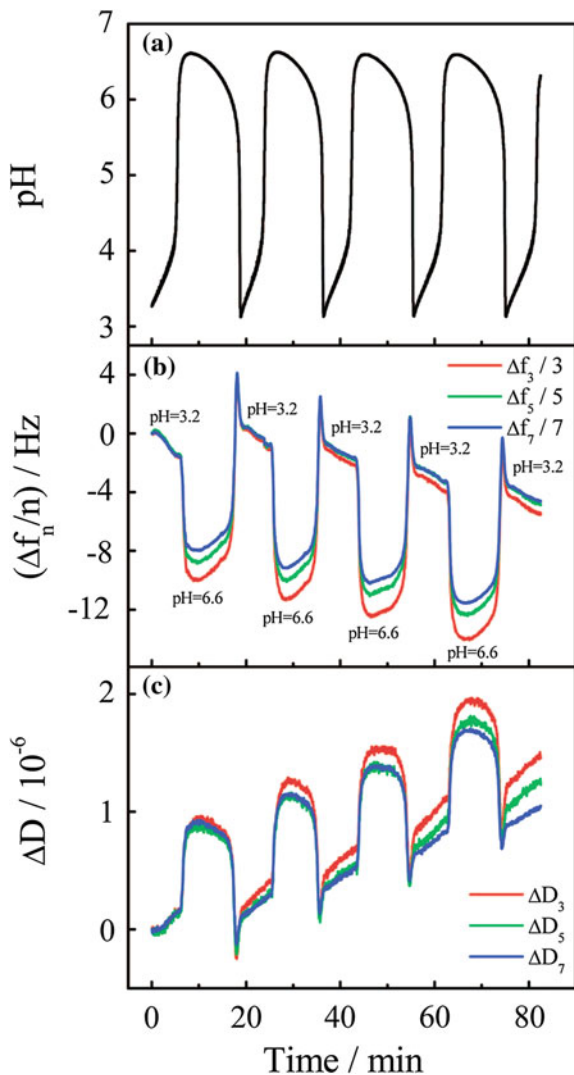
2.5 pH-induced Conformational Change of Grafted Polyelectrolytes

Polyelectrolytes are macromolecules carrying ionic groups, which can dissociate in water or other polar solvents forming charged polymer backbones [40]. When polyelectrolyte chains are grafted on a solid surface, the physical properties of the grafted charged polymer chains are different from that of the grafted uncharged polymer chains [13]. In addition to the intra- and intermolecular interactions involved in the neutral polymer system, electrostatic interactions come into play in the determination of the conformation of polyelectrolyte brushes. It is known that the conformation of polyelectrolyte brushes is strongly influenced by salt concentration and salt type [41]. For the weak polyelectrolytes, the conformation is also influenced by the solution pH [42]. Generally, the switch of conformation of polyelectrolyte brushes is stimulated by manually varied external conditions, that is, the stimuli-responsive properties of the charged polymer layer act in an equilibrium state. However, many physiological behaviors such as heartbeat and brainwaves exhibit rhythmical oscillations. Thus, it is also interesting to see how the conformation of polyelectrolyte brushes is changed driven by a chemical oscillation.

Poly (acrylic acid) (PAA) brushes are prepared on a gold-coated resonator surface by using surface-initiated atom transfer radical polymerization method [21]. The QCM-D measurements on the pH-induced oscillation of PAA brushes under a continuous flow of bromate-sulfite-ferrocyanide (BSF) solution are shown in Fig. 2.11 [21]. Figure 2.11a shows the time dependence of pH of BSF solution. Typically, pH is varied between 3.2 and 6.6. Parts b and c of Fig. 2.11 show the time dependence of shifts in Δf and ΔD of PAA brushes under a continuous flow of BSF solution. Clearly, both Δf and ΔD exhibit obvious oscillations. As pH increases from 3.2 to 6.6, Δf rapidly decreases. Then, Δf sharply increases as pH varies from 6.6 to 3.2. In contrast, the response of dissipation oscillates with pH in an opposite trend. PAA is a weak polyelectrolyte with $pK_a \sim 4.5$ [43]. Therefore, as pH increases from 3.2 to 6.6, more carboxyl groups are ionized, so more water molecules are coupled with PAA chains, leading Δf to decrease. In contrast, as pH decreases from 6.6 to 3.2, Δf increases due to the dehydration of PAA chains. In addition, the slight overtone dependence at pH 3.2 implies PAA brushes are less viscoelastic, whereas the stronger dependence at pH 6.6 indicates that the brushes are more viscoelastic. This can be viewed more clearly from the change in ΔD . As pH increases from 3.2 to 6.6, ΔD increases, indicating that more energy of resonator oscillation is damped by PAA brushes, namely, the brushes become more viscoelastic, whereas the decrease of ΔD with pH varied from 6.6 to 3.2 indicates the collapse of PAA brushes.

Figure 2.12 shows the changes in hydrodynamic thickness (Δt_f), shear viscosity (η_f), and elastic shear modulus (μ_f) of PAA brushes estimated by using the Voigt model. Due to the stretching and collapse of PAA brushes, Δt_f oscillates between

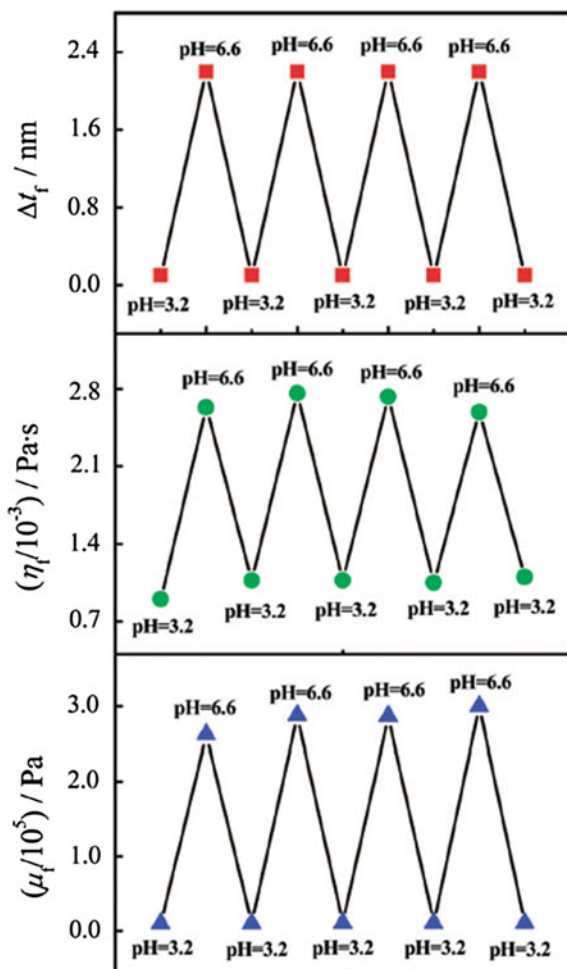
Fig. 2.11 **a** Oscillation of pH of the BSF solution, where $[\text{KBrO}_3] = 0.065 \text{ M}$, $[\text{Na}_2\text{SO}_3] = 0.075 \text{ M}$, $\text{K}_4[\text{Fe}(\text{CN})_6] = 0.02 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.01 \text{ M}$. **b** Time dependence of shift in frequency (Δf_n) of PAA brushes under a continuous flow of BSF solution, where the overtone number $n = 3, 5, 7$. **c** Time dependence of shift in dissipation (ΔD) of PAA brushes under a continuous flow of BSF solution, where the overtone number $n = 3, 5, 7$. Reprinted with the permission from Ref. [21]. Copyright 2008 American Chemical Society



pH 3.2 and 6.6 with amplitude of $\sim 2 \text{ nm}$. At the same time, η_f and μ_f also exhibit oscillations with the change of pH. As pH increases from 3.2 to 6.6, η_f increases from $\sim 1.0 \times 10^{-3}$ to $\sim 2.7 \times 10^{-3} \text{ Pa}\cdot\text{s}$ due to the hydration of PAA chains. On the other hand, the increase of electrostatic repulsions between PAA chains with pH varied from 3.2 to 6.6 leads PAA brushes to adopt a weakly compressible state, so that μ_f increases from $\sim 1.0 \times 10^4$ to $\sim 2.8 \times 10^5 \text{ Pa}$. In contrast, η_f and μ_f decrease with the decreasing pH.

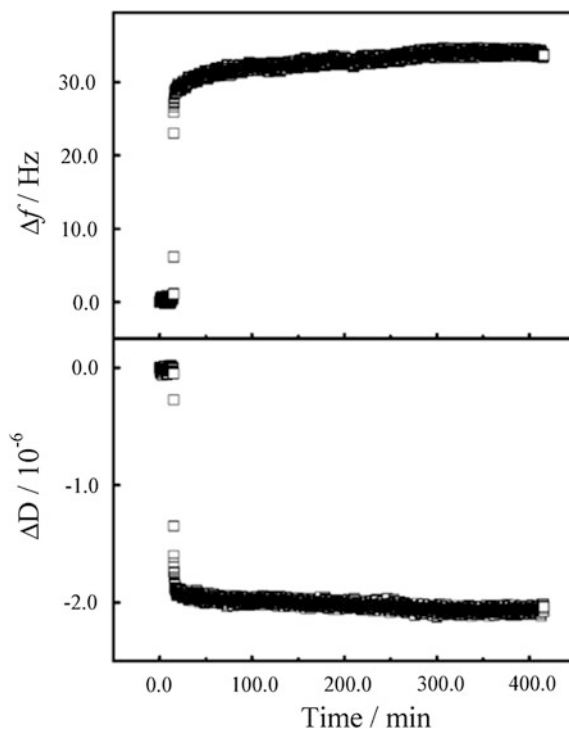
In comparison with the synthetic polyelectrolytes, studies on the conformational change of biopolyelectrolytes (e.g., DNA) have more important implications

Fig. 2.12 Changes in hydrodynamic thickness (ΔL_f), shear viscosity (η_f), and elastic shear modulus (μ_f) of PAA brushes under the oscillation of pH. Reprinted with the permission from Ref. [21]. Copyright 2008 American Chemical Society



for the biological activity of cellular biomacromolecules [44]. DNA with cytidine-enriched sequences can fold into an *i*-motif via intercalated C–C⁺ base pairing in an acidic environment, whereas it unfolds into a random coil in a basic environment [45]. Consequently, the folding and unfolding of DNA can be simply modulated by tuning solution pH. The DNA chains are grafted onto a gold-coated resonator surface at pH 4.5 and 8.5 based on the thiol-gold reaction, which, respectively, gives rise to DNA chains with low and high grafting densities [22]. The grafted DNA chains are immersed in a solution at pH 8.5 first so that they are able to completely unfold. Subsequently, a solution with pH of 4.5 is introduced to the QCM chamber to replace the high pH solution, which will lead to the folding of grafted DNA chains. Figure 2.13 shows Δf quickly increases and then gradually levels off when pH is changed from 8.5 to 4.5. This is an indication of dehydration

Fig. 2.13 Shifts in frequency (Δf) and dissipation (ΔD) for the folding of grafted DNA chains with a low grafting density induced by changing pH, where the overtone number $n = 3$. Reprinted with the permission from Ref. [22]. Copyright 2010 American Chemical Society



during the folding of DNA chains. It is known that the protonated cytidine groups at pH 4.5 would form intra-/interchain hydrogen bonds due to C–C⁺ pairing [46]. The interactions lead to the release of some coupled water molecules from DNA chains, resulting in an increase in Δf . On the other hand, the quick decrease in ΔD indicates the collapse of DNA chains during the folding.

Figure 2.14 shows the shifts in Δf and ΔD for the folding of DNA chains with a high grafting density. Obviously, there are several stages during the folding of grafted DNA chains. Δf increases and ΔD decreases quickly in the initial stage because the pH-induced folding leads to the dehydration and collapse of the DNA chains. Then, Δf and ΔD only slightly change, which might be due to the slight rearrangement of grafted DNA chains. Afterwards, Δf increases and ΔD decreases gradually with time. As stated above, because of the high grafting density, the DNA chains restrict each other to fold into the *i*-motif structure. The DNA chains have to gradually fold as they need to rearrange and shape themselves. After a long time, Δf and ΔD level off, indicating the completion of the folding.

The folding of DNA chains can be viewed in terms of ΔD versus $-\Delta f$ relation (Fig. 2.15). The folding of DNA chains with a low grafting density only involves one kinetic process. This is because the space around DNA chains is enough for their full folding. However, two kinetic processes are observed in the folding of

Fig. 2.14 Shifts in frequency (Δf) and dissipation (ΔD) for the folding of grafted DNA chains with a high grafting density induced by changing solution pH, where the overtone number $n = 3$. Reprinted with the permission from Ref. [22]. Copyright 2010 American Chemical Society

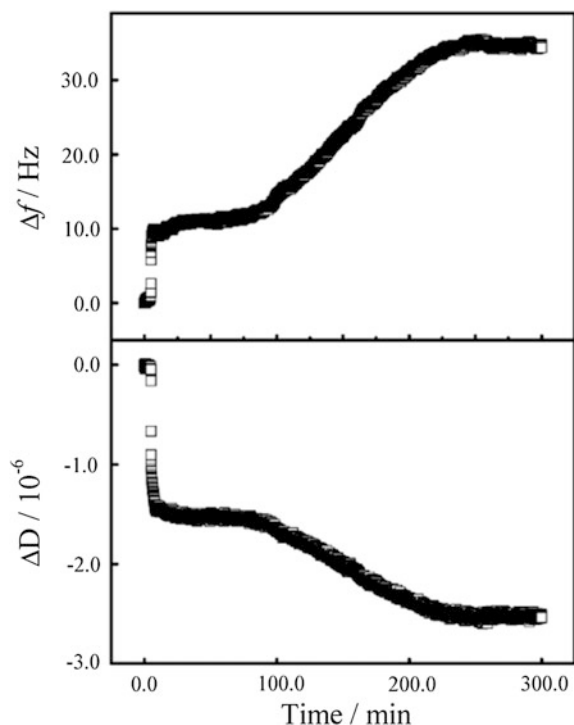
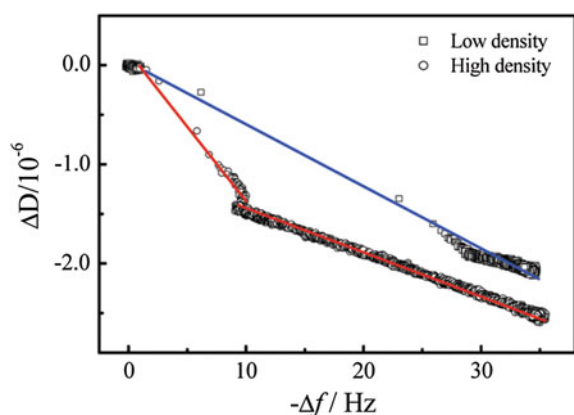


Fig. 2.15 The relation between ΔD and $-\Delta f$ for the folding of DNA chains at different grafting densities, where the overtone number $n = 3$. Reprinted with the permission from Ref. [22]. Copyright 2010 American Chemical Society



DNA with a high grafting density. As discussed above, the DNA chains are expected to partially fold in the first process. In the second process, the DNA chains have to rearrange themselves to have more space for further folding.

2.6 Salt Concentration and Type-induced Conformational Change of Grafted Polyelectrolytes

One interesting and unclear question regarding polyelectrolytes is the reentrant condensation of polyelectrolyte chains upon addition of multivalent salt [47]. Namely, polyelectrolyte chains form a precipitate as the concentration of multivalent salt increases, and the precipitate will redissolve into solution upon the further addition of multivalent salt. The precipitation of polyelectrolyte chains in the presence of multivalent salts limits the insight into the mechanism for the reentrant behavior at the molecular level by using some techniques (e.g., laser light scattering). However, the macroscopic phase separation in the presence of multivalent counterions which occurs for the free chains in solution can be avoided in the QCM-D measurements for the grafted polyelectrolyte chains, so that we can look insight the microscopical mechanism of the reentrant behavior [23].

Figure 2.16 shows the ionic strength (I) dependence of Δf for the resonator grafted with sodium poly(styrene sulfonate) (PSS) chains in different divalent salt solutions. The data obtained in CaCl_2 solution are used as an example to discuss. At $I < 1.5$ M, Δf decreases as I increases from 3.0×10^{-4} to 9.0×10^{-2} M (A to C), indicating the trapping of water molecules by an inhomogeneous layer formed by the grafted PSS chains. From C to D, I increases from 9.0×10^{-2} to 1.5 M, the charges on PSS chains are almost completely neutralized by the counterions. Thus, the chains are dehydrated and collapsed to form a dense and homogenous layer and the trapped water molecules are released out, as indicated by the increase of Δf . At $I > 1.5$ M, Δf decreases again as I increases (D to E), implying that the mass associated with the PSS brushes increases. This is an indication of the rehydration and reexpansion of the grafted PSS chains. For the divalent salts, when the PSS chains collapse into the homogeneous layer, the adsorbed counterions are expected to form a strongly correlated liquid layer at the polyelectrolyte surface due to the strong counterion–counterion correlation [48]. Such a liquid layer has a larger

Fig. 2.16 The ionic strength (I) dependence of frequency shift (Δf) for the resonator grafted with PSS chains in different divalent salt solutions, where the overtone number $n = 3$. Reproduced from Ref. [23] by permission of The Royal Society of Chemistry

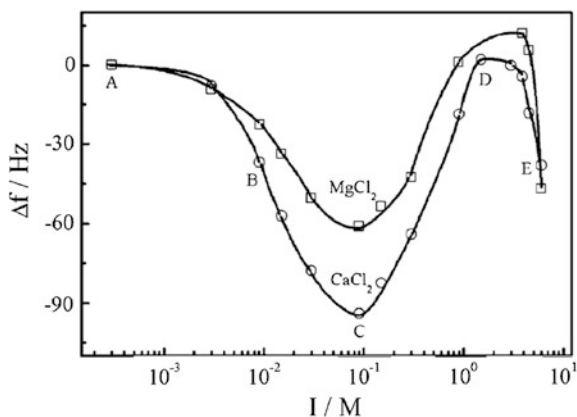
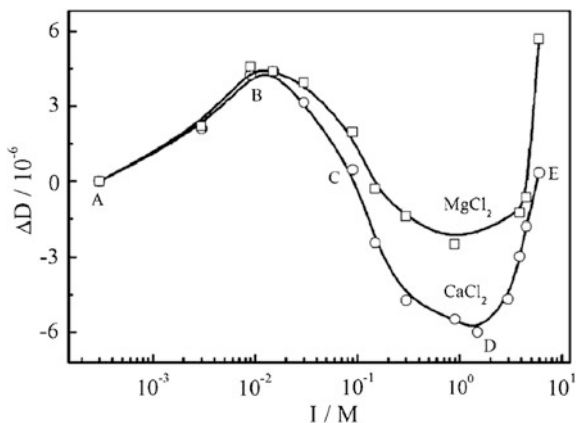


Fig. 2.17 The ionic strength (I) dependence of dissipation shift (ΔD) for the resonator grafted with PSS chains in different divalent salt solutions, where the overtone number $n = 3$. Reproduced from Ref. [23] by permission of The Royal Society of Chemistry

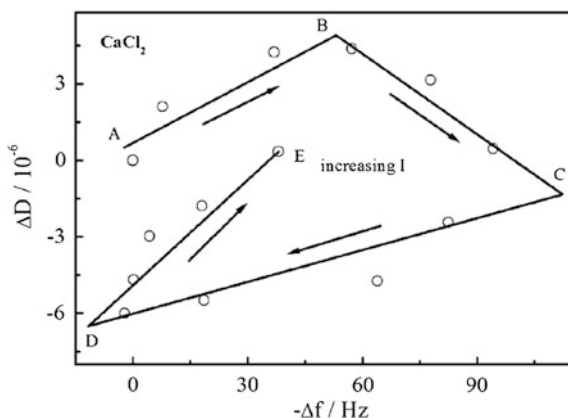


dielectric constant (ϵ_1) than that of water (ϵ_2), therefore the counterions near the polyelectrolyte surface cause polarization of the surface under the liquid layer and produce “image” charges with opposite sign on the polyelectrolyte surface based on the equation $q' = q(\epsilon_2 - \epsilon_1)/(\epsilon_2 + \epsilon_1)$, where q and q' are the original charge and image charge, respectively [48]. At the same time, the repulsion between the incoming counterions and the adsorbed counterions would create some correlation holes [48]. As I increases (D to E), the attractions between the incoming counterions and the image charges give rise to further counterion condensation onto the PSS chains through the correlation holes, which causes the charge inversion of the PSS chains. In other words, the PSS chains now become positively charged. Such a recharging leads to the rehydration of the chains, and the electrostatic repulsion between the PSS chains results in the reexpansion of PSS brushes. This is why Δf decreases from D to E. Additionally, from A to C, a larger change in Δf is observed for CaCl_2 than that for MgCl_2 . This can be explained by the formation of relatively strong ion pairs between Ca^{2+} and the weakly hydrated alkyl sulfonate groups since the strength of hydration of Ca^{2+} is weaker than Mg^{2+} [49].

In Fig. 2.17, the change in ΔD further demonstrates the conformational change of grafted PSS chains in CaCl_2 and MgCl_2 solutions. Specifically, ΔD increases with the increasing I from 3.0×10^{-4} to 9.0×10^{-3} M (A to B), indicating the formation of a loose and inhomogeneous layer. As I increases from 9.0×10^{-3} to 9.0×10^{-2} M (B to C), the decrease in ΔD indicates that the layer becomes denser. Further increasing I from 9.0×10^{-2} to 1.5 M (C to D) leads the grafted PSS chains to form a even more homogeneous and denser layer, as indicated by the further decrease of ΔD from C to D. At $I > 1.5$ M, the increase of I (D to E) leads ΔD to increase again, indicating the reexpansion of the PSS layer due to the charge inversion.

Figure 2.18 shows the $-\Delta f$ dependence of ΔD as a function of ionic strength for the resonator grafted with PSS chains in CaCl_2 solution. ΔD increases with $-\Delta f$ (A to B), implying that the highly extended PSS chains partly shrink into a loose and inhomogeneous structure. From B to C, ΔD decreases but $-\Delta f$ increases, indicating

Fig. 2.18 The frequency shift ($-\Delta f$) dependence of dissipation shift (ΔD) as a function of ionic strength (I) for the resonator grafted with PSS chains in the CaCl_2 solutions, where the overtone number $n = 3$. Reproduced from Ref. [23] by permission of The Royal Society of Chemistry

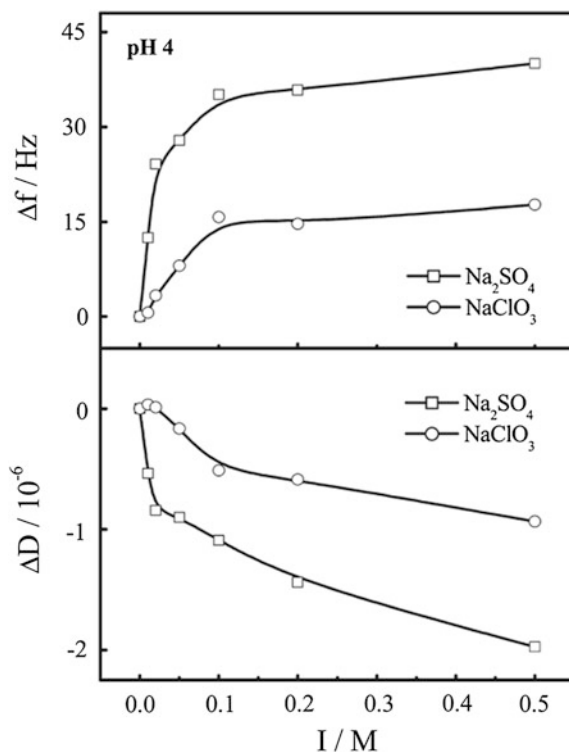


that the inhomogeneous layer forms a relatively dense structure but the water molecules are still trapped in such a structure. Further increasing I (C to D) leads the PSS chains to form a denser and more homogeneous structure, as reflected by the fact that both $-\Delta f$ and ΔD decrease as I increases. The increase in either $-\Delta f$ or ΔD in the last regime (D to E) indicates the rehydration and reexpansion of the grafted PSS chains due to the charge inversion. The conformational change of grafted PSS chains in the presence of trivalent salts has similar results [23].

From discussion above, counterion condensation plays a crucial role in determining polyelectrolyte conformational change. Actually, the extent of counterion condensation is influenced not only by the salt concentration, but also by the charge density of polyelectrolyte chains [50]. For the charged chains, the counterions condense around the oppositely charged groups on the polyelectrolyte chains due to the electrostatic attraction, screening the electrostatic repulsion between the identically charged groups, leading to the collapse of the chains. When the charge density decreases to zero, the polyelectrolytes become uncharged chains. The nonelectrostatic force such as van der Waals force between the ions and nonpolar moiety of polyelectrolyte chains may have effects on the conformational change [51]. In contrast with the electrostatic ion-polar group interaction that gives rise to the “salting-in” effect by charging the group, nonelectrostatic ion-nonpolar surface interaction can result in a “salting-out” effect by dehydrating the nonpolar moiety or a “salting-in” effect by binding onto the nonpolar moiety with respect to different ions [52]. Poly[(2-dimethylamino)ethyl methacrylate] (PDEM) is a weak polyelectrolyte whose charge density can be tuned by pH, and the chains are completely charged, partially charged, and uncharged at pH 4, 7, and 10, respectively [53]. PDEM chains are grafted onto a gold-coated resonator surface by the “grafting to” procedure, and then the conformational change of the grafted PDEM chains can be investigated using QCM-D in salt solutions at different pH [24].

Figure 2.19 shows I dependence of Δf and ΔD for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 4. The increase in

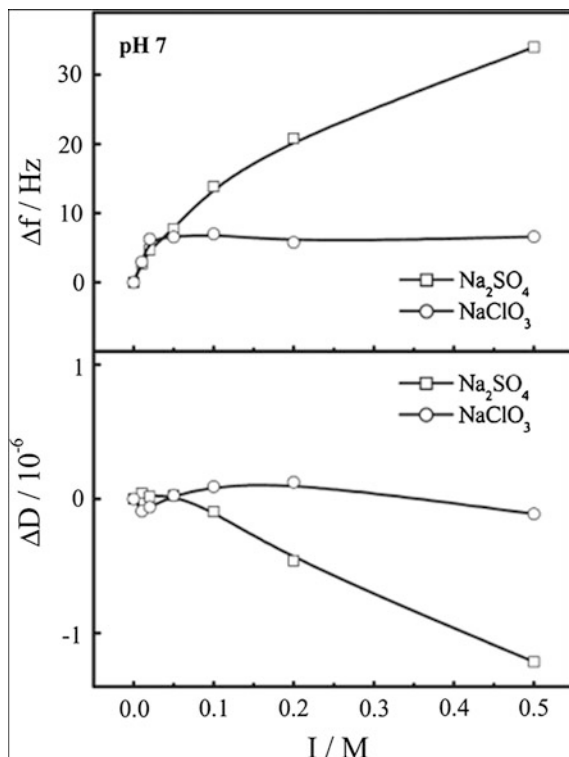
Fig. 2.19 Ionic strength (I) dependence of frequency shift (Δf) and dissipation shift (ΔD) for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 4, where the overtone number $n = 3$. Reprinted with the permission from Ref. [24]. Copyright 2011 American Chemical Society



Δf and decrease in ΔD with the increasing I indicate the dehydration of the grafted chains and the release of water molecules trapped between the chains upon the counterion condensation, which is accompanied by the chain collapse. In the range of $I < 0.1$ M, the grafted chains exhibit a more rapid collapse than that in the higher ionic strength regime, as reflected by the relatively rapid decrease in ΔD in the lower ionic strength regime. On the other hand, for the same ionic strength, SO_4^{2-} can more effectively induce the chain collapse than ClO_3^- does. This is understandable because the divalent counterion can bind with two charged groups at most. As a result, the grafted chains can be cross-linked by SO_4^{2-} , leading to more effective dehydration and chain collapse. Obviously, the conformational change of grafted PDEM chains at pH 4 is dominated by the counterion condensation.

Figure 2.20 shows I dependence of Δf and ΔD for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 7. When pH is increased from 4 to 7, PDEM chains become partially charged and the electrostatic repulsion is weakened, so that the chains adopt partially collapsed conformation. For both salts, Δf gradually increases as I increases, indicating the dehydration of the chains and the release of water molecules from the PDEM layer. This leads the polyelectrolyte chains to further collapse, as indicated by the decrease of

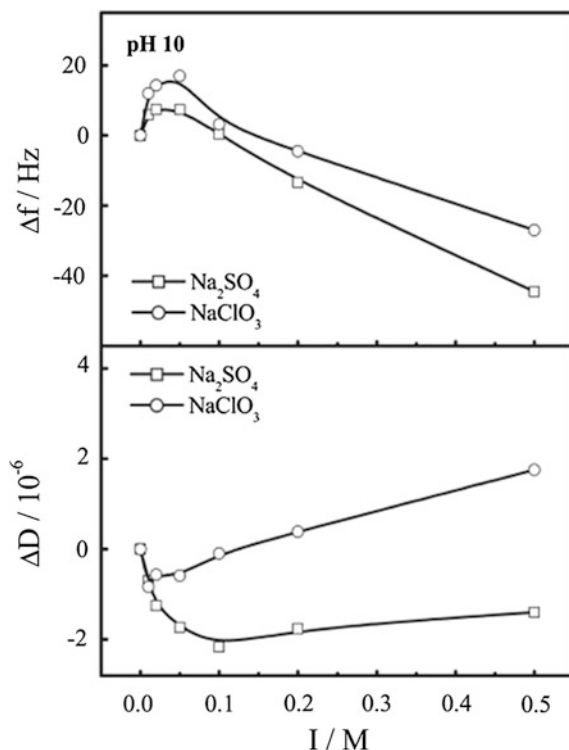
Fig. 2.20 Ionic strength (I) dependence of frequency shift (Δf) and dissipation shift (ΔD) for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 7, where the overtone number $n = 3$. Reprinted with the permission from Ref. [24]. Copyright 2011 American Chemical Society



ΔD . Again, SO_4^{2-} causes larger shifts in Δf and ΔD than ClO_3^- does. However, the difference is smaller than that at pH 4. This is because PDEM chains at pH 7 are already partially collapsed and the addition of salts can only induce limited conformational change of the chains. Clearly, the conformational change of grafted PDEM chains at pH 7 is also dominated by the counterion condensation.

Figure 2.21 shows I dependence of Δf and ΔD for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 10. It can be seen that Δf exhibits a slight increase with I in the range of $I < \sim 0.05$ M, followed by a gradual decrease with the further increase of I for both SO_4^{2-} and ClO_3^- . Likewise, as I increases, ΔD first decreases and then gradually increases. Considering that the nonpolar hydrophobic moiety of polymer chains is hydrated by the surrounding water molecules in aqueous solution, the approach of SO_4^{2-} or ClO_3^- to the nonpolar moiety may dehydrate the surface (salting-out effect) as the adsorption of such two anions would increase the surface tension of the hydrophobic surface [52]. This is why we observe an increase in Δf with the increasing I in the low ionic strength regime. The chain dehydration would strengthen the hydrophobic force between the chain segments, causing a further chain collapse, as indicated by the fact that ΔD decreases with I in the low ionic strength regime. When the ionic strength is above ~ 0.05 M, Δf gradually decreases with I ,

Fig. 2.21 Ionic strength (I) dependence of frequency shift (Δf) and dissipation shift (ΔD) for the resonator grafted with PDEM chains immersed in Na_2SO_4 and NaClO_3 solutions at pH 10, where the overtone number $n = 3$. Reprinted with the permission from Ref. [24]. Copyright 2011 American Chemical Society



suggesting the rehydration of the chains due to the binding of anions onto the dimethylamino groups of PDEM (salting-in effect) [54]. The gradual increase of ΔD with I implies that the bound anions lead to some swelling of the PDEM layer. Besides, Δf decreases and ΔD increases linearly as I increases in the range of $I > 0.05$ M. This is because the strength of the salting-in interaction between ions and polar groups depends on ionic strength [55]. Clearly, the conformational change of the grafted PDEM chains at pH 10 is dominated by the anion–nonpolar moiety interaction and the anion–polar group interaction in the low and high ionic strength regimes, respectively.

2.7 Conclusion

In this chapter, QCM-D is used to investigate the conformational change of the grafted polymer chains. Generally, QCM-D can provide not only the information about the mass change of the grafted chains, but also those about the structural change of the grafted layer. More specifically, Δf is related to the solvation/desolvation of the grafted chains and ΔD is correlated with the stretching/collapse

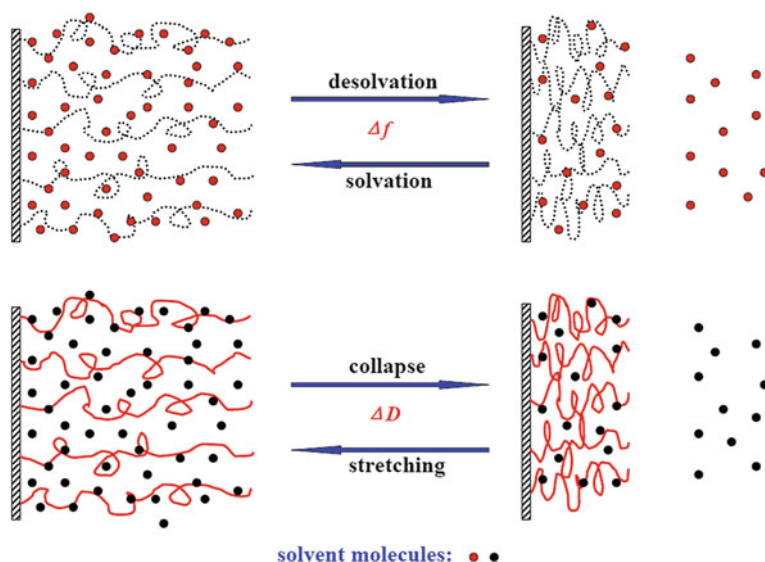


Fig. 2.22 Schematic illustration of the relation between the frequency shift (Δf) and the solvation/desolvation of the grafted polymer chains and the relation between the dissipation shift (ΔD) and the stretching/collapse of the grafted polymer chains

of the grafted chains (Fig. 2.22). The combination of Δf and ΔD can provide more useful information, e.g., the kinetic processes of the conformational change. Based on the Voigt model, QCM-D can also tell how the hydrodynamic thickness, the shear viscosity, and the shear modulus change during the conformational change.

References

1. Bhat RR, Tomlinson MR, Wu T, Genzer J (2006) Surface-grafted polymer gradients: formation, characterization, and applications. *Adv Polym Sci* 198:51–124
2. Ionov L, Minko S (2012) Mixed polymer brushes with locking switching. *Acs Appl Mater Interfaces* 4:483–489
3. Moya S, Azzaroni O, Farhan T, Osborne VL, Huck WT (2005) Locking and unlocking of polyelectrolyte brushes: toward the fabrication of chemically controlled nanoactuators. *Angew Chem Int Ed* 44:4578–4581
4. Neuhaus S, Padeste C, Spencer ND (2011) Versatile wettability gradients prepared by chemical modification of polymer brushes on polymer foils. *Langmuir* 27:6855–6861
5. Barbey R, Lavanant L, Paripovic D, Schuwer N, Sugnaux C, Tugulu S, Klok HA (2009) Polymer brushes via surface-initiated controlled radical polymerization: Synthesis, characterization, properties, and applications. *Chem Rev* 109:5437–5527
6. Zhang GZ, Wu C (2009) Quartz crystal microbalance studies on conformational change of polymer chains at interface. *Macromol Rapid Commun* 30:328–335
7. Alexander S (1977) Adsorption of chain molecules with a polar head a-scaling description. *J Phys-Paris* 38:983–987

8. de Gennes PG (1980) Conformations of polymers attached to an interface. *Macromolecules* 13:1069–1075
9. Milner ST (1991) Polymer brushes. *Science* 251:905–914
10. Halperin A, Tirrell M, Lodge TP (1992) Tethered chains in polymer microstructures. *Adv Polym Sci* 100:31–71
11. Zhao B, Brittain WJ (2000) Polymer brushes: surface-immobilized macromolecules. *Prog Polym Sci* 25:677–710
12. Fleer GJ, Cohen Stuart MA, Scheutjens JMHM, Cosgrove T, Vincent B (1993) *Polymers at Interfaces*. Chapman & Hall, UK
13. R  he J, Ballauff M, Biesalski M, Dziezok P, Grohn F, Johannsmann D, Houbenov N, Hugenberg N, Konradi R, Minko S, Motornov M, Netz RR, Schmidt M, Seidel C, Stamm M, Stephan T, Usov D, Zhang HN (2004) Polyelectrolyte brushes. *Adv Polym Sci* 165:79–150
14. Tagliazucchi M, Szleifer I (2012) Stimuli-responsive polymers grafted to nanopores and other nano-curved surfaces: structure, chemical equilibrium and transport. *Soft Matter* 8:3292–3305
15. Stuart MAC, Huck WTS, Genzer J, Muller M, Ober C, Stamm M, Sukhorukov GB, Szleifer I, Tsukruk VV, Urban M, Winnik F, Zauscher S, Luzinov I, Minko S (2010) Emerging applications of stimuli-responsive polymer materials. *Nat Mater* 9:101–113
16. Dukes D, Li Y, Lewis S, Benicewicz B, Schadler L, Kumar SK (2010) Conformational transitions of spherical polymer brushes: synthesis, characterization, and theory. *Macromolecules* 43:1564–1570
17. Zhang GZ (2004) Study on conformation change of thermally sensitive linear grafted poly (N-isopropylacrylamide) chains by quartz crystal microbalance. *Macromolecules* 37:6553–6557
18. Liu GM, Zhang GZ (2005) Reentrant behavior of poly (N-isopropylacrylamide) brushes in water–methanol mixtures investigated with a quartz crystal microbalance. *Langmuir* 21:2086–2090
19. Liu GM, Zhang GZ (2005) Collapse and swelling of thermally sensitive poly (N-isopropylacrylamide) brushes monitored with a quartz crystal microbalance. *J Phys Chem B* 109:743–747
20. Cheng H, Liu GM, Wang CQ, Zhang GZ, Wu C (2006) Collapse and swelling of poly (N-isopropylacrylamide-co-sodium acrylate) copolymer brushes grafted on a flat SiO₂ surface. *J Polym Sci Polym Phys* 44:770–778
21. Liu GM, Zhang GZ (2008) Periodic swelling and collapse of polyelectrolyte brushes driven by chemical oscillation. *J Phys Chem B* 112:10137–10141
22. Xia HW, Hou Y, Ngai T, Zhang GZ (2010) pH induced DNA folding at interface. *J Phys Chem B* 114:775–779
23. Hou Y, Liu GM, Wu Y, Zhang GZ (2011) Reentrant behavior of grafted poly (sodium styrenesulfonate) chains investigated with a quartz crystal microbalance. *Phys Chem Chem Phys* 13:2880–2886
24. Wang XW, Liu GM, Zhang GZ (2011) Conformational behavior of grafted weak polyelectrolyte chains: effects of counterion condensation and nonelectrostatic anion adsorption. *Langmuir* 27:9895–9901
25. Schild HG (1992) Poly (N-isopropylacrylamide)-experiment, theory and application. *Prog Polym Sci* 17:163–249
26. Wu C, Zhou SQ (1995) Laser-light scattering study of the phase-transition of poly (N-isopropylacrylamide) in water. I Single-chain. *Macromolecules* 28:8381–8387
27. Grest GS, Murat M (1994) Monte carlo and molecular dynamics simulations in polymer science. In: Binder K (ed). Clarendon, Oxford
28. Takei YG, Aoki T, Sanui K, Ogata N, Sakurai Y, Okano T (1994) Dynamic contact-angle measurement of temperature-responsive surface-properties for poly (N-Isopropylacrylamide) grafted surfaces. *Macromolecules* 27:6163–6166
29. Zhang J, Pelton R, Deng YL (1995) Temperature-dependent contact angles of water on poly (N-isopropylacrylamide) gels. *Langmuir* 11:2301–2302

30. Balamurugan S, Mendez S, Balamurugan SS, O'Brien MJ, Lopez GP (2003) Thermal response of poly (N-isopropylacrylamide) brushes probed by surface plasmon resonance. *Langmuir* 19:2545–2549
31. Minko S (2008) Polymer surfaces and interfaces. In: Stamm M. (ed). Springer, Berlin
32. Sauerbrey G (1959) Verwendung von schwingquarzen zur wägung dünner schichten und zur mikrowägung. *Z Phys* 155:206–222
33. Voinova MV, Rodahl M, Jonson M, Kasemo B (1999) Viscoelastic acoustic response of layered polymer films at fluid-solid interfaces: continuum mechanics approach. *Phys Scr* 59:391–396
34. Wu C, Zhou SQ (1995) Thermodynamically stable globule state of a single poly (N-isopropylacrylamide) chain in water. *Macromolecules* 28:5388–5390
35. Winnik FM, Ringsdorf H, Venzmer J (1990) Methanol water as a co-nonsolvent system for poly (N-isopropylacrylamide). *Macromolecules* 23:2415–2416
36. Amiya T, Hirokawa Y, Hirose Y, Li Y, Tanaka T (1987) Reentrant phase-transition of N-isopropylacrylamide gels in mixed-solvents. *J Chem Phys* 86:2375–2379
37. Zhang GZ, Wu C (2001) The water/methanol complexation induced reentrant coil-to-globule-to-coil transition of individual homopolymer chains in extremely dilute solution. *J Am Chem Soc* 123:1376–1380
38. Tanaka F, Koga T, Winnik FM (2008) Temperature-responsive polymers in mixed solvents: competitive hydrogen bonds cause cononsolvency. *Phys Rev Lett* 101:028302
39. Auroy P, Auvray L (1992) Collapse-stretching transition for polymer brushes-preferential solvation. *Macromolecules* 25:4134–4141
40. Forster S, Schmidt M (1995) Polyelectrolytes in solution. *Adv Polym Sci* 120:51–133
41. Zhou F, Hu HY, Yu B, Osborne VL, Huck WTS, Liu WM (2007) Probing the responsive behavior of polyelectrolyte brushes using electrochemical impedance spectroscopy. *Anal Chem* 79:176–182
42. Schuwer N, Klok HA (2011) Tuning the pH sensitivity of poly (methacrylic acid) brushes. *Langmuir* 27:4789–4796
43. Gebhardt JE, Fuerstenau DW (1983) Adsorption of polyacrylic-acid at oxide water interfaces. *Colloid Surf* 7:221–231
44. Williamson DH, Denny PW, Moore PW, Sato S, McCready S, Wilson RJM (2001) The in vivo conformation of the plastid DNA of *Toxoplasma gondii*: implications for replication. *J Mol Biol* 306:159–168
45. Gueron M, Leroy JL (2000) The i-motif in nucleic acids. *Curr Opin Struc Biol* 10:326–331
46. Simmel FC, Dittmer WU (2005) DNA nanodevices. *Small* 1:284–299
47. Hsiao PY, Luijten E (2006) Salt-induced collapse and reexpansion of highly charged flexible polyelectrolytes. *Phys Rev Lett* 97:148301
48. Grosberg AY, Nguyen TT, Shklovskii BI (2002) Colloquium: the physics of charge inversion in chemical and biological systems. *Rev Mod Phys* 74:329–345
49. Collins KD (2004) Ions from the Hofmeister series and osmolytes: effects on proteins in solution and in the crystallization process. *Methods* 34:300–311
50. Manning GS (2007) Counterion condensation on charged spheres, cylinders, and planes. *J Phys Chem B* 111:8554–8559
51. Bostrom M, Williams DRM, Ninham BW (2002) The influence of ionic dispersion potentials on counterion condensation on polyelectrolytes. *J Phys Chem B* 106:7908–7912
52. Satoh M, Kawashima T, Komiyama J (1991) Competitive counterion binding and dehydration of polyelectrolytes in aqueous-solutions. *Polymer* 32:892–896
53. An SW, Thomas RK (1997) Determination of surface pKa by the combination of neutron reflection and surface tension measurements. *Langmuir* 13:6881–6883
54. Maison W, Kennedy RJ, Kemp DS (2001) Chaotropic anions strongly stabilize short, N-capped uncharged peptide helices: a new look at the perchlorate effect. *Angew Chem Int Ed* 40:3819–3821
55. Baldwin RL (1996) How Hofmeister ion interactions affect protein stability. *Biophys J* 71:2056–2063

QCM-D Studies on Polymer Behavior at Interfaces

Liu, G.; Zhang, G.

2013, VIII, 81 p. 59 illus., 19 illus. in color., Softcover

ISBN: 978-3-642-39789-9