

# A study of hydrogel thermal-dynamics using Fourier transform infrared spectrometer

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## Abstract

A rapid and reliable method was presented for studying hydrogel dynamics/kinetics. Two temperature-sensitive hydrogels, poly-*N*-isopropylacrylamide (poly(NIPAAm)) and the copolymer of *N,N*-diethylacrylamide and sodium methacrylate (molar ratio=97:3, poly(NDEAAm-*co*-MAA)) were synthesized. The thermal-behaviors of the gels were studied through the absorbance intensities of both swollen water and gel frame components, and the peak positions of amide band along heating/cooling pathways under dynamic Fourier transform infrared (FTIR) probing. The results showed that the lower critical solution temperature (LCST) of poly(NIPAAm) is about 33–35 °C, which is consistent with reported value of ~34 °C. Compared to poly(NIPAAm), poly(NDEAAm-*co*-MAA) has relatively continuous volume phase transition, starting at ~35 °C and a better thermal-reversibility with similar swelling and deswelling profiles over a larger temperature range (10–80 °C for poly(NDEAAm-*co*-MAA) vs. 10–33 °C for poly(NIPAAm)). The H-bonding water along phase transition was also studied, showing a less reversibility of poly(NIPAAm) compared to poly(NDEAAm-*co*-MAA). In addition, FTIR spectrometer was also used to study the volume changes of poly(NDEAAm-*co*-MAA) under variations in environmental salinity.

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**Keywords:** Hydrogel; FTIR; Thermal-dynamics

## 1. Introduction

Cross-linked hydrogels undergo reversible and discontinuous volume changes in response to changes in environmental conditions such as temperature, pH and salinity [1,2]. When temperature is below a lower critical solution temperature (LCST), the chains of thermo-sensitive hydrogel are substantially soluble and the gel is in a swollen state. As the temperature is increased above LCST, polymer chains of the gel network collapse and aggregate abruptly, and simultaneously, pore water inside the gel is released and the size of the gel dramatically decreases. This behavior of hydrogels in aqueous solutions is considered to be closely related to the destabilization of hydrogen bonds between water molecules and amide groups with increasing temperature [3–5]. The LCSTs can be controlled by copolymerization with other monomers [6]. The addition of hydrophilic monomers

generally increases the LCST whereas the incorporation of more hydrophobic units/groups has the opposite effect.

The dramatic variation in gel volumes due to environmental changes has recently been of interest in development of functional materials and devices for various purposes, e.g. drug delivery systems [7], tissue engineering matrices [8], sensors [9] and actuators [10]. For instance, Freitas and Cussler [1] used poly-*N*-isopropylacrylamide (poly(NIPAAm)) and the copolymer of *N,N*-diethylacrylamide and sodium methacrylate (molar ratio=97:3), poly(NDEAAm-*co*-MAA) to separate proteins by molecular sizes. Poly(NIPAAm) synthesized with rapid swelling and deswelling properties (~30 s, Ref. [11]) and recent progress achieved in micro-patterning of the polymer [12] allow the hydrogels to be applicable in biochemical processes and analyses even at the micro-scale (e.g. hydrogel immobilized microorganisms for further species identification [13], and immobilized biocatalysts for biochemical assays and sensing [14]).

The dynamics as well as kinetics of swelling (or contraction) is an extremely important characteristic in the application of gels to mechanical actuation. Poly(NIPAAm) and poly(NDEAAm-*co*-MAA) are thermo-sensitive hydrogels. The LCSTs of hydrogels can be studied with a variety of experimental techniques, such as turbidity, calorimetry, light

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scattering, nuclear magnetic resonance (NMR) spectroscopy, viscosimetry, fluorescence, and attenuated total reflection (ATR)/Fourier transform infrared (FTIR) spectroscopy [15,16]. Typically, the LCSTs of hydrogels are determined by the measurement of the swelling ratio as a function of temperature [1,14], which is a time-consuming approach that can hardly provide reproducible and precise results [15]. Furthermore, thermodynamics of hydrogels are usually obtained by measuring deswelling extents of the gels through heating the gels, meanwhile the gel deswelling dynamics and kinetics are rarely studied. In addition, a variety of additives such as salts, surfactants, organic solutes and solvents have been reported to affect the phase transition of poly(NIPAAm)/water systems significantly [2,17]. Particularly, the addition of solvents may promote a drastic change in the LCST, which has been demonstrated by Costa and Freitas [18].

In this study, we investigated the thermal-dynamics/kinetics of these two hydrogel systems by using Fourier transform infrared (FTIR) spectrometer. The thermal-reversibilities of the gels and the influence of a saline environment on gel thermodynamics were also studied.

## 2. Experimental

### 2.1. Hydrogel preparation

The synthetic methods of the hydrogels were from Freitas and Cussler [1] with minor modification. Briefly,

4% Poly(NIPAAm). Monomer *N*-isopropylacrylamide (8 g), *N,N*-methylenebisacrylamide (320 mg) as a cross-linking agent and ammonium persulphate (20 mg) as an initiator

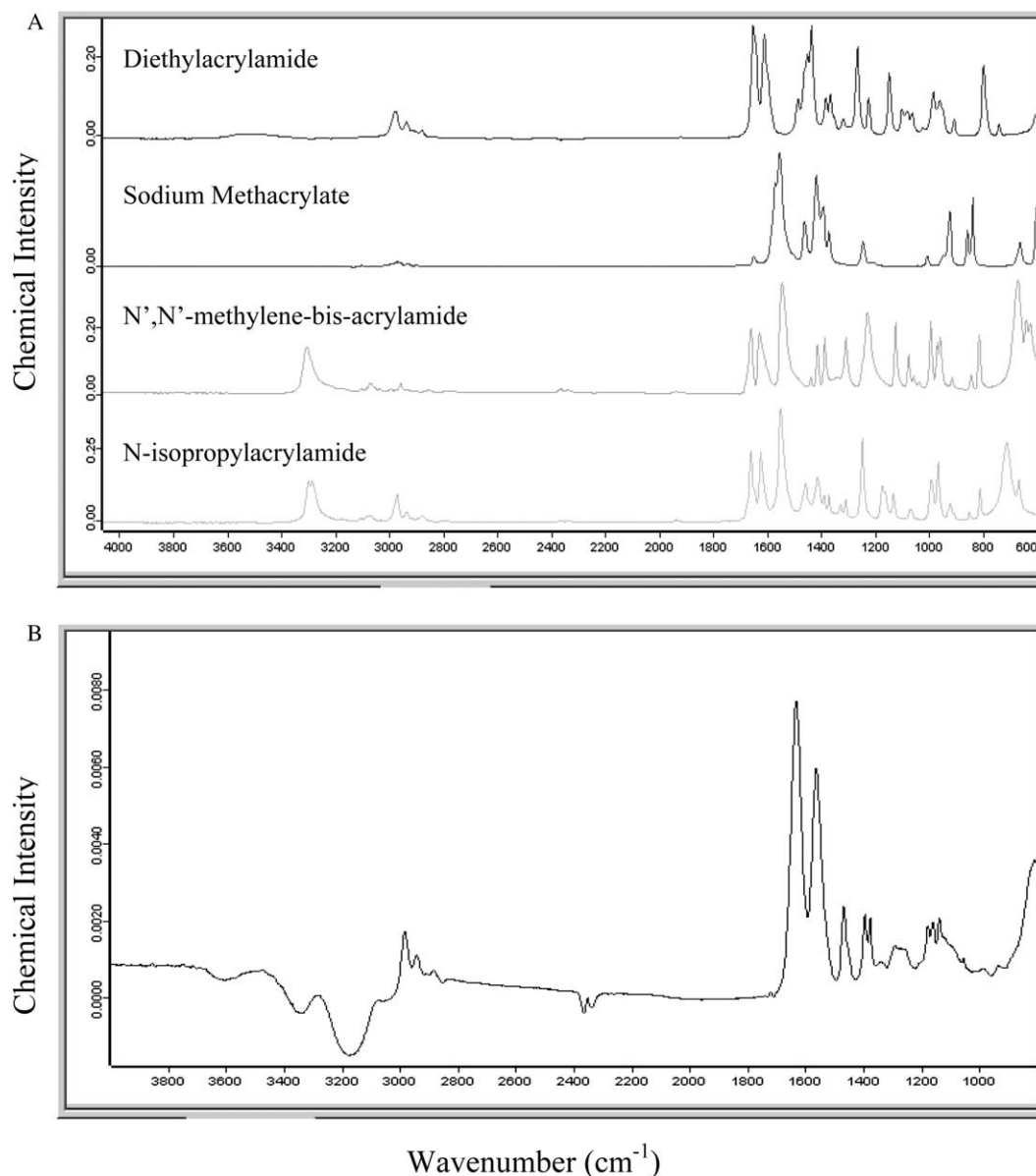


Fig. 1. FTIR spectra of (A) the hydrogel monomers and cross-linker and (B) the swollen poly(NIPAAm) after subtracting water.

were added to 200 mL of water. The solution was sparged with  $N_2$  for 5 min or until the monomer dissolved.  $N,N,N',N'$ -Tetramethylethylenediamine (TEMED, 50  $\mu$ L) was added as an accelerator, then the solution was sparged with  $N_2$  for 1 min. The reaction bottle was sealed and set without disturbance for 1 h for polymerization. The gel was washed with deionized (DI) water and cut into  $\sim 3$  mm pellets, and then dried at 50  $^\circ$ C in a vacuum oven. The gel pellets were stored in a desiccator until use.

**4% Poly(NDEAAm-co-MAA).**  $N,N$ -Diethylacrylamide (8 g), sodium methacrylate (1.2 mL of 1 M solution), and  $N,N$ -methylenebisacrylamide (320 mg), and ammonium persulfate (10 mg) were added to 200 mL of water. The solution was sparged with  $N_2$  for 5 min. TEMED (50  $\mu$ L) was added, then the solution was sparged again with  $N_2$  for 1 min and sealed for 1 h at room temperature for polymerization. The gel was washed with DI water and cut into  $\sim 3$  mm pellets, and then dried at 50  $^\circ$ C in a vacuum oven. The gel pellets were stored in a desiccator until use.

## 2.2. Swell ratio determination

The swell ratios of the hydrogels in saline (0–35‰ NaCl, w/w) solutions were determined as  $(W_e - W_d)/W_d$ , where  $W_e$  is the weight of the gel after the establishment of equilibrium (4 h) and  $W_d$  is the dry weight of the polymer. The poly(NDEAAm-co-MAA) pre-swollen in DI water and 10‰ NaCl solution were labeled as poly(NDEAAm-co-MAA)-0 and poly(NDEAAm-co-MAA)-10, respectively, for convenient reference. The experiments were conducted at 4  $^\circ$ C.

## 2.3. Thermal analysis under FTIR spectrometer

Two sets of experiment have been performed. One was for the thermal behavior of poly(NIPAAm) and poly(NDEAAm-co-MAA). In this setup, an aliquot of the swollen gels ( $\sim 10$  mg) were set in BioATRCell™ II with multiple-bounce silicon crystal for the ATR measurement. The accessory was connected to a Thermostat recirculating water bath ( $-28$  to

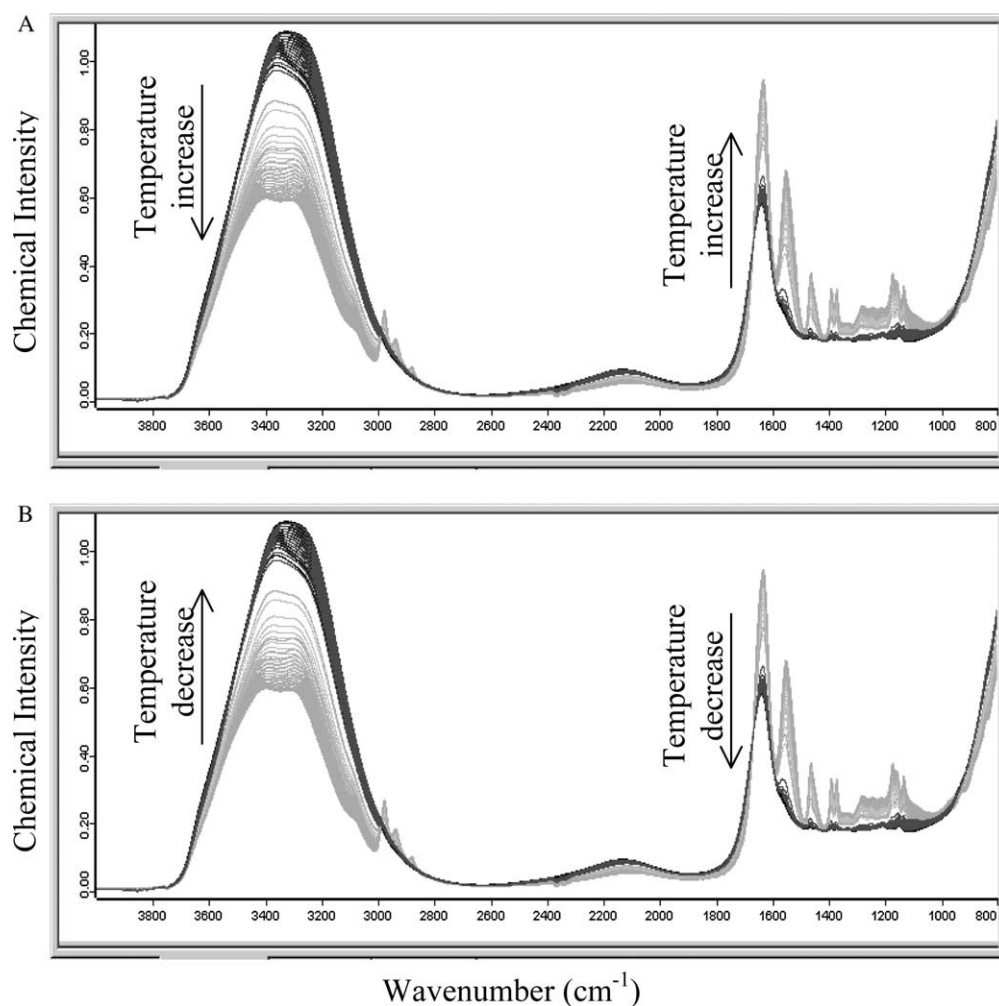


Fig. 2. The scanning FTIR-spectra of swollen 4% poly(NIPAAm) during (A) heating from 10 to 66  $^\circ$ C and (B) cooling from 66 to 10  $^\circ$ C. Water content in the hydrogel is indicated by the absorbance peak at  $\sim 3400$   $cm^{-1}$  and the peaks between 1700 and 1100  $cm^{-1}$  are for gel frame components. Arrows represent the absorbance variation trend with increasing or decreasing temperature.

300 °C, accuracy 0.01 K). Each spectrum was averaged over 128 scans with  $6\text{ cm}^{-1}$  resolution. The gels were heated from 10 to 66 °C for poly(NIPAAm) and to 80 °C for poly(NDEAAm-co-MAA), and then cooled backward to 10 °C. The temperature step was set to 2 °C and at each temperature the samples were measured after being equilibrated to the temperature for 2 min. The measurements at the start point (10 °C), the highest temperature (66 °C for poly(NIPAAm) and 80 °C for poly(NDEAAm-co-MAA)), and the end point (10 °C) were repeated for checking the stability.

The other set of experiments was done at room temperature with single-bounce ATR accessory, not temperature controlled. Dried samples (components of the hydrogels, in Fig. 1(A)) were measured with  $4\text{ cm}^{-1}$  resolution with 128 scans. Hydrogels were measured with the same parameters and buffer subtracted later on.

In both experiments, the chemical intensities were determined under an FTIR (Tensor 27 Powerful mid-IR spectrometer, Bruker

Optics) instrument with a frequency scanning range from 4000 to  $800\text{ cm}^{-1}$ . Water vapor condition was controlled with  $\text{N}_2$  purge through the instrument and the residual water vapor was compensated later on.  $\text{LN}_2$  cooled photovoltaic MCT (Mercury–Cadmium–Telluride) detector was used.

### 3. Results

Fig. 1 shows the FTIR spectra of the frame components of the hydrogels including the gel monomers and cross-linker (Fig. 1(A)), and the poly(NIPAAm) (Fig. 1(B)). All of the organic compounds as well as the polymer have significant absorbance peaks between  $800$  and  $1700\text{ cm}^{-1}$ , which can be used to study the thermo-behaviors of the gels. A double band for isopropyl group at  $1385$  and  $1370\text{ cm}^{-1}$  are a characteristic absorptions of poly(NIPAAm) [19]. In addition, water does not interfere at this frequency. Therefore, band at  $\sim 1385\text{ cm}^{-1}$  was chosen for LCST analyses for both of these two hydrogels.

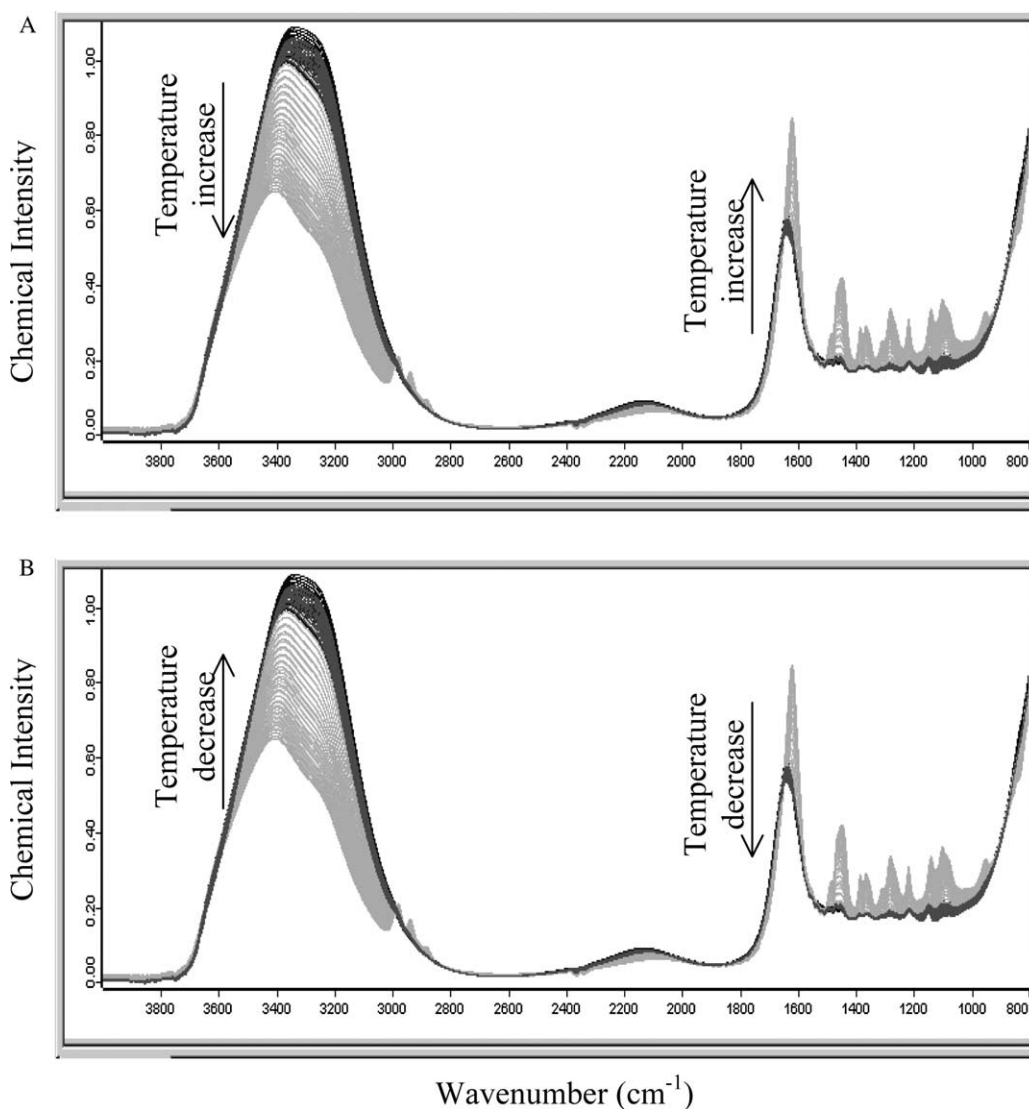


Fig. 3. The scanning FTIR-spectra of 4% poly(NDEAAm-co-MAA)-10 during (A) heating from 10 to 80 °C and (B) cooling from 80 to 10 °C. Water content in the hydrogel is indicated by the absorbance peak at  $\sim 3400\text{ cm}^{-1}$  and the peaks between  $1700$  and  $1100\text{ cm}^{-1}$  are for gel frame components. Arrows represent the absorbance variation trend with increasing or decreasing temperature.

Furthermore, silicon absorption band depends on the temperature, so bands away from the silicon lattice vibration should be selected. The band at about  $1630\text{ cm}^{-1}$  may include three components: (1) intermolecular and (2) intramolecular hydrogen bonded C=O bands, and (3) non-hydrogen bonded C=O band [15,16]. This band was used for the study of H-bonding water. The band at  $\sim 3400\text{ cm}^{-1}$  was used for the study of pore water.

Thermal-related deswelling/swelling of poly(NIPAAm) during heating/cooling was shown in Fig. 2. Time step between measurements was set to 2 K to ensure 2 min resting time for each time step to be enough for stabilization of the hydrogels. With the increase of temperature, pore water inside the poly(NIPAAm) was released as indicated by the decrease in the absorption of OH stretching of water at  $\sim 3400\text{ cm}^{-1}$ , meanwhile the gel-chemical peaks increased (between  $1700$  and  $1100\text{ cm}^{-1}$ ). This reflects that with the gel shrinking, the chemical density of the frame components increased. Here, we propose that a higher intensity is associated with a more packed hydrogel due to the precipitation to the silicon crystal. The opposite process of cooling the gel has shown that with the incorporation of water into the gel, the chemical intensity continuously decreases. Similar results were observed along the heating/cooling pathways of poly(NDEAAm-co-MAA) (Fig. 3).

The relative analysis errors at the start and end points ( $10\text{ }^\circ\text{C}$ ) are  $<1\%$ , indicating that the measurements are repeatable. At the highest working temperatures ( $66\text{ }^\circ\text{C}$  for poly(NIPAAm) and  $80\text{ }^\circ\text{C}$  for poly(NDEAAm-co-MAA)), the relative differences between the two measurements are  $<2\%$ , indicating that the gel volumes are nearly continuous when

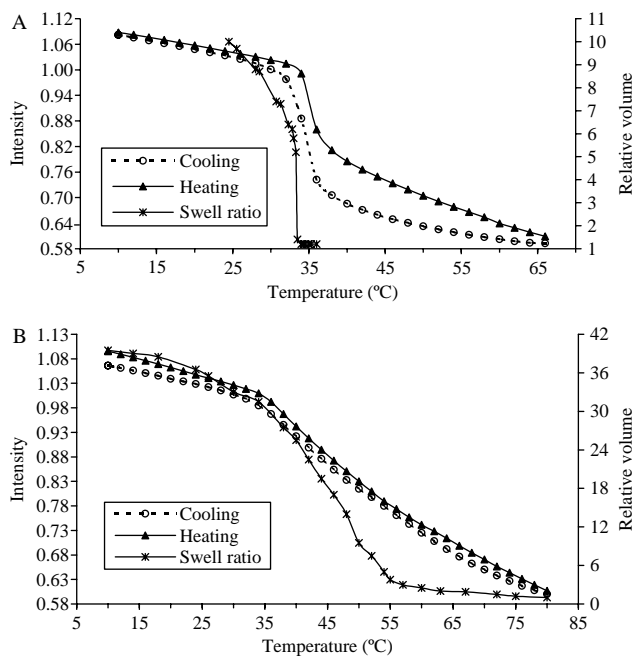


Fig. 4. Water contents in (A) 4% poly(NIPAAm) (pre-swollen in DI water), and (B) 4% poly(NDEAAm-co-MAA-10) analyzed under FTIR spectrometer (shown in intensity at  $\sim 3350\text{ cm}^{-1}$ ) during heating and then cooling. The swell ratios of the hydrogels were obtained by measuring relative volumes (i.e. volumes of swollen gel relative to that at high temperature, replotted from Ref. [1]).

switching from the heating to cooling process (Figs. 4 and 5). All of these data suggest that the gels had reached their corresponding steady states during deswelling/swelling under our working conditions.

## 4. Discussion

### 4.1. LCSTs

The thermal/kinetic behavior of poly(NIPAAm) was obtained by measuring the absorbance of water peaks under FTIR probing (Figs. 4(A) and 5(A)). The LCSTs were obtained by use of tangents (i.e. the cross-points at  $x$ -axis of two trend lines: one is  $10\text{--}32\text{ }^\circ\text{C}$ , and the other is  $34\text{--}38\text{ }^\circ\text{C}$ ). The results showed that the hydrogel has a LCST of  $\sim 35\text{ }^\circ\text{C}$  based on the heating profile, and the cooling profile showed a LCST of  $\sim 33\text{ }^\circ\text{C}$ . Both of these LCSTs are very close to the reported value of  $\sim 34\text{ }^\circ\text{C}$  [1]. Furthermore, the heating profile of the gel is similar to that obtained by measuring gel swell ratios (Fig. 4(A)). The LCSTs of the poly(NDEAAm-co-MAA)-10 gel were obtained similarly to those of the poly(NIPAAm) gel (Fig. 4(B)). The poly(NDEAAm-co-MAA)-10 exhibited relatively continuous contraction during heating from  $10$  to  $80\text{ }^\circ\text{C}$  compared with poly(NIPAAm) (i.e. showing a less sharp variation in volumes during temperature change around its LCST). The LCST of poly(NDEAAm-co-MAA)-10 is  $\sim 36\text{ }^\circ\text{C}$  based on the heating profile, and the cooling profile showed a LCST of  $\sim 35\text{ }^\circ\text{C}$ , which is also similar to that of the reported value (Fig. 4(B)).

The thermal-responses of the hydrogels reflected by the gel chemicals gave similar LCSTs as the swollen water does along heating/cooling pathways (Fig. 5), i.e.  $\sim 34$  and  $32\text{ }^\circ\text{C}$  for poly(NIPAAm) based on heating and cooling profiles,

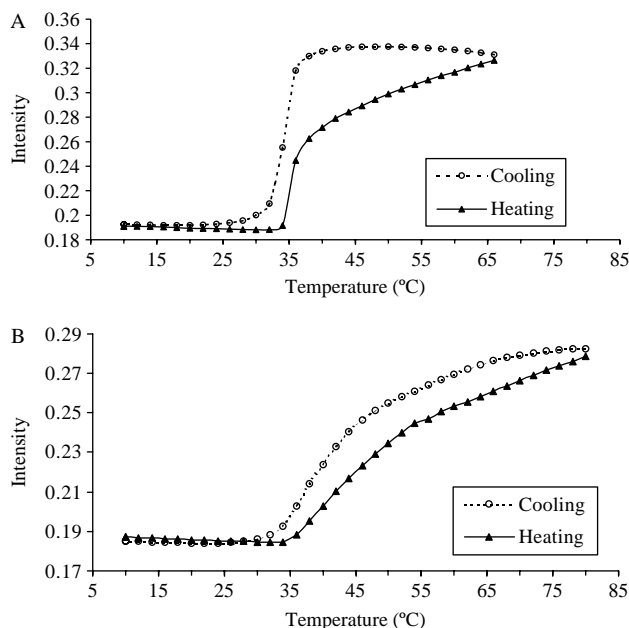


Fig. 5. Chemical intensities of (A) 4% poly(NIPAAm) pre-swollen in DI water and (B) 4% poly(NDEAAm-co-MAA-10) analyzed under FTIR spectrometer at the frequency of  $\sim 1385\text{ cm}^{-1}$  during heating and then cooling.



respectively, and those are 35 and 33 °C for poly(NDEAAm-co-MAA)-10, correspondingly.

The amide I and II bands may be associated with the amide groups on poly(NIPAAm) [15]. The shape and position of these two bands were sensitive to temperature variation at the LCST due to the precipitation occurrence. For both of these hydrogels, at 10 °C, this band was centered at  $\sim 1636 \text{ cm}^{-1}$ . Upon heating, the band peak shifted toward a lower frequency at LCST, and an opposite trend was observed while upon cooling (Fig. 6). In Percot [15], the position of amide I shifted toward higher frequency upon heating. This was explained that the relative intensity of the band associated to intramolecular hydrogen bonding increased (intramolecular hydrogen bonds have a higher frequency band of  $\sim 15 \text{ cm}^{-1}$  than intermolecular hydrogen bonds). In this study, the amide I and amide II bands were not distinguishable. It is likely that the trend of amide II band shift upon heating/cooling (opposite to amide I band) may influence the shift trend of this mixed band.

The thermal variations of the amide band positions were shown in Fig. 6, which was used to determine LCSTs of both poly(NIPAAm) and (NDEAAm-co-MAA). The LCSTs were obtained by use of tangents, which were 33 and 29 °C for poly(NIPAAm) and 35 and 31 °C for (NDEAAm-co-MAA), based on heating and cooling profiles, respectively. The LCSTs obtained by this approach were similar to those obtained from

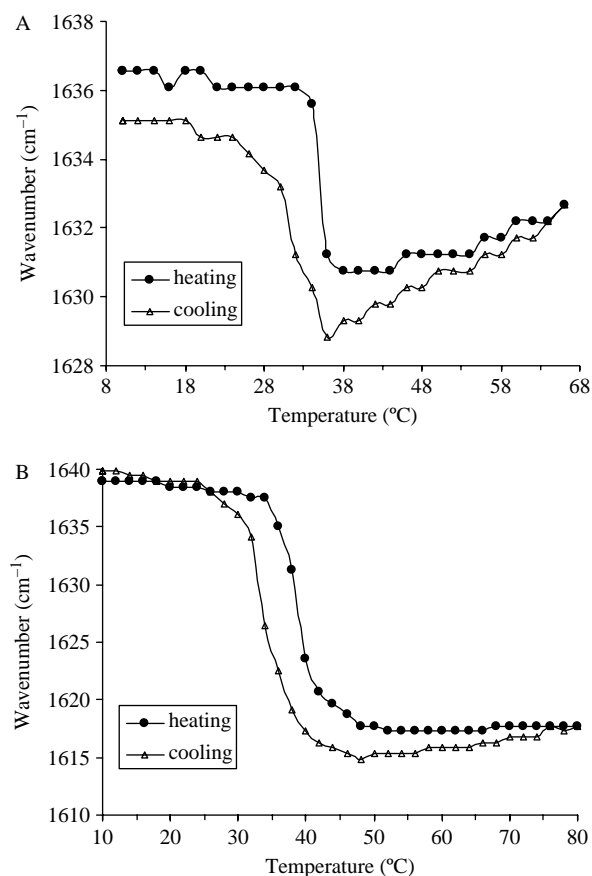


Fig. 6. Thermal variations of the peak positions of the bands at about  $1635 \text{ cm}^{-1}$  which may be associated with hydrogen bonds, (A) 4% of poly(NIPAAm) and (B) 4% of poly(NDEAAm-co-MAA)-10.

the band peak absorbance of both swollen water and gel frame components. Furthermore, the LCSTs of these two hydrogels obtained from heating profiles were also higher ( $\sim 4 \text{ °C}$ ) than those obtained from cooling profiles, correspondingly.

In summary, all of the absorbance profiles of both pore-water and gel chemicals, and band peak positions near  $1635 \text{ cm}^{-1}$  along either heating or cooling pathway showed similar LCSTs which are consistent with previously reported results [1]. However, generally, the LCSTs obtained from the heating profiles showed higher degrees than those obtained from the cooling profiles, 1–2 °C from the absorbance of both water (Fig. 4) or gel chemicals (Fig. 5) and 3–4 °C from the band positions at  $\sim 1630 \text{ cm}^{-1}$  (Fig. 6). Apparently, the differences in LCSTs are mainly due to kinetic (offsets in  $x$ -axis) instead of thermodynamic (offsets in  $y$ -axis) factors. In detail, the kinetic factors result in differential LCSTs of poly(NIPAAm) of 1.7–1.9, and 0.4–0.6 °C due to the dynamic factors based on the mathematic analysis of the Figs. 4 and 5. The p(NDEAAm-co-MAA) gel has more hydrophilic bonds than the poly(NIPAAm) gel, which should have a quicker response to environment changes. This assumption was supported by our experimental results, i.e. compared to poly(NIPAAm), (NDEAAm-co-MAA) has (1) less difference in LCSTs obtained by heating and cooling the gel; (2) more kinetically reversible.

#### 4.2. Thermo-reversibility

A previous study [20] has shown that contraction of poly(NIPAAm) reaches a steady state within 1 min when heating from 22 to 50 °C. In this study, the measuring interval was 2 min between each temperature variation of 2 °C, presumably, the gels had already reached steady states, and the discussion of thermo-reversibility here is based on this assumption.

Previous study on poly(NIPAAm) [2] showed quantitative differences in the water content of the hydrogel along the swelling and deswelling pathways in the presence of additives. This behavior was hypothesized to be an osmotically driven phenomenon. Harmon and Frank [18] found that the thermo-deswelling kinetics changed as a function of cross-linking density, and by how much free polymer chains were added (e.g. molecular size, hydrophobicity, etc.). The authors concluded that the incorporation of free polymer chains into thermo-responsive poly(NIPAAm) gels altered the kinetics of the LCST volume phase transition. Furthermore, faster kinetics were associated with higher levels of free polymer chains and more hydrophilic polymers.

In this study, we also found that the poly(NIPAAm) exhibited relatively irreversible swelling/deswelling behavior at the temperatures above LCST—apparently, the gel expelled lesser quantities of water during heating or/and imbibed lesser amounts of water during cooling compared to the imaginary central line between the heating and cooling profiles (reflected as the heating profiles are positioned always above the cooling profiles for pore-water, but they are below the cooling profiles for gel chemicals, Figs. 4 and 5). This may be explained due to

Table 1  
Swell ratios of the hydrogels under different salinities (NaCl solutions) at 4 °C

NaCl (% <i>v/v</i> , w/w)	4% Poly(NIPAAm)	4% Poly(NDEAAm-co-MAA)
0.0	30.7 ± 1.9	142.0 ± 6.1
2.5		36.8 ± 3.0
5.0		32.6 ± 0.3
10.0		22.7 ± 2.4
17.5		20.1 ± 2.0
35.0	30.6 ± 1.8	2.1 ± 0.5

the non-uniform collapse of the gel network [21] since gels intrinsically have inhomogeneities [22]. The gel near the surface collapses first, forming a dense layer of hydrophobic gel. Because swelling or deswelling of gels is governed by an osmotic process, the formation of this hydrophobic layer slows the diffusion of water through it [20]. Since, poly(NIPAAm) has a relatively larger hydrophobic component compared to poly(NDEAAm-co-MAA) [20], poly(NIPAAm) should have a faster initial rate of collapse when temperature is increased just above LCST (reflected by sharper changes near LCST, Figs. 4 and 5), which results in less water expelled than it should because of the rapid build-up of outer surrounding hydrophobic barriers. Similarly, when the temperature decreases, the shrunken poly(NIPAAm) gel absorbs less water due to the existing of such barriers. As a result, the poly(NIPAAm) gel shows different shrinking/swelling routes during a thermo-cycle of heating followed by cooling (Figs. 4 and 5).

Fig. 6 showed that at higher temperature upon either heating or cooling route, the position of the band peak shifted toward lower frequency when less H-bonding water binds with the polymer chains. Compared the heating with cooling profiles of these two hydrogels, it is obviously that both of the cooling

profiles were sit below the heating profiles, correspondingly. This suggests that the hydrogels may absorb less water (H-bonding) upon cooling. This is consistent with our results discussed previously in this paper. In addition, again, the poly(NDEAAm-co-MAA) is more reversible compared to poly(NIPAAm) based on H-bonding water content during a cycle of heating followed by cooling.

Compared to poly(NDEAAm-co-MAA), poly(NIPAAm) gel has a lesser kinetic-reversibility (different heating and cooling profiles). Presumably, this is due to the rapid formation of hydrophobic layer near its surface resulting in slower kinetics. Note, that the irreversibility of the gels is referred to as the route (kinetically). However, as indicated by the relative intensity differences between the start and the end points (<1% for both of the gels), the gels are considered thermally reversible after a cycle of heating up to 80 °C followed by cooling backward to the initial status.

#### 4.3. Influence of salinity

The poly(NDEAAm-co-MAA) gel is also salinity-sensitive. The swell ratios of poly(NDEAAm-co-MAA) at 4 °C are 142 in DI water and 2.1 in 35% NaCl solution, while, those of poly(NIPAAm) do not change within this salinity range (Table 1). With the increase of salinity, the poly(NDEAAm-co-MAA) gel initially shows the sharpest volume decrease, then, volume shrinkage gradually becomes slower. FTIR spectra showed an increase in chemical intensity at  $\sim 1600\text{ cm}^{-1}$  with the increase of salinity (Fig. 7), reflecting the decrease of gel volume. From this initial demonstration, we propose that FTIR spectrometer can be an effective method to study the responses of gels to other environmental changes, such as salinity.

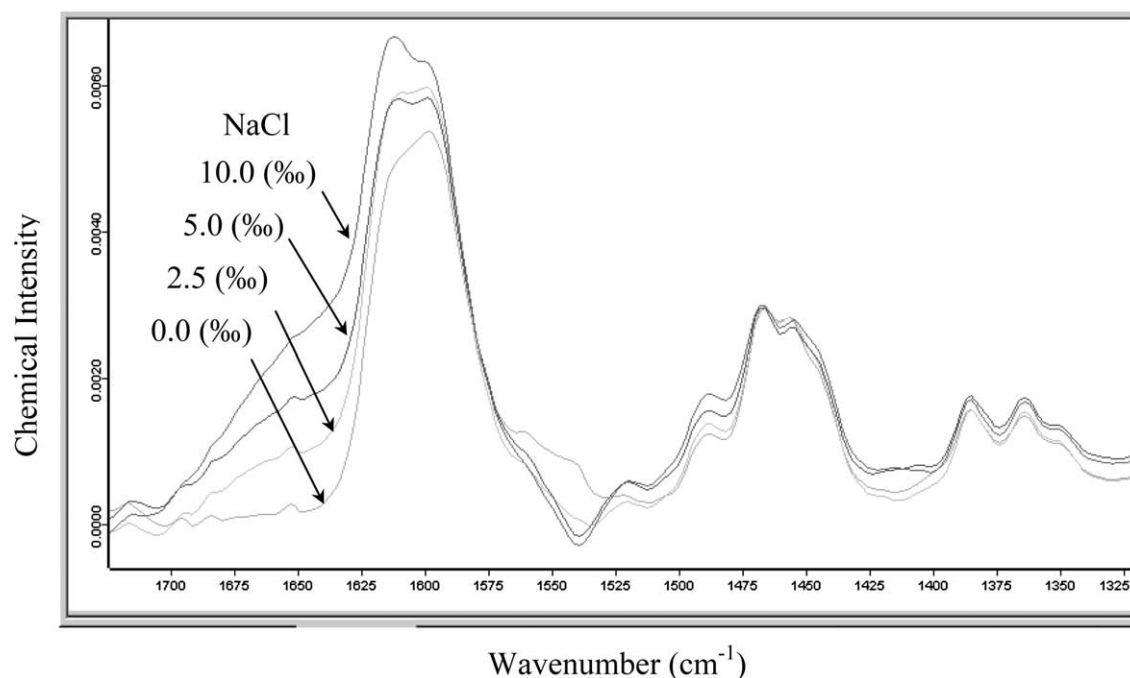


Fig. 7. Spectra of 4% poly(NDEAAm-co-MAA) equilibrated in different NaCl solutions.

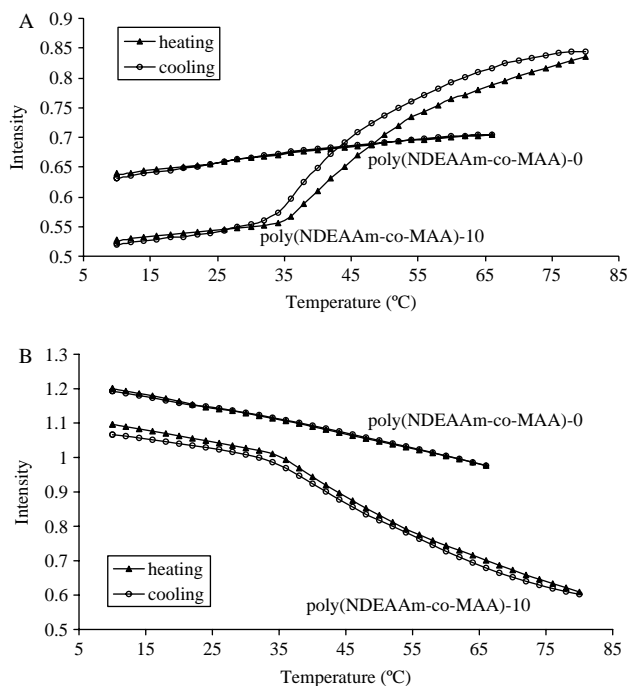


Fig. 8. Comparison of gel contraction and swelling of 4% of poly(NDEAAm-co-MAA)-0 and poly(NDEAAm-co-MAA)-10 analyzed under FTIR spectrometer at the frequencies of (A)  $1630\text{ cm}^{-1}$  for gel chemicals and (B)  $3350\text{ cm}^{-1}$  for pore-water.

Fig. 8 is the comparison of poly(NDEAAm-co-MAA)-0 and poly(NDEAAm-co-MAA)-10 in the study of thermo-dynamics under FTIR spectrometer. Generally, both of the spectra show the same trends of gel shrinking/swelling during heating/cooling. However, poly(NDEAAm-co-MAA)-10 shows greater variations in the absorbance of both pore-water (Fig. 8(B)) and gel chemicals (Fig. 8(A)), and a more significant LCST. Here, we proposed that because poly(NDEAAm-co-MAA)-10 has approximately an order of magnitude lower swell ratio than poly(NDEAAm-co-MAA)-0 at  $4\text{ }^{\circ}\text{C}$  (Table 1), the more compacted poly(NDEAAm-co-MAA)-10 gel with higher content of gel chemicals: (1) likely has a greater tendency to rapidly develop ‘hydrophobic barriers’ at the gel surface, showing an apparent thermo-irreversibility as discussed previously in this article; (2) is presumably more sensitive to temperature change especially when temperature is close to its LCST, thus showing a clearer LCST and (3) has greater variation in relative volume changes. Therefore, poly(NDEAAm-co-MAA)-10 was used in this study for investigating the thermal-dynamics and kinetics of poly(NDEAAm-co-MAA).

## 5. Conclusions

Thermal dynamics/kinetics of hydrogels are very important for the design and engineering of hydrogels as drug deliverers,

biosample separators and actuators, since accuracy in gel volume as well as mesh size is the key factor for gel performance. We demonstrated that FTIR spectrometer is a powerful tool to study hydrogel volume transitions under environmental changes in a quick and reliable way. Our results showed that hydrogels with fast volume changes from environment stimuli tend to have less reversibility along the swelling/deswelling pathways. We propose that rapid volume variations (usually happening near gel surfaces, initially) results in non-homogeneity of the polymers, which leads to differential diffusion of water. In addition, the heating and cooling profiles of both gels examined mirrored those of the water content very well, suggesting that the FTIR peak absorbance of gel chemicals can also be used to study gel thermal-dynamics, especially for the hydrogels with low swell ratios. Furthermore, peak positions of amide band can also be used to study H-bonding water as well as LCSTs. All of these three approaches give consistent results.

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