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Water and Moisture Uptake by Plasma Polymerized Thermoresponsive Hydrogel Films

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ABSTRACT: Water and moisture uptake characteristics of plasma polymerized *N*-isopropylacrylamide (pNIPAAm) hydrogel films, deposited under different reactor process conditions, have been studied using a quartz crystal microbalance with dissipation monitoring. Trends in frequency and dissipation values during water/moisture sorption studies indicated that the pNIPAAm thin films were thermoresponsive. Deposition at higher substrate temperatures and lower reactor pressures, where electron and ion temperatures are high, yielded films with relatively high moisture uptake capacity under ambient humidity conditions. In contrast, pNIPAAm films deposited at lower substrate temperatures and higher pressures, where cross-link densities are reduced, showed relatively low moisture uptake. These results are consistent with the hydrogen-bonding characteristics of the pNIPAAm films.

Introduction

Hydrogels are three-dimensional polymer networks that swell in aqueous solutions while maintaining their integrity. "Intelligent" hydrogels respond to a variety of stimuli such as pH,[1] temperature,[2] electric field,[3] light,[4] and stress[5] through volume or conformation changes. The macroscopic changes are a result of fast, reversible changes at the microscopic level and have led to novel applications in drug delivery,[6,7] bioseparations,[8] sensors,[9] and intelligent surfaces.[10] Poly(*N*-isopropylacrylamide) (poly(NIPAAm)), a widely studied thermoresponsive polymer, exhibits inverse temperature solubility in aqueous solutions as a result of a volume phase transition analogous to lower critical solution transition (LCST) temperature in single linear chains. While a variety of techniques are available to study the LCST transition in bulk hydrogels, the number of analytical methods to characterize the thermoresponsive properties of thin films is limited. Furthermore, the presence of a constraining substrate in thin films makes interpretation of the results difficult. Nevertheless, several investigators have studied the LCST type of transition in poly(NIPAAm) thin films using optical techniques such as surface plasmon resonance[11−13] and ellipsometry,[14] surface analytical techniques such as static[15] and dynamic contact angle[16−18] measurements, and atomic force microscopy.[19]

In addition to the analytical techniques mentioned above, temperature-dependent quartz crystal microbalance (QCM) measurements may be used to study mass changes associated with NIPAAm thin films upon exposure to water vapor (moisture) and liquid water. Early applications of the QCM were in air or vacuum to monitor adsorption and deposition processes. On the basis of the well-known Sauerbrey relationship, it was possible to relate frequency changes of the QCM to added mass through the crystal constant.[20] After the development of oscillation circuits to ensure stable operation in liquids,[21] the QCM technique gained more widespread use, especially in electrochemistry[22] and as a transducer for gravimetric sensors in the biomedical field.[23] With the advent of the quartz crystal microbalance with dissipation (QCM-D) technique, QCM methods can be used to monitor not only the frequency changes associated with mass changes of a thin film on the oscillating crystal but also the dissipation factor, which provides information on the mechanical properties of thin films.[24]

The dissipation factor, *D*, which is defined as the reciprocal of the quality factor, *Q*, of the oscillation of the quartz crystal, represents the ratio of the energy dissipation to the stored energy during an oscillation. Thus, when the oscillation of a quartz crystal is damped by the presence of a lossy material, the dissipation factor will be higher than when the oscillation is not damped. Since immersion of a quartz crystal in a liquid will damp the oscillation, the dissipation factor in liquids is higher than that in air or vacuum. Furthermore, a viscoelastic polymer layer on a QCM will show greater dissipation than a rigid, elastic film. Therefore, the dissipation factor may be used to determine mechanical properties of various materials coated on a quartz crystal in a QCM.

The QCM-D method has been used to study absorption, swelling kinetics, and mechanical properties of various polymer films and gels.[25−29] Furthermore, temperature-dependent QCM-D studies have been performed to study the swelling and conformation changes associated with un-cross-linked, solution polymerized NIPAAm chains grafted to SiO_2-coated quartz crystal resonators.[30−33] On the basis of the frequency and dissipation changes at various temperatures, the authors were able to study the coil-to-globule transition in the grafted NIPAAm chains; in contrast to the sharp coil-to-globule transition found in linear NIPAAm chains in solution, the grafted NIPAAm chains showed a continuous transition in the temperature range 20−38 °C.

Plasma polymerization produces randomly cross-linked polymeric networks; properties of plasma polymers (e.g., cross-link density) can be controlled by variation of reactor conditions such as substrate temperature, reactor operating pressure, applied RF power, and precursor flow rates. We reported previously that plasma polymerized NIPAAm thin films, referred to as pNIPAAm hereafter, obtained under different process conditions of reactor pressure and substrate temperature showed different chemical bonding characteristics.[34] In particular, films obtained at higher reactor pressures and lower substrate temperatures showed strong intermolecular hydrogen bonding and a high percentage loss in film thickness upon exposure to liquid water

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possibly due to lack of adequate cross-linking. Conversely, pNIPAAm films obtained at lower reactor pressures and higher substrate temperatures showed negligible intermolecular hydrogen bonding and a negligible or positive change in film thickness upon exposure to water.

Previous reports on pNIPAAm films have focused on characterizing the thermoresponsive properties through a variety of surface analytical techniques,[19,35−37] but details on the bulk material properties such as water and moisture uptake characteristics were not provided. Specifically, we are not aware of any QCM-D studies of water and moisture uptake characteristics of pNIPAAm films. Furthermore, to our knowledge, no attempts were made to vary the cross-link density of plasma polymerized hydrogel films by changing the reactor processing conditions. In this study, we correlate the water and moisture uptake characteristics of NIPAAm films prepared under different reactor conditions to their physicochemical properties through QCM-D studies and thus confirm the existence of an LCST type of transition. Knowledge of moisture and water uptake characteristics of plasma polymerized hydrogel films will assist in the development of chemical/biomolecule sensitive films for sensor applications. Since pNIPAAm films are deposited from the vapor phase, the necessary cross-linking and adhesion properties may be built into the films during deposition. With this approach, the incorporation and integration of these films into sensors and other electronic devices is facilitated relative to grafting or spin-casting methods of film formation.[38,39]

Experimental Section

Plasma polymerized NIPAAm thin films were prepared in a 13.56 MHz, parallel plate reactor at temperatures of either 120 or 175 °C and pressures of either 93.3 or 133.3 Pa. A 1:1 volumetric mixture of argon and NIPAAm vapor was fed into the reactor. Details of the reactor configuration, thin film deposition methods, and film characterization have been published previously.[34,40] To investigate the water uptake and moisture sorption characteristics of the pNIPAAm films obtained under different process conditions, QCM-D studies were performed at various temperatures between 20 and 40 °C.

pNIPAAm thin films were deposited onto quartz crystal sensors (QCM) (Q-Sense, Newport Beach, CA) coated with ∼50 nm silicon/silicon dioxide (Si/SiO_2) to study their water uptake and moisture sorption characteristics. Immediately after deposition, the films were rinsed in deionized water three times to remove the un-cross-linked monomers or polymer chains. Subsequently, the film thickness was measured using variable angle spectroscopic ellipsometry. All pNIPAAm films used in this study had a nominal thickness of 100 nm.

The behavior of pNIPAAm thin films in liquid water was monitored at different temperatures through frequency and dissipation changes in the QAFC 302 flow cell of the QCM-D apparatus. First, a quartz crystal coated with pNIPAAm was mounted in the QCM-D flow cell; the temperature of the flow cell was allowed to stabilize at 20 ± 0.1 °C; subsequently, deionized (DI) water flow was initiated. After this initial purge, the flow of DI water was terminated and the pNIPAAm-coated QCM exposed to a constant quantity of liquid water (∼80 μL) for the remainder of the experiment. Since the flow of DI water caused a temperature change, additional time was allowed for the temperature to stabilize at the set point. After temperature stabilization, frequency and dissipation data were acquired. Data acquisition continued at a given temperature until stable readings of the frequency and dissipation data were attained. Similarly, frequency and dissipation data were acquired at other temperatures between 18 and 40 °C. According to the manufacturer, temperature stability of the QAFC 302 flow cell is ±0.02 °C; however, in our laboratory, temperatures were stable up to ±0.1 °C. At each temperature, the time required for the frequency and dissipation values to stabilize was ∼20 min.

Moisture sorption experiments were also performed in the QAFC 302 flow cell at three different temperatures: 18 ± 0.1 °C, 25 ± 0.1 °C, and 35 ± 0.1 °C. After loading a pNIPAAm-coated quartz crystal into the QCM-D apparatus, the flow cell base and the crystal were brought to the set temperature. Subsequently, the flow cell was purged with dry N_2 for 30 min to remove background moisture contained in the pNIPAAm films. At the end of 30 min and while dry N_2 was still flowing, data acquisition was initiated. Dry N_2 flow continued for an additional 5 min before the QCM was exposed to ambient humidity. The relative humidity in the laboratory during these experiments was ∼40%; all future references to ambient humidity in this paper should be taken to mean a relative humidity of ∼40%. The data values recorded in the dry N_2 environment served as a baseline for subsequent measurements. Frequency and dissipation values of the pNIPAAm coated quartz crystal were recorded in ambient humidity for ∼60 min after the N_2 flow was terminated. At this point, the rate of decrease in the frequency due to moisture uptake had slowed to less than 2 Hz every 15 min. Following exposure to ambient humidity, the quartz crystal was exposed to dry N_2 to remove the sorbed moisture from the pNIPAAm films.

All frequency and dissipation factor changes reported in this study were determined by subtracting the value of frequency or dissipation of the bare crystal from the value measured for the pNIPAAm coated quartz crystal at each temperature. Since the frequency and dissipation factor of the bare quartz crystal can vary with temperature, the values of frequency and dissipation were determined at various temperatures between 20 and 40 °C prior to depositing pNIPAAm on the quartz crystal resonators.

Results and Discussion

Water and moisture uptake measurements of pNIPAAm thin films were obtained for films deposited under four different conditions of substrate temperature and reactor pressure: 120 °C, 133.3 Pa (process condition A), 120 °C, 93.3 Pa (process condition (B), 175 °C, 133.3 Pa (process condition C), and 175 °C, 93.3 Pa (process condition D). However, because of film dissolution during water rinsing, only results from films prepared using the latter three process conditions are presented below. That is, when pNIPAAm thin films prepared at a substrate temperature of 120 °C and a reactor pressure of 133.3 Pa are exposed to liquid water to remove un-cross-linked chains and monomer from the network, the film thickness decreases to ∼15% of its original value, apparently due to the lack of adequate cross-linking. The reduction in film thickness causes considerable roughening of the film surface; as a result, it can no longer be considered a homogeneous overlayer on the quartz crystal. Thus, thickness measurements with variable-angle spectroscopic ellipsometry were not possible due to scattering from the rough surface of the pNIPAAm films. Furthermore, we believe that the QCM-D data from such films may not be reliable since the increased surface area of the film can enhance water retention.

Water Uptake Measurements. The normalized frequency and dissipation values for overtones 3, 5, and 7 of quartz crystals coated with pNIPAAm prepared using process conditions B, C, and D are shown in Figures 1, 2, and 3, respectively. Since the trend in the fundamental frequency and dissipation factor with temperature was inconsistent with that observed in the case of 3rd, 5th, and 7th overtones, they were not included in the following analysis. Indeed, such behavior, believed to be caused by poor energy trapping due to the small size of the crystal, has been reported by other investigators.[28,41] Furthermore, in a previous study, the authors use only the 3rd overtone of the frequency and dissipation to draw conclusions on the conformation changes in poly(NIPAAm) chains with temperature.[31,32] Since the normalized frequency values for the three different

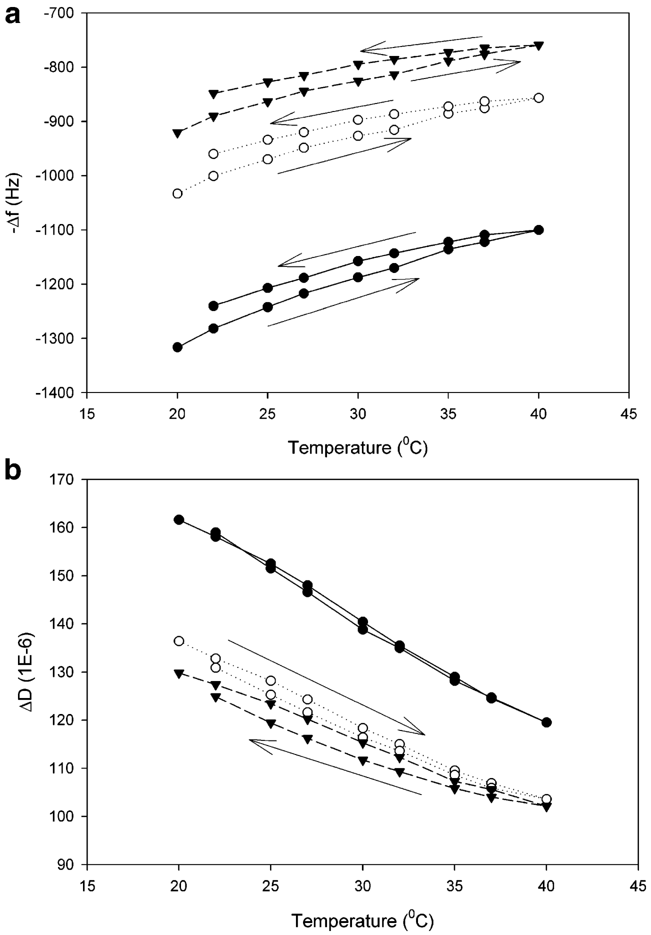

Figure 1. Process condition B (substrate temperature = 120 °C; reactor pressure = 93.3 Pa). Variation of $-\Delta f$ (a) and ΔD (b) with temperature: $n = 3$ (●); $n = 5$ (○); $n = 7$ (▼).

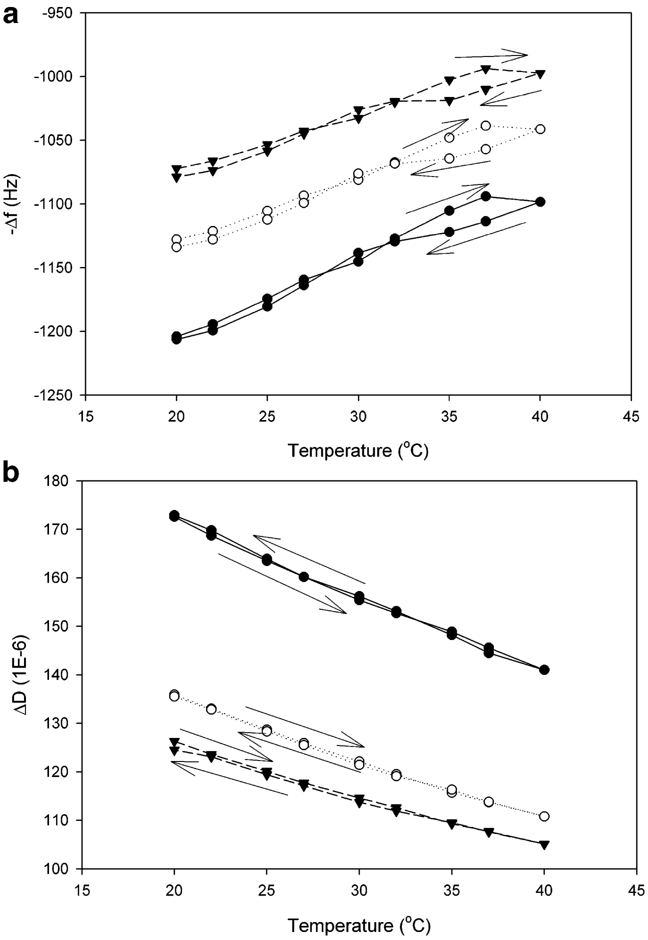

Figure 2. Process condition C (substrate temperature = 175 °C; reactor pressure = 133.3 Pa). Variation of $-\Delta f$ (a) and ΔD (b) with temperature: $n = 3$ (●); $n = 5$ (○); $n = 7$ (▼).

overtones do not collapse to a single set of values, the pNIPAAm films are frequency-dependent and hence may be viscoelastic. Therefore, the Sauerbrey formalism to determine water uptake capacities is not applicable.

Figures 1, 2, and 3 indicate that frequency and dissipation values of the pNIPAAm films are temperature-dependent. The values of $|\Delta f|$ are higher at lower temperatures and decrease as temperature increases. This indicates that the pNIPAAm films take up water at the lower temperatures and reject it at higher temperatures. In the temperature range studied, the transition between the hydrophilic and hydrophobic states appears continuous and essentially reversible. Similarly, the values of ΔD decrease with an increase in temperature. The trend in dissipation values supports the inference from $|\Delta f|$ values: when the pNIPAAm films are hydrophilic at lower temperatures, increased water absorption causes the films to show greater deviation from a pure elastic behavior, resulting in greater dissipation. At higher temperatures, the observed lower dissipation values are consistent with a more rigid polymeric network with reduced water content as indicated by the frequency changes. The overall change in Δf with temperature, as a result of the hydration/dehydration of the pNIPAAm network, is ~150 Hz and is comparable to the change observed in NIPAAm chains grafted to the QCM surface; however, the overall change in ΔD with temperature is higher than that reported in previous investigations.[31,32]

Previous studies have demonstrated that plots of ΔD vs $-\Delta f$ or $-\Delta D/\Delta f$ vs temperature display changes in D (possibly due to structure or conformation changes) and f (due to changes in coupled mass) and therefore permit the two processes to be monitored simultaneously.[42] The importance of such approaches has been demonstrated for surface grafted poly(NIPAAm) chains; although the variation of $-\Delta f$ and ΔD with temperature was continuous, plots of ΔD vs $-\Delta f$ and $-\Delta D/\Delta f$ vs temperature revealed changes in the slope at ~30 °C, close to the well-accepted LCST temperature of NIPAAm chains in water.[30−33] On the basis of these changes in slope, swelling and collapse behavior of poly(NIPAAm) chains was inferred.

Figure 4 shows the variation of $-\Delta D/\Delta f$ (based on the 3rd overtone) with temperature for pNIPAAm films deposited under process conditions B, C, and D. Except for minor changes in the slopes, variation of $-\Delta D/\Delta f$ appears continuous with temperature, suggesting that hydration/dehydration of the NIPAAm network and the corresponding mechanical property changes occur simultaneously. At higher temperatures, $-\Delta D/\Delta f$ is reduced relative to that at lower temperatures, suggesting that the dissipation per unit mass is lower at higher temperatures. This is consistent with the LCST type of transition expected for NIPAAm films. Furthermore, at all temperatures studied, the value of $-\Delta D/\Delta f$ was highest for pNIPAAm films prepared under process condition D, indicating that these films show the highest dissipation per unit mass of coupled water, possibly due to greater water uptake relative to that of the other films. The results from Figure 4 are in contrast to previous results reported for surface grafted poly(NIPAAm) chains,[31] where $-\Delta D/\Delta f$ was constant with temperature in the range of 20−30 °C but increased at $T > 30$ °C. An explanation for such a transition was not offered. However, in a different study on conformation

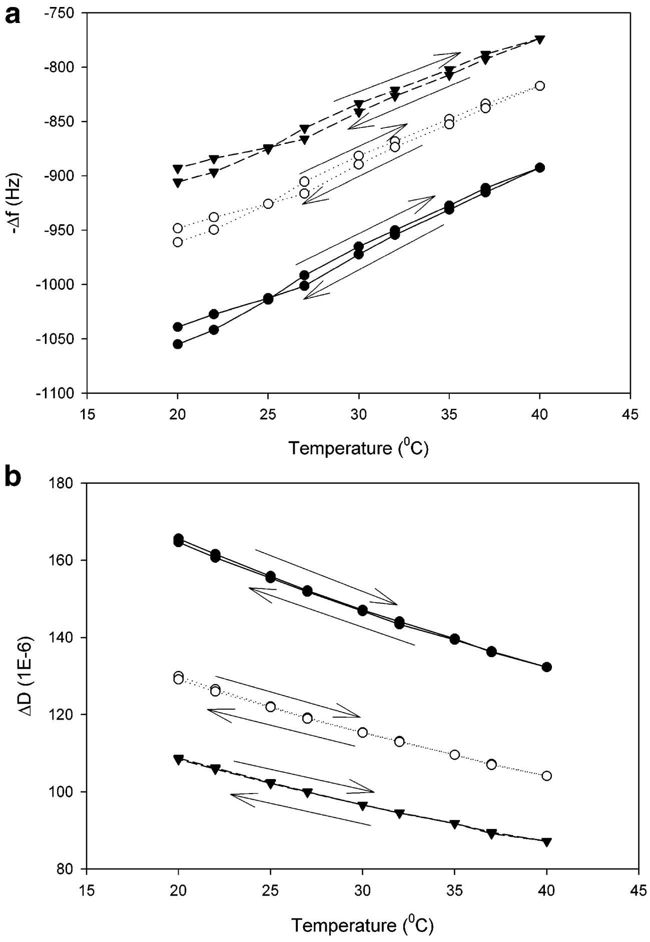

Figure 3. Process condition D (substrate temperature = 175 °C; reactor pressure = 93.3 Pa). Variation of $-\Delta f$ (a) and ΔD (b) with temperature: $n = 3$ (●); $n = 5$ (○); $n = 7$ (▼).

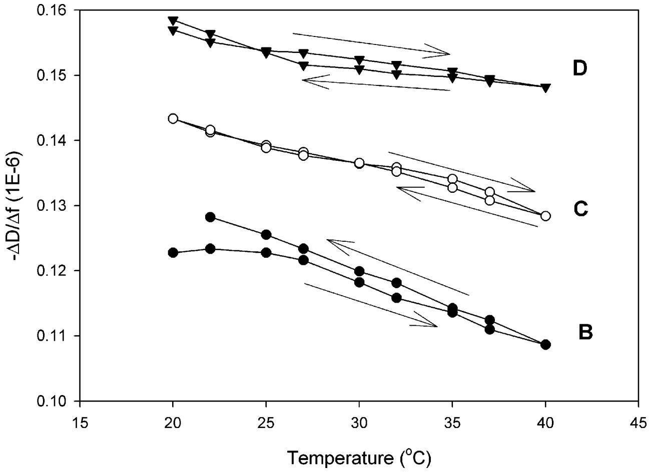

Figure 4. Plot of $-\Delta D/\Delta f$ with temperature: process condition B (120 °C, 93.3 Pa) (●); process condition C (175 °C, 133.3 Pa) (○); process condition D (175 °C, 93.3 Pa) (▼).

changes in adsorbed poly(NIPAAm) chains on QCM surfaces, the variation of $-\Delta D/\Delta f$ with temperature was similar to our results in that $-\Delta D/\Delta f$ varied continuously with temperature; in addition, the range of values obtained for $-\Delta D/\Delta f$ in our study (∼0.16−0.10) match those obtained in their study.[30] The values of $-\Delta D/\Delta f$ obtained in this study are also in close agreement with the theoretical value of 0.13 predicted for the 3rd overtone, based on a quantitative analysis of the oscillation of the quartz crystal resonator in liquids.[43,44]

Over the temperature range studied in the current investigation, the existence of a continuous rather than a discontinuous transition for the pNIPAAm films is plausible. In fact, temperature-dependent sessile contact angle measurements on the pNIPAAm films showed the existence of a broad transition with transition temperatures (at the inflection points of the sigmoidal curves) below 20 °C.[34] Since plasma polymerization is likely to produce a randomly cross-linked network with a broad range of polymer chain lengths between cross-links, a wide spectrum of collapse rates may be expected. In addition to the continuous transition that is expected in inhomogeneous networks,[45] the constraint due to adhesion of the films to the substrate causes continuous transitions that are controlled by kinetic rather than purely thermodynamic processes.[46]

Moisture Sorption Experiments. The results from moisture sorption experiments performed on pNIPAAm films prepared using conditions B, C, and D are shown in Figure 5a−c. Specifically, Figure 5a−c shows the variation of the swelling factor, *Q*, with time$^{1/2}$ at three different temperatures. The swelling factor, *Q*, at a given temperature may be defined[47] as the ratio of the frequency of pNIPAAm-coated quartz crystal exposed to ambient humidity to the frequency of pNIPAAm-coated quartz crystal measured in dry N_2; both frequencies are expressed relative to that of the bare crystal. The swelling factor, *Q*, was calculated for all three process conditions from changes in the 3rd overtone of the fundamental frequency (∼15 MHz) of the QCM data. Since the normalized frequencies for all overtones collapsed to that of the fundamental frequency, it is possible to use the Sauerbrey relationship to calculate the moisture uptake capacity.

Figure 5a−c demonstrates that the moisture sorption process in pNIPAAm thin films follows non-Fickian kinetics since the initial portion of the integral sorption curve is not linear with the square root of time. Furthermore, there is no definitive saturation level in the sorption curve; at the end of 60 min, the sorption process appears to reach a pseudo-equilibrium state. The observed nonlinear sorption process is consistent with sigmoidal behavior at short times and two-stage sorption at longer times.[48] Sigmoidal sorption processes occur due to a time dependence of the penetrant surface concentration and slow establishment of equilibrium at the surface.[49] The variable surface concentration (VCS) model, which assumes a constant diffusivity for Fickian diffusion and a variable surface concentration, gives a satisfactory description of the sigmoidal behavior. The two-stage sorption is believed to occur due to polymer relaxation effects.[50]

In addition to the kinetics of the sorption process, it is important to consider the moisture uptake capacities of the pNIPAAm films at different temperatures. Values of the swelling ratio, *Q*, at the end of the 60 min sorption process are plotted in Figure 6 as a function of the process condition employed to prepare NIPAAm films; the error bars in Figure 6 are fractional errors in the swelling ratio computed from systematic errors in the measured frequency values. Uncertainty in the measured frequency values was determined by measuring the frequency by mounting and dismounting the quartz crystal resonator in the flow cell several times. Indeed, other investigators have reported on the introduction of such systematic errors in the measurement of frequency values.[28,41]

From Figure 6, it is clear that for pNIPAAm films prepared at 175 °C the sorption capacity of the films decreases continuously from 18 to 35 °C, thus confirming the thermoresponsive properties of the films. However, for the pNIPAAm film obtained at 120 °C, 93.3 Pa, while the sorption capacity is

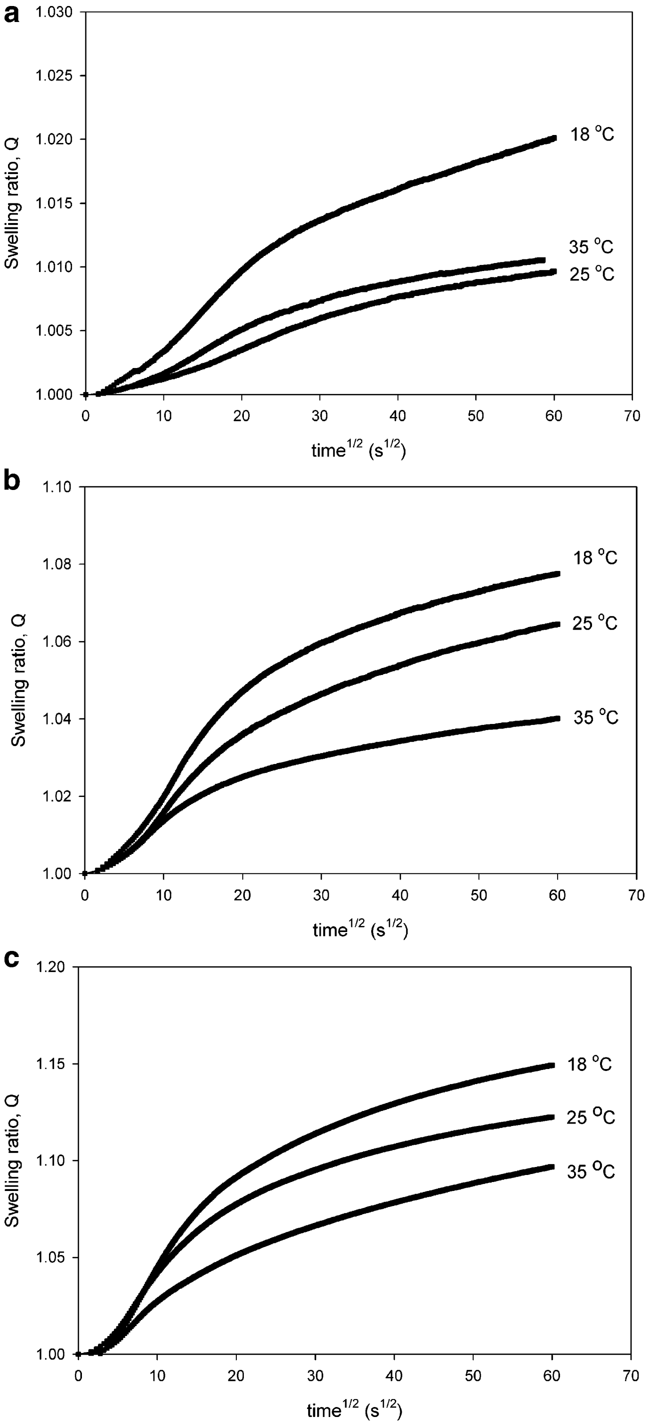

Figure 5. (a) Process condition B (substrate temperature = 120 °C, reactor pressure = 93.3 Pa): absorption kinetics from ambient air (relative humidity ~ 40%). (b) Process condition C (substrate temperature = 175 °C, reactor pressure = 133.3 Pa): absorption kinetics from ambient air (relative humidity ~ 40%). (c) Process condition D (substrate temperature = 175 °C, reactor pressure = 93.3 Pa): absorption kinetics from ambient air (relative humidity ~ 40%).

highest at 18 °C, the sorption capacities at 25 and 35 °C differ only by 0.1%; the value of Q at 25 °C is 1.01, whereas at 35 °C it is 1.011. We believe that this discrepancy may be due to the difficulty involved in accurately determining swelling ratios that are already small (swelling ratio = 1.02 at 18 °C).

Furthermore, Figure 6 shows that at all temperatures the swelling ratio is highest for pNIPAAm films prepared using condition D. At first glance, this result seems counterintuitive because our previous results[34] suggested that due to the greater electron and ion energies in the plasma reactor at increased substrate temperatures and low reactor pressures, the resulting pNIPAAm films possess higher cross-link density. In fact, when such films are exposed to liquid water immediately after the deposition to extract the un-cross-linked chains, there is either a positive or negligible change in the film thickness; in contrast, similar studies on pNIPAAm films deposited at lower substrate temperatures and higher reactor pressures resulted in large negative changes in the film thickness. Since films with greater cross-link density are able to exert greater elastic forces, they resist the expansion of the polymer matrix due to water/moisture uptake. Therefore, films with greater cross-link density should show lower swelling ratios.

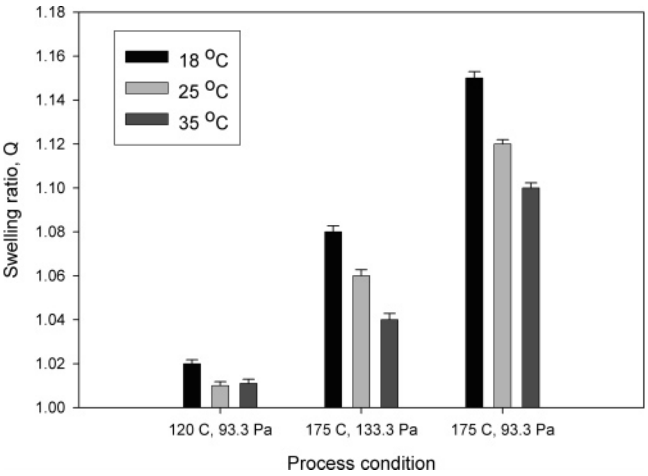

Figure 6. Comparison of moisture uptake capacities, through swelling ratio, Q.

In addition to the differences in cross-link densities, it is necessary to consider the changes in chemical bonding characteristics of pNIPAAm films prepared under different process conditions. We have previously shown that based on the positions of amide I and II bands in the Fourier transform infrared spectra deposition at higher substrate temperatures and lower reactor pressures generate pNIPAAm films with weak hydrogen-bonding characteristics.[34] Conversely, pNIPAAm films deposited at lower substrate temperatures and higher reactor pressure display stronger hydrogen bonding. The existence of strong intermolecular hydrogen bonding can hinder the ingress of moisture or water in the polymeric network since the polar groups are not available for hydrogen bonding with the penetrant.

Indeed, the effect of hydrogen bonding on moisture and water uptake capacity has been studied in other polymeric systems. Because of strong intermolecular hydrogen bonding at pH values less than the critical pH of a cross-linked network of poly(vinylpyrrolidinone)−poly(acrylic acid), the swelling ratio of the network was considerably lower relative to the swelling ratio in a solution with pH higher than the critical pH of the network.[51] At higher values of pH, because of ionization of the carboxylic acid groups of acrylic acid, the intermolecular hydrogen bonding diminishes and thus causes greater swelling.

Other studies have demonstrated that although a decrease in water uptake capacity with increase in cross-linking in partially cross-linked hydrogels (based on carboxymethylcellulose) is observed, the completely cross-linked hydrogel showed the greatest water uptake capacity.[52] Furthermore, the partially cross-linked hydrogels showed pH-dependent swelling behavior due to the ionization of carboxylic acid groups, whereas the 100% cross-linked hydrogel did not. This behavior has been attributed to the effects of hydrogen bonding; the partially cross-linked hydrogels possessed considerable hydrogen bonding which diminished the water uptake capacity. On the other hand, the completely cross-linked hydrogel showed negligible hydrogen bonding and thus was able to swell to a greater extent. Again, evidence of hydrogen bonding in the hydrogels was obtained from amide I and II bands of the FTIR spectra.

Thus, pNIPAAm films expected to possess greater cross-link density have greater moisture uptake capacity, possibly due to the lower extent of intermolecular hydrogen bonding. Conversely, pNIPAAm films with a high degree of intermolecular hydrogen bonding show smaller moisture uptake capacity. However, it is important to note that the dry N_2 purge used to dehydrate pNIPAAm films prior to moisture absorption studies may not have removed all the moisture trapped in the polymer network. It is therefore possible that the pNIPAAm film from process condition B possessed irremovable water,[53] thereby preventing the uptake of any additional moisture. This conclusion is in contrast to pNIPAAm films prepared using process condition D, which may contain less residual moisture after the dry N_2 purge and hence may allow a greater moisture uptake. In any case, it is clear that the complex interplay of hydrogen bonding and cross-link density controls the moisture uptake capacity of the pNIPAAm films.

Conclusions

Liquid water and moisture uptake characteristics of pNIPAAm films were studied between 20 and 40 °C using the QCM-D technique. Measurements in liquid water indicated that the pNIPAAm films are viscoelastic because they show frequency-dependent response. In the temperature range studied, Δf and ΔD varied continuously with temperature such that the values of $|\Delta f|$ and ΔD were higher at higher temperatures, thereby confirming the existence of an LCST type of transition. Moisture absorption studies showed that pNIPAAm films followed anomalous, non-Fickian kinetics. Intermolecular hydrogen bonding controlled the moisture uptake capacity; pNIPAAm films with a high degree of intermolecular hydrogen bonding exhibited lower moisture uptake capacities.

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