Spectral interpretation of thermally irreversible recovery of poly(N-isopropylacrylamide-co-acrylic acid) hydrogel†

Shengtong Sun, Jun Hu, Hui Tang and Peiyi Wu*

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The thermally induced volume phase transition process of poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) hydrogel is studied using FT-IR spectroscopy in combination with the perturbation correlation moving window (PCMW) technique and two-dimensional correlation spectroscopy (2Dcos) analysis. According to PCMW spectra analysis, an elevation of volume phase transition temperature (VPTT) due to an extra equilibrium of repulsive electrostatic interactions of acrylic acid moieties in hydrogel from 34 °C to ca. physiological temperature (37 °C) is determined. 2Dcos helps us to conclude that the dehydration of hydrogel responds earlier in the process of network collapse than hydrogen bond variations of AA and NIPAM moieties during heating, while the hydrogen bonds of NIPAM and AA moieties change before the network swelling in the cooling process. Furthermore, relatively stable inner hydrogen bonds of AA moieties restrict the complete expansion of PNIPAM-co-AA hydrogel, resulting in a unique irreversible recovery during cooling.

Introduction

Linear poly(N-isopropylacrylamide) (PNIPAM) experiences a coil-to-globule phase transition around lower critical solution temperature (LCST, ~32 °C), attributing from the distribution changes of hydrogen bonds and hydrophobic interactions in aqueous solution.1–5 Moreover, cross-linking of linear PNIPAM chains by introducing variable amounts of cross-linkers or comonomers can produce PNIPAM-based hydrogels, which undergoes a shrinking/swelling volume phase transition (VPT) around VPTT.6–12 Furthermore, an incorporation of proper comonomers can tune the thermal phase transition temperature over a range about 10 °C. It makes the VPTT of PNIPAM-based hydrogels around physiological temperature appear feasible and stimulates enormous investigations for a better understanding of the mechanism of volume phase transition behavior.13–18 These results also enlighten researchers in the design of functional hydrogel particles, especially in mimicking biological functional systems for controlled drug delivery applications.19–25

Generally, the copolymerization of hydrophilic monomers such as acrylic acid (AAc), sodium acrylate, acrylamide, N-vinyl-2-pyrrolidinone can increase the VPTT of PNIPAM-based hydrogels,13 while the reverse is true when the hydrophobic monomers are used.26 Up to the present, modification of PNIPAM-based hydrogels has attracted extensive interests of both theoretical and experimental researchers. Hirotsu et al. investigated ionized PNIPAM hydrogels showing a surprising discontinuous phase transition during thermal treatment compared to nonionic ones.27 However, Beltran et al. came to the opposite conclusion.28 Kawasaki and his collaborators studied the effects of ionization of acrylic acid on volume phase transition behavior of PNIPAM-co-AA hydrogel. They summarized that the VPT of the hydrogel was discontinuous below pH 6.3 while continuous above pH 7.5. It will be of great value to understand the VPT nature of dually thermo- and pH-sensitive PNIPAM-co-AA hydrogel.29 Shibayama et al. reported that PNIPAM-co-AA hydrogel had a microscopic separation below the temperature of macroscopic transition during heating.11,12 In addition, PNIPAM-co-AA microgels exhibited a two-step VPT when the AA content and charge intensity increased gradually.30 It is widely accepted that the VPT nature of PNIPAM-co-AA hydrogel is resulting from a subtle equilibrium between attractive hydrophobic interactions of NIPAM moieties and repulsive electrostatic interactions of acrylic acid moieties.30 Except for the incorporation of acrylic acid, various external stimuli have variable influences on the shrinking/swelling behavior of PNIPAM-co-AA hydrogels.31,32

A variety of methods have been used to study volume phase transition behavior of hydrogels, including dynamic light scattering (DLS), nuclear magnetic resonance (NMR), small-angle neutron scattering (SANS), cryogenic transmission electron microscopy (cyro-TEM), Raman spectroscopy, and
infrared (IR) spectroscopy. However, to the best of our knowledge, few investigations of the irreversible VPT behavior of PNIPAM-co-AA hydrogel in the heating and cooling cycle process have ever been reported.

In this paper, we attempt to study the volume phase transition behavior of PNIPAM-co-AA hydrogel with FT-IR in combination with two-dimensional correlation spectroscopy (2Dcos) and perturbation correlation moving window (PCMW) technique. 2Dcos is a mathematical method whose basic principles were first proposed by Noda in 1986. Up to the present, 2Dcos has been widely used to study spectral variations of different chemical species under various external perturbations (e.g., temperature, pressure, concentration, time, electromagnetic field, etc.). Due to the different responses of different species to external variables, additional useful information about molecular motions or conformational changes can be extracted which cannot be obtained straight from conventional 1D spectra. PCMW is a newly developed technique, whose basic principles can date back to conventional moving window proposed by Thomas and Richardson, and later in 2006 Morita et al. improved this technique to much wider applicability through introducing the perturbation variable into the correlation equation. Except for its original ability in determining transition points as conventional moving window did, PCMW can additionally monitor complicated spectral variations along the perturbation direction. A combination of PCMW and 2Dcos analysis helps us to successfully monitor the microscopic variations of complex interactions in PNIPAM-co-AA hydrogel during the entire thermal process and a proposed irreversible recovery mechanism is also presented. The partially irreversible nature seems to be arising from relatively stable inner hydrogen bonds of acrylic acid moieties formed at the collapsed state of PNIPAM-co-AA hydrogel. This may be helpful in further understanding the volume phase transition behavior of complex hydrogel and in modifying the properties of various kinds of functional hydrogels.

Experimental section

Materials

N-Isopropylacrylamide (NIPAM) is purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and recrystallized from cyclohexane before use. Acrylic acid is purchased from Aladdin reagent Co. and purified by passing through a short alumina column. N,N',N'-tetramethylethylenediamine (TEMED), ammonium persulfate (APS) and N,N'-methylenebisacrylamide (MBAA) (cross-linker) are all purchased from Aladdin reagent Co. and used as received. D2O is purchased from Cambridge Isotope Laboratories Inc. (D-99.9%).

Preparation of PNIPAM-co-AA hydrogel

NIPAM and AAc were dissolved in deionized water followed by the addition of N,N'-methylenebisacrylamide (MBAA) and ammonium persulfate (APS). After three freeze–thaw cycles, the polymerization was initiated with N,N',N'-tetramethylethylenediamine (TEMED) at room temperature (15 °C) and lasted for 10 h. The reaction and chemical structures are shown in Fig. 1.

Besides, the feed ratio is [NIPAM]/[AA]/[APS]/[MBAA] = 1.92 : 0.32 : 0.06 : 0.01 mol L−1. The hydrogel obtained was dialyzed with deionized water for one week and freeze-dried to dry gel before use.

Fourier transform infrared spectroscopy

PNIPAM-co-AA dry gel was swollen in D2O at 4 °C for a week to ensure complete deuteration of all the N–H and O–H protons and sufficient swelling of the hydrogel before FT-IR measurement.

The sample of PNIPAM-co-AA hydrogel for FT-IR measurements was prepared by sealing it between two CaF2 tablets. FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm−1, and 32 scans were available for an acceptable signal-to-noise ratio. Variable-temperature spectra were collected between 30 and 43 °C with an increment of 0.5 °C (accuracy: 0.1 °C, 27 spectra in all for both heating and cooling processes). In addition, the process of baseline correction was performed by the software Omnic, ver.6.1a.

Methods

Perturbation correlation moving window

FT-IR spectra collected with an interval of 0.5 °C are used to perform perturbation correlation moving window analysis. Primary data processing was carried out with the method provided by Morita and further calculation was performed by the software 2D Shige, ver. 1.3 (© Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004–2005). Furthermore, the final contour maps are obtained by Origin program, ver. 8.0. Wherein, warm colors (red and yellow) represent positive intensities while cool colors (blue) are for negative ones. An appropriate window size (2m + 1 = 11) was chosen to generate PCMW spectra with good quality.

Two-dimensional correlation analysis

The above FT-IR spectra are also used to perform 2D correlation analysis by the same software 2D Shige, ver. 1.3 (© Shigeaki Morita, Kwansei-Gakuin University, Japan, 2004–2005). Similarly, the results are plotted into corresponding contour maps with the same significations as PCMW analysis by Origin program, ver. 8.0.
Results and discussion

Conventional IR analysis

It should be noted that D$_2$O is chosen as the solvent rather than H$_2$O to eliminate the overlap of the $\delta$(O–H) band of water around 1640 cm$^{-1}$ with the $\nu$(C–O) band of PNIPAM-co-AA hydrogel as well as the broad $\nu$(O–H) band of H$_2$O around 3300 cm$^{-1}$ with $\nu$(C–H) bands of the hydrogel.$^{41}$ As reported, the transition temperature of PNIPAM gel in D$_2$O is 0.7 °C higher than that in H$_2$O.$^{42}$ However, the deuterium isotopic substitution has little influence on the magnitude of hysteresis.$^{42}$ Thus, using D$_2$O as the solvent proves to be reasonable for the phase transition analysis of PNIPAM-based hydrogels.

The variations of FT-IR spectral intensity as a function of temperature during heating and cooling are plotted in Fig. 2. For clarity, not all the spectra are plotted here. Three regions, including C–H stretching bands in 3030–2840 cm$^{-1}$, C═O stretching bands of AA moieties in 1740–1680 cm$^{-1}$ and NIPAM moieties in 1674–1572 cm$^{-1}$, are mainly focused in this paper.

C–H stretching bands shift to lower wavenumbers during heating and return to their original positions in the cooling process, attributing to the dehydration and hydration of hydrophobic polymer chains.$^{41}$ However, in the two C═O stretching regions, several obvious irreversible variations during heating and cooling can be observed. In the AA-related C═O stretching region a binary change occurs, as a result the spectral intensity of the band around 1728 cm$^{-1}$ increases during heating while that of the band around 1687 cm$^{-1}$ decreases. Interestingly, spectral variations in this region are comparatively unnoticeable during cooling, even though the tendency is still opposite in a magnifying view. This difference during heating and cooling shows a distinctive variation behavior which is closely related to an incorporation of AA moieties. On the other hand, the binary spectral changes of the NIPAM-related amide I region in 1675–1570 cm$^{-1}$ exhibit good recovery during heating and cooling from 1DIR spectra.

The temperature dependence of the wavenumber shifts of $\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$ during heating and cooling as shown in Fig. 3 suggests that all the C–H stretching bands in 3030–2840 cm$^{-1}$ shift to lower wavenumbers during heating due to the dehydration of polymer chains. The reverse is true for the cooling process. However, both the wavenumber shifts of $\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$ do not show a drastic change making it hard for us to determine the VPTT of PNIPAM-co-AA hydrogel.

What's more, the determination of VPTT of the hydrogel becomes even more difficult in the C═O stretching region. To quantitatively evaluate their spectral variations, the integral areas of the two regions are calculated, respectively, as a function of temperature as shown in Fig. 3. As expected, an obvious distinction between heating and cooling processes can be observed in the region 1745–1680 cm$^{-1}$. In 1DIR spectra, the integral area of spectral intensity in the region remains unchanged during cooling, apparently different from a nearly linear increase during heating. Additionally, in the region of 1674–1572 cm$^{-1}$, the integral area shows a steady increase during cooling which differs from the tendency during heating. The variations in these two regions may be closely related to each other. It is presumed that the interactions of acrylic acid moieties with themselves and AA moieties with NIPAM moieties have a significant impact on the VPT nature of the hydrogel.

For the amide I region, the integral area in this region increases to a higher value during cooling. It might have

Fig. 2 Variable-temperature FT-IR spectra of PNIPAM-co-AA hydrogel (D$_2$O) during heating and cooling between 31 and 43 °C.

Fig. 3 Temperature dependence of the wavenumber shifts of $\nu_{as}(CH_3)$ around 2980 cm$^{-1}$ and $\nu_{as}(CH_2)$ around 2940 cm$^{-1}$ as well as the integral area of the regions 1740–1680 cm$^{-1}$ and 1675–1572 cm$^{-1}$ during heating and cooling.
resulted from an increase of interactions concerning NIPAM moieties owing to distinctive variations regarding AA moieties during cooling, which requires further confirmation. It demonstrates that VPT behavior of PNIPAM-co-AA hydrogel has a few intrinsic differences from pure PNIPAM hydrogel due to the incorporation of AA moieties. An initial analysis from FT-IR spectra helps us to reach a preliminary conclusion that the shrinking/swelling volume phase transition of PNIPAM-co-AA hydrogel is irreversible during the heating and cooling circle. However, conventional 1DIR analysis cannot provide us a clear explanation for the distinctive VPT behavior from pure NIPAM hydrogel which will be further traced and clarified by following PCMW and 2Dcos analysis.

Perturbation correlation moving window

To determine the VPTT of PNIPAM-co-AA hydrogel not exactly obtained from conventional 1DIR analysis, the PCMW technique is applied. PCMW is especially helpful to monitor spectral variations of different chemical systems, particularly weak phase transitions hard to observe by other methods. Generally, two spectra, synchronous and asynchronous, can be generated by PCMW. The rules of PCMW are as follows: in the case of perturbation increment, positive synchronous correlation stands for increasing spectral intensity variation while negative one to a concave variation. Positive synchronous correlation is also generated by PCMW. The rules of PCMW are as follows: in the case of perturbation increment, positive synchronous correlation stands for increasing spectral intensity variation while negative one to a concave variation. Positive synchronous correlation can be generated by PCMW. The rules of PCMW are as follows: in the case of perturbation increment, positive synchronous correlation stands for increasing spectral intensity variation while negative one to a concave variation. In this paper, only the synchronous spectra of PCMW are presented in Fig. 4 for the determination of VPT during heating and cooling.

Despite slight differences read from different bands due to their different thermo-responsibilities, VPTTs during heating and cooling can be easily determined to be about 38 °C and 36 °C respectively. It’s worth noting that the VPT during cooling is slightly lower than that in the heating process, indicating a hysteresis of the hydrogel after thermal treatment. It indicates that PCMW is indeed a good method to find transition points, especially for chemical systems with complicated spectral variations like PNIPAM-co-AA hydrogel in this paper. Additionally, it is worth noting that the VPTT read from AA-related bands is slightly lower than that of NIPAM-related bands during heating, indicating that AA moieties may have an earlier response than NIPAM moieties in the chain collapse procedure of PNIPAM-co-AA hydrogel. It can also be confirmed by later 2Dcos analysis.

Two-dimensional correlation analysis

To further obtain the information of group motions in VPT of PNIPAM-co-AA hydrogel, all the spectra between 30 and 43 °C are used to perform 2Dcos analysis. Two spectra, synchronous and asynchronous, can also be generated. The two spectra are both represented by two wavenumber axes (ν1, ν2) and one spectral intensity correlation axis. 2D synchronous spectra reflect the degree of in-phase response with the corresponding correlation spectral intensity, while the asynchronous one can demonstrate the degree of out-phase response similarly. According to Noda’s rule, when the cross-peak {Φ(ν1, ν2)} (assuming ν1 > ν2) in synchronous spectra has the same symbol as the cross-peak {Ψ(ν1, ν2)} in asynchronous spectra, the response at band ν1 should be prior to or earlier than that at band ν2 and vice versa. For the convenience of discussion, spectral assignments of the bands for 2Dcos analysis are listed in Table 1.

Analysis of the heating process. From 2D synchronous and asynchronous spectra during heating, we can differentiate the bands that might be unnoticeable in conventional 1DIR spectra due to their enhanced spectral resolution of 2D correlation spectroscopy. In consideration of the relatively lengthy details of determining the order of spectral peaks, we only present the final sequence here for the heating process of PNIPAM-co-AA hydrogel. Operation details can be found in the ESI. The order is listed as follows (> stands for prior to or earlier than): 2927 cm⁻¹ > 2899 cm⁻¹ > 2970 cm⁻¹ > 1728 cm⁻¹ > 1713 cm⁻¹ > 1720 cm⁻¹ > 2873 cm⁻¹ > 1653 cm⁻¹ > 2987 cm⁻¹ > 1691 cm⁻¹ > 2943 cm⁻¹ > 1687 cm⁻¹ > 1601 cm⁻¹ > 1684 cm⁻¹ > 1624 cm⁻¹ > 2883 cm⁻¹ > 2931 cm⁻¹, as shown in Fig. 5.

I C–H region. Extracted from the order above, the response sequence in the C–H region is: 2927 cm⁻¹ > 2899 cm⁻¹ > 2970 cm⁻¹ > 2873 cm⁻¹ > 2987 cm⁻¹ > 2943 cm⁻¹ > 1728 cm⁻¹ > 1713 cm⁻¹ > 1720 cm⁻¹ > 2873 cm⁻¹ > 1653 cm⁻¹ > 2987 cm⁻¹ > 1691 cm⁻¹ > 2943 cm⁻¹ > 1687 cm⁻¹ > 1601 cm⁻¹ > 1684 cm⁻¹ > 1624 cm⁻¹ > 2883 cm⁻¹ > 2931 cm⁻¹, as shown in Fig. 5.

II AA-related C–O region. Similarly, an order of 1728 cm⁻¹ > 1713 cm⁻¹ > 1720 cm⁻¹ > 1691 cm⁻¹ > 1687 cm⁻¹ > 1684 cm⁻¹ can be extracted from above. It can be interpreted as: ν(C=OAA...D–N(NIPAM)) > ν(C–OAA...D–OAA) (dimeric form) > ν(C=OAA...2D–N(NIPAM)) > ν(C–OAA...D–OAA) (oligomeric form) > ν(C–OAA...D–OAA). In short, it’s...
v(C=O\text{AA} \cdots D-N\text{NIPAM}) > v(C=O\text{AA} \cdots D-O\text{AA}) > v(C=O\text{AA} \cdots D_2\text{O}). Therefore, the variations of hydrogen bonds between AA moieties and NIPAM moieties have an earlier response than those of inner hydrogen bonds in dimeric or oligomeric forms of AA moieties; changes of the bands that correspond to interactions of AA moieties with D_2O lag behind in the heating process. Additionally, it manifests itself as a binary spectral intensity change in the region 1745–1680 cm\(^{-1}\) during heating.

### III Amide I region.

The simple order in the amide I region can be summarized as 1653 cm\(^{-1}\) > 1601 cm\(^{-1}\) > 1624 cm\(^{-1}\), or v(C=O\text{NIPAM} \cdots D-N\text{NIPAM}) > v(C=O\text{NIPAM} \cdots 2D_2\text{O}) > v(C=O\text{NIPAM} \cdots D_2\text{O}). It reveals that the transformation from...
water-associated hydrogen bonds to inner hydrogen bonds experiences two steps. In other words, hydrogen bonds of $\nu(C=O_{\text{NIPAM}}-2D_2O)$ transformed to those of $\nu(C=O_{\text{NIPAM}}\cdots D_2O)$ before the inner hydrogen bonds are formed. It also manifests itself as a binary spectral intensity change in the region 1674–1572 cm$^{-1}$ during heating.

IV Summary. Analyzing all the bands in the heating process comprehensively, the order can be summarized as: $\text{CH}_3 > \text{CH}_2 > \nu(C=O_{\text{AA}}\cdots D_{\text{NIPAM}}) > \nu(C=O_{\text{AA}}\cdots D_{\text{AA}})$ (dimeric form) > $\nu(C=O_{\text{AA}}\cdots 2D_{\text{NIPAM}})$ > $\nu(C=O_{\text{NIPAM}}\cdots D_{\text{NIPAM}})$ > $\nu(C=O_{\text{NIPAM}}\cdots D_{\text{AA}})$ (oligomeric form) > $\nu(C=O_{\text{NIPAM}}\cdots D_{2O}) > \nu(C=O_{\text{NIPAM}}\cdots 2D_{2O})$. Therefore, during heating, the dehydration of the backbone responds to temperature first initiating preliminary collapse of PNIPAM-co-AA hydrogel. Meanwhile, the repulsive electrostatic interaction of carboxyls from AA moieties is unfavorable for the swollen hydrogel to collapse compared to pure PNIPAM hydrogel, driving the VPTT of PNIPAM-co-AA hydrogel to be higher. From 1DIR, PCMWM, 2DIR analyses with the assignments of the major changing bands during heating, we can draw the conclusion as follows. (1) The variations of the interactions between AA moieties and NIPAM moieties as well as water molecules occur in advance, which reach the equilibrium fast in the form of inner hydrogen bonds of AA moieties. This agrees with a lower transition temperature of AA from above PCMWM spectra during heating. (2) The variations of NIPAM moieties have a slower response which also agrees with a higher transition temperature first initiating preliminary collapse of PNIPAM-co-AA hydrogel. Finally, the entire shrinking phase transition process is driven by the thermally induced dehydration of hydrophobic groups.

Analysis of the cooling process. Similarly, the sequence in the cooling process can also be deduced as: $2968$ cm$^{-1}$ > $2873$ cm$^{-1}$ > $1714$ cm$^{-1}$ > $1705$ cm$^{-1}$ > $2939$ cm$^{-1}$ > $2931$ cm$^{-1}$ > $2926$ cm$^{-1}$, as shown in Fig. 5.

I C–H region. To put it simply, the order of responses in the C–H region can be summarized as: $\text{CH}_3 > \text{CH}_2$. Thus, we may reach the conclusion that, during cooling, water molecules diffuse into the hydrogel network first encompassing relatively free methyl groups to form the so-called “water cage” before permeating the polymer chains and interacting with inside methylene groups, which is opposite to that during heating.

II AA-related C–O region. Here, a clear result is obtained: $\nu(C=O_{\text{AA}}\cdots D_{\text{NIPAM}}) > \nu(C=O_{\text{AA}}\cdots D_{\text{AA}}) > \nu(C=O_{\text{AA}}\cdots D_{2O})$. Obviously, without considering the interactions concerning water molecules, this changing order is opposite to that of the heating process.

III Amide I region. In the region 1680–1570 cm$^{-1}$, the sequence can be interpreted as $\nu(C=O_{\text{NIPAM}}\cdots D_{\text{NIPAM}}) > \nu(C=O_{\text{NIPAM}}\cdots D_{2O}) > \nu(C=O_{\text{NIPAM}}\cdots 2D_{2O})$. In contrast, the transformation of hydrogen bonds concerning NIPAM moieties shows a two-step process, including the hydrogen bond of $\nu(C=O_{\text{NIPAM}}\cdots 2D_{2O})$ as well.

IV Summary. Combining all the bands during cooling entirely, the order is summarized as: $\text{CH}_3 > \nu(C=O_{\text{NIPAM}}\cdots D_{\text{NIPAM}}) > \nu(C=O_{\text{NIPAM}}\cdots D_{2O}) > \nu(C=O_{\text{NIPAM}}\cdots 2D_{2O}) > \nu(C=O_{\text{NIPAM}}\cdots D_{\text{NIPAM}}) > \nu(C=O_{\text{AA}}\cdots D_{\text{AA}}) > \nu(C=O_{\text{AA}}\cdots D_{2O}) > \nu(C=O_{\text{NIPAM}}\cdots D_{\text{NIPAM}})$ > $\nu(C=O_{\text{NIPAM}}\cdots D_{\text{AA}})$ > $\nu(C=O_{\text{NIPAM}}\cdots D_{2O})$. Therefore, water molecules diffuse into PNIPAM-co-AA hydrogel first during cooling while variations concerning the hydrogel network backbone reflected by $\nu(\text{CH}_2)$ responds much slower. The breaking of inner hydrogen bonds regarding NIPAM moieties show an earlier response than those concerning AA moieties. Finally, the backbone of PNIPAM-co-AA hydrogel recovers to some extent mainly due to NIPAM moieties.

Judging from an earlier response of AA-related inner hydrogen bonds than that of NIPAM-related ones during heating and a slower response during cooling from 2DIR, we can deduce that the AA-related inner hydrogen bonds are much more stable than NIPAM-related ones. Thus, recovery of NIPAM moieties will be driven favorably without consideration of entanglement of polymer chains. However, relatively stable inner hydrogen bonds of AA moieties prevent the collapsed network from recovery. It is apparently confirmed by the larger integral area of the region 1674–1572 cm$^{-1}$ or higher spectral intensity of $\nu(C=O_{\text{NIPAM}}\cdots D_{2O})$ at 1622 cm$^{-1}$.
indicating an increase of water-associated NIPAM hydrogen bonds due to residual interactions of AA moieties in swelling hydrogel. Interestingly, the distinctive hydrogel structures during heating and cooling agree well with previous results. In other words, differing from the shrinking process involving both NIPAM and AA moieties, the swelling process of the PNIPAM-co-AA hydrogel network is mainly comprised of NIPAM moieties, leading to the partially irreversible recovery of the VPT behavior of PNIPAM-co-AA hydrogel in the cooling process, as illustrated in Fig. 6.

In summary, during heating, water molecules are expelled from the network of PNIPAM-co-AA hydrogel first followed by the formation of stable AA inner hydrogen bonds; then transformation from water-associated hydrogen bonds to inner ones of NIPAM moieties occurs at last. During cooling, NIPAM moieties start to expand due to the formation of water-associated hydrogen bonds. However, relatively stable inner hydrogen bonds of AA moieties limit complete stretching of the hydrogel network according to the above analysis. Subsequent swelling of the backbone results from the diffusion of water molecules.

Conclusions

In this paper, we focus on the investigation of the distinct VPT nature of PNIPAM-co-AA hydrogel in D_2O by FT-IR spectroscopy in combination with the PCMW technique and 2Dcos. The PCMW technique helps us to determine the VPTTs to be about 38 °C during heating and 36 °C during cooling, which are around the physiological temperature. The elevation of VPTT is attributed from strong repulsive electrostatic interactions of AA moieties or Donnna osmotic pressure.

A combination of 1DIR spectra, PCMW technique and 2D analysis helps us to put forward a mechanism of the VPT nature of PNIPAM-co-AA hydrogel. During heating, dehydration of hydrogel has an earlier response than hydrogen bond variations of AA and NIPAM moieties, while the transformation from inner hydrogen bonds of NIPAM moieties to water-associated ones drives the swelling process of the hydrogel network in the cooling process. Interestingly, inner hydrogen bonds of acrylic acid moieties are relatively stable in the hydrogel network limiting the complete stretching of NIPAM moieties, which mainly accounts for a unique thermally irreversible recovery of the PNIPAM-co-AA hydrogel network.

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References

14 W. Xue, S. Champ and M. B. Huglin, Polymer, 2000, 41, 2575.
15 W. Xue, S. Champ and M. B. Huglin, Polymer, 2001, 42, 3665.