The unusual volume phase transition behavior of the poly(N-isopropylacrylamide)–poly(2-hydroxyethyl methacrylate) interpenetrating polymer network microgel: different roles in different stages†

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Dynamic thermal phase transition behavior of a well-defined poly(N-isopropylacrylamide)–poly(2-hydroxyethyl methacrylate) (PNIPAM–PHEMA) interpenetrating polymer network (IPN) microgel in D2O synthesized by two-step precipitation polymerization was studied by means of IR spectroscopy in combination with the perturbation correlation moving window (PCMW) technique and two-dimensional correlation spectroscopy (2Dcos) analysis. Due to the hydrophobic and non-thermo-responsive properties of PHEMA and the special IPN structure, the IPN microgel exhibited an unusual thermally induced collapse process. The introduction of PHEMA would lower the volume phase transition temperature (VPTT) and the volume phase transition degree. 2Dcos was finally employed to discern the sequence order of all the group motion during heating and cooling processes. PHEMA plays different roles in different stages during the volume phase transition. Additionally, as PHEMA exhibits only a slight response to temperature, it would provide the PNIPAM–PHEMA IPN microgel with good reversibility.

Introduction

Microgels or nanogels, with the size ranging from tens of nanometres to several microns, are cross-linked polymeric particles which could swell in a good solvent.1–3 Microgels that can conventionally undergo a volume change in response to environmental stimuli, including temperature,4,5 pH,6 light7,8 and electric field,9 are called “intelligent” or “smart” microgels. Compared with macroscopic gels, microgels show a rather faster variation in their volume upon external stimuli due to their smaller size.10–12 Because of their excellent and attractive stimuli responsive properties, smart microgels have been widely used in many fields, such as controlled drug delivery,3,13,14 tissue engineering,15 catalysts,16 imaging,17 and sensing,18 to name a few.

Among various synthetic thermo-sensitive microgels, the poly(N-isopropyl acrylamide) (PNIPAM) microgel is the most studied example with a negative thermal response or a lower critical solution temperature (LCST, ∼32 °C).2,19 Below LCST, the PNIPAM microgel absorbs a high amount of water and swells well in the solution. When the temperature goes up to above LCST, PNIPAM undergoes a drastic, discontinuous volume phase transition and exists in a collapsed state above LCST. Similar to the coil-to-globule phase transition of PNIPAM aqueous solution, the swelling and deswelling transition of the PNIPAM microgel is also thermally reversible. The transition is generally considered to be the competitive result of the hydrophobic interaction of pendent isopropyl groups and backbones and the hydrogen bonding association between amide groups and water molecules.20

To widen the application field of PNIPAM-based polymers, many different ways such as simple random copolymerization and interpenetrating copolymerization have been utilized. Generally, the copolymerization of hydrophilic monomers such as acrylic acid (AAc), sodium acrylate, acrylamide, and N-vinyl-2-pyrrolidinone can increase the VPTT of PNIPAM-based polymers,21 while the reverse is true when poly(2-hydroxyethyl methacrylate) is introduced in the system.22 Up to now, modification of PNIPAM-based microgels has attracted extensive interest of both theoretical and experimental researchers. The PNIPAM-co-HEMA microgel was synthesized and used as a new type of injectable cell scaffold by Zhang’s group.22,23 30 mol% of HEMA was incorporated into the PNIPAM microgel and the VPTT of the PNIPAM-co-HEMA microgels was determined to
be 29 °C, which is about 3 °C lower than that of the pure PNIPAM microgels (∼32 °C). This phenomenon was attributed to the hydrogen-bonding between the hydroxyl groups in HEMA and amide groups in NIPAM, which makes the copolymer microgels more hydrophobic.\textsuperscript{22,23} Phase transition behavior of the PNIPAM-co-PHEMA microgel was also studied by Tang and Ma.\textsuperscript{24} In their studies, the incorporation of HEMA causes the VPTT of the PNIPAM-co-PHEMA microgels to shift to a lower temperature and the deswelling ratio of the microgels to increase first and then decrease with the increase of the feed ratio. Special attention has been paid to IPN microgels due to their special structure.\textsuperscript{25–30} In contrast to the simple blend or copolymerization, the two different parts in IPN usually interact with each other by hydrogen bonds, electrostatic interactions, etc. IPN microgels can be synthesized with two kinds of cross-linked polymer networks and they exhibit properties of both the polymers. The IPN microgel of PNIPAM–PAAc was synthesized by Hu, which had the same VPTT as the PNIPAM microgel and also showed a response to pH. It can also self-assemble into an ordered structure, displaying bright colors and can be used for drug delivery.\textsuperscript{28,29}

Another class of two-component networks similar to IPNs, amphiphilic co-networks, with their special structure and anomalous swelling behaviour have also been studied by a variety of techniques.\textsuperscript{31–34} In our previous study, we synthesized PNIPAM–PHEMA IPN microgels and discussed the factors affecting the polymerization. Usually, the VPTT of an IPN microgel containing a PNIPAM matrix remains the same as the PNIPAM microgel;\textsuperscript{28} however, the VPTT of the PNIPAM/PHEMA IPN microgel shows an unusual decrease due to the incorporation of PHEMA chains. We proposed a possible mechanism for this interesting phenomenon, but more direct evidence might be needed for detailed explanation.\textsuperscript{30}

A variety of methods have been used to study volume phase transition behavior of microgels, including experimental methods such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), light scattering,\textsuperscript{39} neutron scattering,\textsuperscript{40,41} nuclear magnetic resonance (NMR)\textsuperscript{42,43} and some theoretical modelling.\textsuperscript{44} However, to the best of our knowledge, no investigation of the VPT behavior of PNIPAM–PHEMA IPN microgels in the heating and cooling cycle has ever been reported.

In this paper, we have attempted to study the volume phase transition behavior of PNIPAM–PHEMA IPN microgels by FT-IR in combination with two-dimensional correlation spectroscopy (2Dcos) and the perturbation correlation moving window (PCMW) technique. For the IPN microgels, FTIR is the technique of choice for exploring the behavior of the two parts in the IPN structure during the volume phase transition as the characteristic peaks of the two parts can be separately probed using the IR spectra. In this way, we are able to differentiate the roles of the two parts of the microgels during the volume phase transition process. Furthermore, both PCMW and 2Dcos have also been proved to be effective methods in elucidating dynamic phase transition behavior of thermal responsive polymers such as PNIPAM,\textsuperscript{26} PVCL,\textsuperscript{45} poly(vinyl methyl ether) (PVME)\textsuperscript{46} and OEG(M)A-based linear polymers.\textsuperscript{47} A combination of PCMW and 2Dcos analyses helps us to gain additional information on microscopic variations of complicated interactions in the microgels during the volume phase transition process, and therefore a more comprehensive understanding of the relationship between the structure and the thermal responsive properties of the microgels can be achieved.

**Experimental**

**Materials**

\(N\)-Isopropyl acrylamide (NIPAM) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and recrystallized from cyclohexane before use. 2-Hydroxyethyl methacrylate (HEMA) was purchased from Aladdin reagent Co. and purified by passing through a short alumina column. \(N,N,N',N'\)-Tetramethylethylenediamine (TEMED), dodecyl sulfate sodium salt (SDS), potassium persulfate (KPS) and \(N,N'\)-methylenebisacrylamide (MBAA) were all purchased from Aladdin reagent Co. and used as received. \(D_2\)O was purchased from Cambridge Isotope Laboratories Inc. (D-99.9%) and used as received.

**IPN microgel preparation**

PNIPAM–PHEMA IPN microgels (the chemical structure as shown in Scheme 1) were synthesized according to previous reports.\textsuperscript{30} First, we prepared PNIPAM microgels by precipitation polymerization. NIPAM (3.8 g), MBAA (0.066 g), and SDS (0.15 g) were dissolved together in distilled water (240 mL). The solution was put into a three-neck flask equipped with a magnetic stirrer. The solution was purged with nitrogen for 1 h before being placed in a 70 °C hot bath. KPS (0.166 g), which was dissolved in 20 mL water, was then added to initiate the emulsion polymerization. The reaction lasted for 4 h under a nitrogen atmosphere with the reaction temperature being kept at 70 °C. All PNIPAM particles were purified via dialysis (MWCO 14 000) against frequent changes of stirring water for 2 weeks at room temperature. The final PNIPAM microgel concentration was adjusted to \(3.2 \times 10^{-2} \text{ g mL}^{-1}\).

Second, we used PNIPAM microgels as seeds to prepare PNIPAM–PHEMA IPN microgels. 1.576 g as-prepared PNIPAM microgel solution, 0.05 g MBAA and 0.415 g HEMA were added into a three-neck flask. Distilled water was added to make the final solution volume to 35 mL. The solution was kept at 4 °C for 2 days. The solution was bubbled for 1 h with nitrogen gas and then precipitated into a three-neck flask, which was filled with a total of 35 mL of 100 °C water. The precipitate was then washed with methanol and water and lyophilized to form PNIPAM–PHEMA IPN microgels. The chemical structure of PNIPAM–PHEMA IPN microgels is shown in Scheme 1.

![Scheme 1](View Article Online)
before further operation. The initiator (0.024 g KPS) and accelerator (0.02 g TEMED) were separately dissolved in water and added rapidly to the solution, bringing the final solution volume to 37 mL. The reaction lasted for 10 min under a nitrogen atmosphere, and the temperature was well regulated at 23 °C with a water bath. The obtained IPN microgels through dialysis (MWCO 14000) for 2 weeks was freeze-dried to dry gel before use.

**Instruments and measurements**

The particle size was measured by dynamic light scattering (DLS) using a zetasizer nano instrument (Malvern, England). The scattering angle of all the measurements is 90°. The concentration of PNIPAM–PHEMA IPN microgels in D2O was fixed to 10 wt% and placed at 4 °C for a week before FT-IR measurements to ensure that they are completely swollen. The sample of PNIPAM–PHEMA IPN microgel solution for FT-IR measurements was prepared by sealing between two CaF2 tablets. All the time-resolved FTIR spectra at variable temperatures were recorded using a Nicolet Nexus 6700 FTIR spectrometer equipped with a DTGS detector. 32 scans at a resolution of 4 cm⁻¹ were accumulated to obtain an acceptable signal-to-noise ratio. The temperature was manually controlled with an electronic cell holder at a rate of ca. 0.3 °C min⁻¹ with an increment of 1 °C (accuracy: 0.1 °C). Baseline correction was performed by the OMINIC 6.1a software.

**Investigation methods**

**Perturbation correlation moving window (PCMW).** FTIR spectra recorded with an increment of 0.5 °C were used to perform PCMW analysis. Primary data processing was carried out with the method provided by Morita and further correlation calculation was conducted using the 2D Shige ver. 1.3 software (Shigeaki Morita, Kwansei Gakuin University, Japan, 2004–2005). The final contour maps were plotted using Origin Program ver. 8.0, with the red colors being defined as positive intensities and the green colors as negative ones. An appropriate window size (2m + 1 = 11) was chosen to generate PCMW spectra with good quality.

**Two-dimensional correlation analysis (2Dcos).** The temperature-dependent FTIR spectra recorded at an interval of 1 °C in certain wavenumber ranges were selected to perform 2D correlation analysis. 2D correlation analysis was conducted using the same 2D Shige ver. 1.3 software (Shigeaki Morita, Kwansei Gakuin University, Japan, 2004–2005) and was further plotted into the contour maps using Origin Program ver. 8.0. In the contour maps, red colors are defined as positive intensities, while the blue colors are defined as negative ones.

**Results and discussion**

**DLS measurements**

Fig. 1 shows the size distributions of hydrodynamic radii of PNIPAM and IPN microgels at 25 °C. The polymer concentration of the PNIPAM and IPN microgel dispersions was the same as 5.0 × 10⁻⁶ g mL⁻¹ at pH = 7. The radius of the IPN microgel is smaller than that of the PNIPAM microgel because of the addition of the hydrophobic PHEMA polymer network, making the microgel absorb less water at room temperature.

As shown in Fig. 2, the black and red lines correspond to the volume phase transition of PNIPAM and IPN microgels. We take the point with the most drastic size change as VPTT. So the VPTTs of PNIPAM and IPN microgels are respectively 32 °C and 29 °C. An obvious decrease of VPTT could be detected in the IPN system compared to PNIPAM.

**Conventional FTIR analysis**

Temperature-dependent FT-IR measurements of IPN microgels in D2O (10 wt%) were performed during a heating-and-cooling cycle between 21 and 40 °C to elucidate the dynamic mechanism of the thermo-responsive behavior, as shown in Fig. 3. It should be noted that we used D2O, rather than H2O, as the solvent in order to eliminate the overlap of the v(O–H) band of H2O around 1640 cm⁻¹ with v(C=O) of PNIPAM as well as the broad v(O–H) band of H2O around 3300 cm⁻¹ with v(C–H) bands. For the thermo-responsive PNIPAM segments, the transition temperature in D2O is ca. 0.7 °C higher than that in H2O. Thus, the deuterium isotope effect can be considered to cause no obvious changes on the phase separation of PNIPAM–PHEMA IPN microgels.
Herein, we specifically focus on the following two spectral regions: the C–H stretching region (3030–2840 cm$^{-1}$) and the C=O stretching region (1755–1580 cm$^{-1}$). In this way, we are able to trace almost all the group motion of IPN microgels during the volume phase transition. As shown in Fig. 3, during the heating process, all the C–H stretching bands shift to lower frequency, indicating the changes of interactions between the hydrophobic moieties of the polymer and water molecules in the system. As is known, water clathrates exist around the hydrophobic moieties of water-soluble polymers in a well-ordered structure and more water molecules surrounding C–H groups would result in higher vibrational frequency.50,51 Thus we believe that the C–H groups undergo dehydration with increasing temperature, which should mainly arise from the PNIPAM segments. As shown in Fig. 3, during heating, the amide I groups of PNIPAM show a binary spectral intensity change, similar to the spectral variation of pure PNIPAM in D$_2$O.20 Generally, the $\nu$(C=O) band can be roughly considered to be the combination of two bands at 1626 and 1651 cm$^{-1}$, which can be assigned to C=O stretching vibrations in C=O/D$_2$O and C=O/D–N hydrogen bonds, respectively. Thus the binary change of amide I in the PNIPAM segments during heating can be explained by the transformation of the hydrogen bonds of C=O from being with water to being self-associated ones.51–53 However, the phase transition is relatively smooth compared to that of pure PNIPAM. No obvious abrupt change could be detected in this system, which could be attributed to the introduction of PHEMA. The existence of the PHEMA network slows down the collapse of PNIPAM microgels and restricts the phase transition of PNIPAM microgels. Compared to the amide I group of PNIPAM, the intensity of the ester carbonyl group of PHEMA is similar while the degree of change is relatively weak. It is reasonable because PHEMA possesses no temperature-responsive properties under this condition. Thus, together with the increase in the hydrophobicity of the polymer chains, water molecules are expelled out of the polymer chains at the same time, as can be detected in the temperature-resolved FTIR spectra. During the cooling process, the case is just opposite to that of the heating.

To quantitatively describe the two volume phase transition processes during heating and cooling, the temperature-dependent frequency shifts of $\nu_{as}(\text{CH}_3)$ and $\nu_{as}(\text{CH}_2)$ as well as the half integral area of two kinds of C=O have been plotted and shown in Fig. 4. All the C–H stretching bands in the 3030–2840 cm$^{-1}$ range shift to lower wavenumbers during heating due to the dehydration of polymer chains. The reverse is true for the cooling process. However, the change of both the wavenumber shifts of $\nu_{as}(\text{CH}_3)$ and $\nu_{as}(\text{CH}_2)$ is not that drastic making it hard for us to determine the VPTT of the IPN microgel.

Additionally, the determination of VPTT of the microgel 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. 4. In the region 1755–1680 cm\(^{-1}\), the area change is relatively little and the same trend could be detected in the cooling process, which is in good accordance with the 1D IR spectra. As PHEMA possesses no temperature-responsive properties in this temperature region, the weak change could be referred to as “driven phase transition behaviour”, which is due to the driving effect of the volume phase transition of PNIPAM.

In the region of 1674–1580 cm\(^{-1}\), the integral area shows an unusual change during both heating and cooling processes. In the heating process, the integral area experiences a “decrease–increase–further decrease” process, which is totally different from other PNIPAM-based systems.\(^\text{20,52,53}\) During cooling, the integral area experiences an “increase–decrease” process, which shows a different trend from that in the heating process. Additionally, the integral area during the cooling process is larger than that in the heating process and the changing level is relatively weak. As PHEMA would form hydrogen bonds with PNIPAM and possesses no thermo-responsive properties, the changing level would be thus reduced. The non-thermo-responsive properties of PHEMA would help the IPN microgel to retain some water at high temperatures, which would lead to a more hydrophilic environment in the beginning of the cooling process and thus a larger integral area.

Another noticeable phenomenon is the good reversibility during the volume phase transition process. Both the temperature-dependent frequency shifts of \(v_{\text{as}}(\text{CH}_3)\) and \(v_{\text{as}}(\text{CH}_2)\) and the integral area of two kinds of C=O could return to the original point. This could be attributed to the special IPN structure. The PHEMA part in the IPN system would act as a skeleton in the microgel.\(^\text{30}\) In the heating process, it would restrict the phase transition of PNIPAM. However, in the cooling process, the non-thermo-responsive PHEMA network behaves as a soft and non-collapsing gel in the IPN, which could “memorize” the condition before the phase transition and thus help the IPN microgel to return to the original state. However, conventional 1DIR analysis cannot provide us a clear explanation for the unusual VPT behavior which will be further traced and clarified by following PCMW and 2Deos analysis.

**Perturbation correlation moving window (PCMW)**

To obtain more detailed spectral variations and accurate phase transition temperatures for the different groups in the PNIPAM–PHEMA IPN microgel, 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 intensities, while negative one for decreasing; positive asynchronous correlation corresponds to a convex spectral intensity variation while negative one corresponds to a concave variation. In this paper, only the synchronous spectra of PCMW are presented in Fig. 5 for the determination of VPTT 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 29 °C and 26 °C, respectively. It is worth noting that the VPTT during cooling is slightly lower than that in the heating process, indicating a hysteresis of the microgel 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 the PNIPAM–PHEMA IPN microgel in this paper. Additionally, it is worth noting that the synchronous spectra of the C=O group of PHEMA in PCMW are relatively weak, which means the phase transition degree is relatively low. This could be attributed to the non-thermo-responsive properties of PHEMA, which is also in good accordance with previous 1D IR studies. Interestingly, the blank part of the synchronous spectra of the C=O group of PHEMA (around 29 °C) corresponds to the most dramatic part of other groups. It is presumed that this phenomenon could be attributed to the redistribution of different hydrogen bonds in the system. Detailed information could be obtained in the following 2Dcos analysis.

Two-dimensional correlation spectroscopy (2Dcos)

2Dcos is a mathematical method whose basic principles were first proposed by Noda in 1986. 2Dcos has been considerably applied to interpret spectroscopic intensity fluctuations under different types of external perturbations (e.g. temperature, pressure, concentration, time, and electromagnetism) ever since. By spreading the original spectra along a second dimension, features not readily visible in conventional analysis can be sorted out, and hence spectral resolution enhancement can be achieved. In addition, 2Dcos can be applied to deduce the specific sequence order of different chemical groups under a certain physical or chemical variable which cannot be obtained straight from conventional 1D spectra.

All the FTIR spectra in heating and cooling between 21 and 40 °C with an increment of 0.5 °C are applied to generate the 2Dcos spectra and the obtained synchronous and the asynchronous spectra are shown in Fig. 6.

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**Fig. 5** PCMW synchronous spectra of PNIPAM–PHEMA IPN microgel during heating and cooling. Warm colors (red) refer to positive intensities, while cold colors (blue) refer to negative intensities.
2D synchronous spectra provide information on simultaneous changes between two wavenumbers. For instance, the bands related to the C=O group of PNIPAM segments have negative cross-peaks, indicating that they display opposite sensitivities to temperature perturbation, that is, one decreases while the other is increasing during heating determined from raw spectra. 2D asynchronous spectra can significantly enhance the resolution of the original spectra. In Fig. 6, many subtle bands such as the bands at 1733 cm$^{-1}$ and 1600 cm$^{-1}$ attributed from $\nu$(C=OH) and $\nu$(C=ON⋯D$_2$O) that cannot be determined in the 1D analysis have been identified. These additionally observed bands related to subtle group conformations could provide more detailed information and significantly assist in figuring out the mechanism of the complex phase transition process. For clarity, all the bands found in asynchronous spectra and their corresponding assignments are presented in Table 1.

In addition to enhancing the spectral resolution, 2Dcos can also provide useful information on the specific sequence order of the chemical groups taking place under external perturbation. The judging rule can be summarized as Noda’s role, that is if cross-peaks ($\nu_1$, $\nu_2$, assume $\nu_1 > \nu_2$) in the synchronous and asynchronous maps have the same symbol, both positive

![2D Synchronous and Asynchronous Spectra](image)

**Fig. 6** 2D synchronous and asynchronous spectra of the PNIPAM–PHEMA IPN microgel during heating and cooling. Warm colors (red) refer to positive intensities, while cold colors (blue) refer to negative intensities.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>2985</td>
<td>$\nu_{as}$(hydrated CH$_3$)</td>
</tr>
<tr>
<td>2971, 2967</td>
<td>$\nu_{as}$(dehydrated CH$_3$)</td>
</tr>
<tr>
<td>2946, 2935</td>
<td>$\nu_{as}$(dehydrated CH$_2$)</td>
</tr>
<tr>
<td>2925</td>
<td>$\nu$ (CH)</td>
</tr>
<tr>
<td>2871</td>
<td>$\nu$(CH$_3$)</td>
</tr>
<tr>
<td>1773</td>
<td>$\nu$(C=OH)</td>
</tr>
<tr>
<td>1716</td>
<td>$\nu$(C=O⋯D−N$_N$)</td>
</tr>
<tr>
<td>1699</td>
<td>$\nu$(C=O⋯D$_2$O)</td>
</tr>
<tr>
<td>1658, 1652</td>
<td>$\nu$(C=O⋯D−N$_N$)</td>
</tr>
<tr>
<td>1645</td>
<td>$\nu$(C=O⋯D−O$_H$)</td>
</tr>
<tr>
<td>1625</td>
<td>$\nu$(C=O⋯D$_2$O)</td>
</tr>
<tr>
<td>1606, 1600</td>
<td>$\nu$(C=O⋯2D$_2$O)</td>
</tr>
</tbody>
</table>
or both negative, then we can conclude that a change at \(v_1\) occurs prior to that at \(v_2\) with the perturbation, whereas if cross-peaks \((v_1, v_2)\) in the synchronous and asynchronous maps have different symbols, one positive and the other negative, then we can infer that peak \(v_2\) varies prior to peak \(v_1\).\(^{59}\)

**Analysis of the heating process**

In consideration of the relatively lengthy details for the determination of the sequence of spectral peaks, we decided to present the final order for the heating and cooling process in ESL\(^{†}\). The detailed order is listed as follows (\(-\) means earlier than or prior to): \(1699 \text{ cm}^{-1} \rightarrow 1600 \text{ cm}^{-1} \rightarrow 2946 \text{ cm}^{-1} \rightarrow 1645 \text{ cm}^{-1} \rightarrow 2971 \text{ cm}^{-1} \rightarrow 1652 \text{ cm}^{-1} \rightarrow 1625 \text{ cm}^{-1} \rightarrow 2925 \text{ cm}^{-1} \rightarrow 2871 \text{ cm}^{-1} \rightarrow 1733 \text{ cm}^{-1} \rightarrow 2985 \text{ cm}^{-1} \rightarrow 1716 \text{ cm}^{-1}\).

This sequence order can be interpreted as the following three aspects:

1. Considering separately C–H related vibrations, the sequence can be extracted as follows: \(2946 \text{ cm}^{-1} \rightarrow 2971 \text{ cm}^{-1} \rightarrow 2925 \text{ cm}^{-1} \rightarrow 2871 \text{ cm}^{-1} \rightarrow 2985 \text{ cm}^{-1}\), that is, \(v_{as}(\text{hydrated CH}_2) \rightarrow v_{as}(\text{dehydrated CH}_3) \rightarrow v_{as}(\text{dehydrated CH}_2) \rightarrow v_{as}(\text{CH}_3) \rightarrow v_{as}(\text{hydrated CH}_3)\). Without considering the differences in stretching modes, the sequence can be described as \(\text{CH}_2 \rightarrow \text{CH}_3\). However, the \(\text{CH}_2\) group exists both in the side chain of PHEMA and the backbone of PNIPAM, which cannot be clearly separated under this condition. Thus no direct conclusion could be drawn on this region. On the other hand, if we consider only stretching modes, an interesting sequence can be found for the methyl group that the asymmetric stretching vibration had an earlier response than the symmetric stretching vibration. As previously reported, the direction of asymmetric stretching vibration is parallel to the polymer chain axis while that of symmetric stretching vibration is vertical to the polymer chain axis.\(^{60}\) Therefore, we can conclude that the IPN microgel had the chain collapsed along the backbone first before water molecules were expelled outside the network.

2. Considering separately C=O related vibrations, the sequence can be extracted as follows: \(1699 \text{ cm}^{-1} \rightarrow 1600 \text{ cm}^{-1} \rightarrow 1645 \text{ cm}^{-1} \rightarrow 1652 \text{ cm}^{-1} \rightarrow 1733 \text{ cm}^{-1} \rightarrow 1716 \text{ cm}^{-1}\); that is, \(v(C=O) \rightarrow v(C=O) \rightarrow v(C=O) \rightarrow v(C=O) \rightarrow v(C=O) \rightarrow v(C=O)\). In the heating process, the hydrogen bond between C=O of PHEMA and water broke down first, which could be due to the hydrophobic properties of PHEMA. Thus some water would be expelled out of the IPN microgel and a hydrophobic environment was created. In this relatively hydrophobic environment, the hydrogen bond between C=O of PNIPAM and water would break down more easily compared to the pure PNIPAM hydrogel,\(^{58}\) which could be responsible for the decrease of VPTT of the IPN microgel compared to the PNIPAM microgel. Dehydrated C=O and C=O forming hydrogen bonds with PNIPAM responded to temperature after the phase transition of PNIPAM, which implies that the PHEMA segments are indirectly influenced and exhibit “driven phase transition behaviour”. Overall, the hydrophobic PHEMA created a hydrophobic environment, which induced the phase transition of PNIPAM, and the phase transition of PNIPAM drives the PHEMA to respond to the heating temperature in turn. The special IPN structure plays an important role in this process, which makes PNIPAM and PHEAM interact with each other at the molecular level.

Another noticeable phenomenon is that both the 2D synchronous and asynchronous spectra of PHEMA segments during heating are blank, only the cross peak between the C=O group of PHEMA and PNIPAM could be detected, implying that the phase transition behavior of PHEMA was closely connected to PNIPAM, as discussed before.

3. Combining C=H and C=O related stretching vibrations, the whole sequence can be summarized as follows: \(\text{C}=\text{O}_\text{H} \rightarrow \text{C}=\text{O}_\text{N} \rightarrow \text{CH}_2 \rightarrow \text{CH}_3\). Combining our previous discussion, we can conclude that the driving force for chain collapse of the IPN microgel during heating was the breakage of the hydrogen bond between HEMA and water.

**Analysis of the cooling process**

Similarly, the sequence of group motion of the PNIPAM hydrogel in the cooling process can also be deduced as follows: \(1699 \text{ cm}^{-1} \rightarrow 1606 \text{ cm}^{-1} \rightarrow 1733 \text{ cm}^{-1} \rightarrow 1658 \text{ cm}^{-1} \rightarrow 1645 \text{ cm}^{-1} \rightarrow 2985 \text{ cm}^{-1} \rightarrow 1625 \text{ cm}^{-1} \rightarrow 2967 \text{ cm}^{-1} \rightarrow 2871 \text{ cm}^{-1} \rightarrow 2925 \text{ cm}^{-1} \rightarrow 1716 \text{ cm}^{-1} \rightarrow 2935 \text{ cm}^{-1} \rightarrow 2883 \text{ cm}^{-1} \rightarrow 2946 \text{ cm}^{-1}\).

We adopted the same analysis method as that in the heating process.

1. For C–H related stretching vibrations, the sequence can be extracted as follows: \(2985 \text{ cm}^{-1} \rightarrow 2967 \text{ cm}^{-1} \rightarrow 2871 \text{ cm}^{-1} \rightarrow 2925 \text{ cm}^{-1} \rightarrow 2935 \text{ cm}^{-1} \rightarrow 2883 \text{ cm}^{-1} \rightarrow 2946 \text{ cm}^{-1}\); that is, \(v_{as}(\text{hydrated CH}_3) \rightarrow v_{as}(\text{dehydrated CH}_3) \rightarrow v_C(\text{CH}_3) \rightarrow v_{as}(\text{dehydrated CH}_2) \rightarrow v_{as}(\text{hydrated CH}_3) \rightarrow v_C(\text{CH}) \rightarrow v_{as}(\text{hydrated CH}_2)\). Without considering the differences in stretching modes, the sequence can be described as \(\text{CH}_3 \rightarrow \text{CH}_2\), indicating that during cooling the response order is opposite to that of the heating process. However, due to the same reason stated in our previous study, no more details could be simply obtained. To carefully compare the 2D synchronous and asynchronous spectra of the CH region during the cooling process with that of the heating process, we can find that more peaks could be obtained in the cooling process, such as the peaks at \(2935 \text{ cm}^{-1}\) and \(2883 \text{ cm}^{-1}\), which are attributed to \(v_{as}(\text{hydrated CH}_2)\) and \(v_C(\text{CH}_3)\). In the heating process, the IPN microgels are well swelled and the environment is uniform for both PNIPAM and PHEAM segments. The difference between the \(\text{CH}_2\) group of the side chain of PHEMA and the \(\text{CH}_2\) group of the backbone of PNIPAM could not be distinguished. However, after the phase transition is complete, the PNIPAM segments would greatly collapse while the phase transition degree of PHEMA segments was little. The environment would be inhomogeneous and the two different \(\text{CH}_2\) groups could be well separated. This also reveals the non-thermo-responsive properties of PHEMA, as discussed before.

2. For C=O related vibrations, the sequence can be extracted as follows: \(1699 \text{ cm}^{-1} \rightarrow 1606 \text{ cm}^{-1} \rightarrow 1733 \text{ cm}^{-1} \rightarrow 1658 \text{ cm}^{-1} \rightarrow 1645 \text{ cm}^{-1} \rightarrow 2985 \text{ cm}^{-1} \rightarrow 1625 \text{ cm}^{-1} \rightarrow 2967 \text{ cm}^{-1} \rightarrow 2871 \text{ cm}^{-1} \rightarrow 2925 \text{ cm}^{-1} \rightarrow 1716 \text{ cm}^{-1} \rightarrow 2935 \text{ cm}^{-1} \rightarrow 2883 \text{ cm}^{-1} \rightarrow 2946 \text{ cm}^{-1}\); that is,
and cooling processes. This journal is © The Royal Society of Chemistry 2014

Proposed dynamic mechanism of the volume phase transition of the PNIPAM–PHEMA IPN microgel

Based on the analysis above, we can clearly understand the volume phase transition dynamics of PNIPAM–PHEMA IPN during the heating and cooling processes. For a more intuitive understanding of the dynamic mechanism, we present a schematic illustration in Scheme 2. At a lower temperature below LCST, as the aliphatic groups were surrounded by water molecules and carbonyl groups formed hydrogen bonds with water molecules, PNIPAM–PHEMA IPN microgels would be well swollen. Herein, the existence of PHEMA segments would have two effects on the IPN microgels. Firstly, PHEMA is hydrophobic compared to PNIPAM, PHEMA segments would drive the water away from the PNIPAM microgel. Secondly, the carbonyl group and hydroxyl group on the side chain of HEMA would form hydrogen bonds with the amide group on the side chain of NIPAM, which also helps pump water from the PNIPAM microgel to the surrounding environment. With the temperature increase, PHEMA segments would help create a hydrophobic environment, which could account for the decrease of VPTT. However, as PHEMA exhibits only slight response to temperature, PHEMA behaves as a soft, non-collapsing gel in the IPN. The non-collapsing gel would play the role of a skeleton at high temperatures, which reduces the collapse degree of the volume phase transition. This could account for the results that the size of the IPN microgel after the volume phase transition is bigger than that of the PNIPAM microgel, as shown in Fig. 2. During the heating process, PHEMA would act as an “initiator” in the beginning of the volume phase transition, as an independent segment in the process of the volume phase transition and as a “controller” in the end of the volume phase transition. In the sequential cooling process, PHEMA plays similar roles in the beginning, in the process and in the end of the volume phase transition. Additionally, as PHEMA exhibits only a slight response to temperature, it maintains its original size in the whole phase transition, which would help PNIPAM to return to its original condition. Our proposed mechanism for the volume phase transition of PNIPAM–PHEMA IPN discerned for the first time the specific order taking place between the physical diffusion of water molecules and hydrogen bonding association among groups and additionally identified the driving force of each process.

In copolymer systems, such as poly(N-isopropylacrylamide-co-acrylic acid) (PNIPAM-co-AA) hydrogels, AA would take part in the volume phase transition in the whole process. However, PNIPAM–PHEMA IPN microgels, as we state before,
contain two parts which are connected with each other only by hydrogen bonds. The phase transition of IPN is really unusual, PHEMA would act as an “initiator” in the beginning of the volume phase transition, as an independent segment in the process of the volume phase transition and as a “controller” in the end of the volume phase transition.

Conclusions

In this paper, we performed DLS and FTIR measurements, in combination with PCMW and 2Dcos, to investigate the thermally induced volume phase transition behavior of the PNIPAM–PHEMA IPN microgels by in situ tracing at the molecular level. An unusual volume phase transition behavior could be observed in the DLS measurements. These phenomena can also be observed in the temperature-dependent FTIR spectra and the corresponding quantitative analysis as well as in the PCMW spectra. Finally, 2Dcos was employed to elucidate the thermally dynamic hydration mechanism of PNIPAM–PHEMA IPN microgels. During the phase transition, PHEMA acts as an “initiator” in the beginning of the volume phase transition, as an independent segment in the process of the volume phase transition and as a “controller” in the end of the volume phase transition. Additionally, due to the hydrophobic and non-thermo-responsive properties of PHEMA and the special IPN structure, the volume phase transition temperature and the volume phase transition degree could be decreased.

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Notes and references