Toward the dynamic phase transition mechanism of a thermoresponsive ionic liquid in the presence of different thermoresponsive polymers†

Ge Wang and Peiyi Wu*

The influence of two thermoresponsive polymers, poly(N-isopropylacrylamide) (PNIPAM) and poly(N-vinylcaprolactam) (PVCL), on the phase transition behavior of a thermoresponsive ionic liquid, tributylhexylphosphonium 3-sulfopropylmethacrylate ([P4,4,4,6][MC3S]), was investigated. An obvious distinction was observed in the LCSTs and morphologies of [P4,4,4,6][MC3S]–PNIPAM and [P4,4,4,6][MC3S]–PVCL aqueous solutions, indicating their large differences in dynamic transition processes. In general, PNIPAM can “break” the water structure of [P4,4,4,6][MC3S] to decrease the transition temperature, while PVCL can “make” the water structure to increase it. Surprisingly, [P4,4,4,6][MC3S] has an unusual over-hydration behavior before dehydration while PNIPAM experiences a two-step transition process in [P4,4,4,6][MC3S]–PNIPAM aqueous solution, which has never been reported so far. Further studies revealed that the formation of strong intra-/inter-molecular hydrogen bonds C=O⋯D–N in PNIPAM is the driving force for the LCST phenomenon of [P4,4,4,6][MC3S]–PNIPAM solution, while it is the [P4,4,4,6][MC3S] that dominates the phase separation of [P4,4,4,6][MC3S]–PVCL solution.

Introduction

Ionic liquids (ILs) are organic salts whose melting points are very low (below 100 °C or even at room temperature).1,2 They have many unique properties (excellent ionic conductivities, broad electro-chemical window, high thermal and chemical stability, negligible vapor pressure, etc.), which can be flexibly tuned by combining different cations and anions. According to an estimation, more than a million potential cation/anion combinations are available that provide the unlimited possibility for ILs to be applied in many specific areas.3 Hence, the research into ILs is booming. ILs have been widely investigated in various fields including organic synthesis,4–6 catalysis,6–8 electrochemistry,9,10 analytical chemistry,11,12 separation13,14 and polymer chemistry.15–18

As a typical example of charged organic materials, ILs have multiple interactions with many substances including solvents,19 celluloses,20 proteins21 and polymers especially thermoresponsive polymers.22–24 Among a great variety of thermoresponsive polymers, poly(N-isopropylacrylamide) (PNIPAM) with a lower critical solution temperature (LCST ~ 32 °C) close to the physiological temperature has been widely studied. In 2011, Venkatesu et al. investigated the effect of an imidazolium-based IL, 1-benzyl-3-methylimidazolium tetrafluoroborate ([Bzmim][BF4]), on the LCST behavior of PNIPAM in an aqueous solution.22 Their experimental results elucidated that [Bzmim][BF4] destabilizes the hydrated macro-molecule structure and reduces the LCST of PNIPAM. Our group observed that 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF4]) acts as the “destroyer” and the “constructor” for the phase behavior of PNIPAM.23 Besides PNIPAM, poly(N-vinylcaprolactam) (PVCL) is another well-studied thermoresponsive polymer. Lately, we investigated the thermodynamic phase behavior of PVCL solution in the presence of different hydrophilic/hydrophobic ILs.24 The addition of hydrophilic ILs hardly affects the transition temperature of PVCL, while the addition of hydrophobic ILs, such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Emin][NTf2]), can increase it. In general, related studies are rare and have focused on ternary composite systems, in which the interactions are versatile and complex. However, only conventional ILs are involved in these systems and ILs are used merely as additives.

Recently, thermoresponsive ionic liquids, especially LCST-type ILs, have been attracting much interest in the IL science. As a distinct subclass of ILs, LCST-type ILs exhibit unique advantages in many applications.25–27 More and more studies have focused on the phase separation behavior of ILs, or even poly(ionic liquid)s (PILs). In 2007, the LCST-type phase transition of amino-acid-based ILs was reported by Ohno’s group.28 To the
best of our knowledge, this system is the first example for LCST-type behavior of IL/water mixtures. By adjusting the balance between hydrophilicity and hydrophobicity, a series of LCST-type ILs have been synthesized. In 2012, Ohno’s group first reported the LCST phase transition behavior of PILs in pure water. More recently, a series of new LCST-type ILs (TVBP-CsS) and their polymers, cationic PILs, were reported by Yuan’s group. Nevertheless, the study of thermostressive ILs is still in its infancy, and current research studies are confined to binary systems that only involve the thermostressive ILs and solvents (water in most cases). Moreover, there has been no report on studying the interactions between thermostressive ILs and thermostressive polymers so far, let alone on the integrated mechanism of the phase transition on the molecular level. Studying the interactions between thermostressive ILs and thermostressive polymers is helpful for comparing the difference between them, as well as for further understanding the transition behavior of ILs. In consideration of the unique properties of ILs and thermostressive polymers, the combination of thermostressive polymers with LCST-type ILs could not only broaden their own applications, but also be proposed for the application in new fields. Under this circumstance, comprehension of the interactions between LCST-type ILs and thermostressive polymers becomes very essential and attractive to study.

In the present work, we designed a ternary composite system composed of a LCST-type IL, tributylhexylphosphonium 3-sulfopropylmethacrylate ([P4,4,4,6][MC3S]), thermostressive polymers and water to explore the effect of thermostressive polymers on the LCST behavior of ILs and the interactions between the IL and the polymers at the same time. Moreover, the phase separation mechanism of [P4,4,4,6][MC3S] has been clarified recently, which provides the convenience for studying thermostressive IL-included ternary complex systems. As for thermostressive polymers, we chose PNIPAM and PVCL as two typical examples. PNIPAM is the most familiar LCST-type polymer whose phase separation undergoes a coil–globule transition. As a type I thermostressive polymer, PVCL shows a continuous phase transition behavior with liquid–liquid phase separation (LLPS). The influence of different thermostressive polymers on the LCST-phase transition of [P4,4,4,6][MC3S] solution was first elucidated by DSC, optical microscopy, and NMR and FT-IR spectroscopy in combination with the perturbation correlation moving window (PCMW) technique, which is very helpful to further understand the interactions of other thermostressive ILs involved systems.

**Experimental**

**Materials**

N-Isopropylacrylamide (NIPAM) was purchased from Aladdin Reagent Co. and recrystallized from cyclohexane prior to polymerization. N-Vinylcaprolactam (VCL) was obtained from Alfa Aesar Co. and purified by passing through a short alumina column prior to use. 2,2'-Azobis(2-isobutynitrile) (AIBN; Aladdin Reagent Co.) was recrystallized from ethanol. Tributylhexylphosphonium bromide ([P4,4,4,6]Br); Beijing HWRK Chem Co.), potassium 3-sulfopropylmethacrylate ([K][MC3S]; Aladdin Reagent Co.) and deuterium oxide (D2O, D-99.9%; Cambridge Isotope Laboratories Inc.) were used as received.

**Sample preparation**

The detailed synthesis procedures are shown in the ESI.

**Differential scanning calorimetry (DSC)**

Calorimetric measurements were performed on the Mettler-Toledo differential scanning calorimetry (DSC) thermal analyzer with a scanning rate of 10 °C min⁻¹. Additionally, the testing temperature for DSC ranged from 10 to 70 °C.

**Optical microscopy**

Optical microscopy observations were carried out on a Leica DM2500P polarizing microscope with a Linkam THMS600 hot stage to control the experimental temperature, whose sensor accuracy is 0.1 °C. The heating rate is 0.5 °C min⁻¹ for [P4,4,4,6][MC3S]–PNIPAM and [P4,4,4,6][MC3S]–PVCL aqueous solutions.

**Temperature-variable ¹H nuclear magnetic resonance (¹H NMR) analysis**

Temperature-variable ¹H NMR spectra of [P4,4,4,6][MC3S]–D2O solution (20% (w/v)) and 20% (w/v) [P4,4,4,6][MC3S]–D2O with 4% (w/v) PNIPAM or PVCL (polymers/IL = 20 wt%) were recorded on a Varian Mercury plus (400 MHz) spectrometer at a rate of 0.5 °C min⁻¹. For [P4,4,4,6][MC3S]–PNIPAM–D2O solution, the testing temperature ranged from 15 to 40 °C; while for [P4,4,4,6][MC3S]–D2O and [P4,4,4,6][MC3S]–PVCL–D2O solutions, the heating range was 25 to 50 °C. All the spectra were obtained using the same instrumental parameters.

**Fourier transform infrared spectroscopy (FT-IR)**

The solutions of 20% (w/v) [P4,4,4,6][MC3S]–D2O with 4% (w/v) PNIPAM and 20% (w/v) [P4,4,4,6][MC3S]–D2O with 4% (w/v) PVCL were sealed between two ZnS tablets for FT-IR measurements. All temperature-dependent FT-IR spectra were collected on a Nicolet Nexus 6700 spectrometer with a DTGS detector. 32 scans at a resolution of 2 cm⁻¹ were accumulated to achieve acceptable high-quality spectra. Temperatures were controlled using an electronic cell holder at a rate of 0.5 °C min⁻¹ with an increment of 1 °C (accuracy is 0.1 °C). After all spectra were collected, the original spectra were baseline-corrected using Omnic 6.1a software. FT-IR spectra collected from 15 to 40 °C for [P4,4,4,6][MC3S]–PNIPAM and 25 to 50 °C for [P4,4,4,6][MC3S]–PVCL were used for conventional analysis and further two-dimensional analysis.

**Perturbation correlation moving window (PCMW)**

The temperature-dependent FT-IR spectra of different chemical groups at certain wavenumber ranges were selected to carry out the PCMW analysis. The method provided by Morita was utilized to process the raw data. Further correlation information was calculated using the software 2D Shige, ver. 1.3 (©Shigeaki...
Morita, Kwansei Gakuin University, Japan, 2004–2005) with an appropriate window size \((2m + 1 = 11)\) to generate quality PCMW spectra. Finally, the contour maps were plotted using Origin Program \(8.0\) with warm colors (red and yellow) indicating positive intensities while cool colors (blue) indicating the negative ones.

**Results and discussion**

**Calorimetric measurements**

To elucidate the effect of different thermoresponsive polymers on the phase transition behavior of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solution, differential scanning calorimetric measurements were performed. Fig. 1 presents the heating curves of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solutions with different weight ratios of PNIPAM (a) and PVCL (b). The phase separation of pure IL solution (20 wt%) occurs at ca. 37 °C with a broad and asymmetric endothermic peak. Due to the lack of strong self-associated hydrogen bonds, \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) experiences a gradual change above the LCST similar to PVCL.\(^{36}\) By adding 4% (w/v) PNIPAM or PVCL, the transition temperatures of the PNIPAM-involved IL solutions rise drastically to 25 °C, which is lower than the pure IL solution (ca. 37 °C) and pure PNIPAM solution (ca. 32 °C, in Fig. S2(a), ESIF). With the weight ratio of PNIPAM to IL increasing from 20 to 100 wt%, the transition temperatures of the PNIPAM-involved IL solutions are maintained at 25 °C. The endothermic peaks tend to increase and become narrow and symmetric, whose shape approaches those of pure PNIPAM solutions (seen in Fig. S2(a), ESIF). As a result, we surmise that PNIPAM dominates the phase separation of PNIPAM-involved IL solutions, even if the weight ratio of PNIPAM is low. The case is totally different for the PVCL-involved system, the LCST of IL solution mixed with 4% (w/v) PVCL (PVCL/IL = 20 wt%) is 39 °C, which is the middle of pure IL solution (ca. 37 °C) and pure PVCL solution (ca. 41 °C, in Fig. S2(b), ESIF). However, the distinction is small in comparison to the PNIPAM-involved system. What is more, the transition temperatures of the PVCL-involved IL solutions rise gradually as the weight ratio of PVCL to IL increases from 20 to 100 wt%, which is similar to the tendency of pure PVCL solutions (seen in Fig. S2(b), ESIF). Different from the PNIPAM-involved system, the endothermic peaks of PVCL-involved IL solutions are broad and asymmetric and the sizes are almost unchanged. This phenomenon reveals that the phase separation of PVCL-involved IL solution is a gradual dehydration process and large amounts of IL dominate the LCST behavior of PVCL-involved IL solutions.

Generally, the addition of PNIPAM to \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solution can drastically decrease the LCST of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\), while the addition of PVCL increases it. It is well known that the combination of salts with a polymer or protein would affect the behavior of salts and the polymer or protein through their interactions with water.\(^{37,40}\) The thermoresponsive polymers added into the \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solution can interact with water and induce changes in the interaction between the IL and water. This indirect effect of the polymers may alter the transition temperatures of LCST-type IL solutions. Specifically, PNIPAM can “break” the water structure to decrease the transition temperature of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solution, while PVCL can “make” the water structure to increase it. Moreover, the phase diagrams in Figs. S3 and S4 (ESI†) illustrate the LCST variation of IL-included ternary systems and pure thermoresponsive polymer solutions with different concentrations, respectively. To further study the distinction between PNIPAM and PVCL on the phase transition behavior of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\), we chose 20% (w/v) \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) with 4% (w/v) PNIPAM or PVCL (polymers/IL = 20 wt%) for the following experiments.

**Optical microscopy**

Optical microscopy was performed to directly observe the temperature-induced phase transition of IL-included ternary systems. The optical microscopy photographs of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM (15–40 °C) and \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL (25–50 °C) solutions are shown in Fig. 2. When the temperature reaches a specified degree (24 °C for \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM and 39 °C for \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL), the visual field becomes cloudy as a result of phase transition. A multitude of small particles are formed from the homogeneous solutions and they disappear again after the cooling process (Fig. S5, ESI†). Interestingly, the morphologies of the particles in \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM and \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL are different, which means that PNIPAM and PVCL have different effects on the phase transition behavior of \([\text{P}4,4,4,6][\text{MC}3\text{S}]\). The particles in \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM are irregular and fragmented, which is similar to the pure \([\text{P}4,4,4,6][\text{MC}3\text{S}]\) solution (Fig. S6, ESI†). While the particles that stemmed from \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL are regular and globular, which are called “droplets” customarily. More importantly, the appearance of the droplets is a sign of the LLPS phenomenon.\(^{37,42}\) This phenomenon will be further explained by the following FT-IR analysis. In other words, the addition of PVCL makes LLPS occur in the IL-included ternary system, while PNIPAM does not. Moreover, the information about the formed IL-rich domains and the water-rich matrix is given in Fig. S7 and Table S1 (ESI†). The results show that ca. 82% solute remains in the aqueous solution in \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM, while that percentage is about 60% in \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL. As for IL-rich domains, ca. 85% of water remains in the \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PNIPAM system and ca. 47% water remains in the \([\text{P}4,4,4,6][\text{MC}3\text{S}]\)–PVCL one. These data are in good agreement with the following temperature-variable \(^1\text{H} \text{NMR} \) analysis which determined that a

![Fig. 1](image-url)
weaker dehydration process happens in the IL after the addition of PNIPAM.

Temperature-variable $^1$H NMR analysis

Fig. 3 shows the $^1$H NMR spectra of (a) [P$_{4,4,4,6}$][MC3S], (b) [P$_{4,4,4,6}$][MC3S]–PNIPAM and (c) [P$_{4,4,4,6}$][MC3S]–PVCL in D$_2$O ([P$_{4,4,4,6}$][MC3S]/D$_2$O = 20% (w/v), polymers/[P$_{4,4,4,6}$][MC3S] = 20 wt%) and the assignment of various protons according to previous reports. In Fig. 3(b) and (c), we can distinguish the $H_l$ and $H_m$ of PNIPAM and $H_n$ of PVCL from the characteristic peaks ($H_a$, $H_b$, $H_c$, $H_d$, and $H_f$ in anions, $H_g$, $H_h$, and $H_i$ in cations and $H_{e,k}$ in both anions and cations) of the IL, which provide the convenience for tracing different parts of the mixed solutions during the phase separation process.

$^1$H NMR measurement has the advantage of distinguishing the protons located in different chemical environments and tracing the change rule of them during the phase transition process, which is difficult to achieve by other testing methods. Temperature-variable $^1$H NMR spectra of [P$_{4,4,4,6}$][MC3S] (from 25 to 50 °C), [P$_{4,4,4,6}$][MC3S]–PNIPAM (from 15 to 40 °C) and [P$_{4,4,4,6}$][MC3S]–PVCL (from 25 to 50 °C) solutions are presented in Fig. 4(a)–(c), respectively. Normalization was performed referencing to the integrated intensity of HDO. All the peaks shift toward a lower field with a drastic decrease in intensity during the heating process, indicating the formation of aggregates in which the protons are wrapped after phase transition. To describe the degree of phase transition and distinguish the differences between the IL and polymers, quantitative analysis is necessary.

The phase separation fraction $p$ was defined and employed to quantitatively characterize the degree of dehydration as well as phase transition. The definition of $p$ is:

$$p = 1 - (I/I_0)$$

where $I$ is the integrated intensity of the selected resonance peak in the $^1$H NMR spectra and $I_0$ is the integrated intensity of this peak when no phase separation occurs. In this work, we took the integrated intensity obtained from the initial test temperature ([P$_{4,4,4,6}$][MC3S]–PNIPAM for 15 °C, [P$_{4,4,4,6}$][MC3S] and [P$_{4,4,4,6}$][MC3S]–PVCL for 25 °C) as $I_0$. $H_a$, $H_b$, $H_i$, and $H_j$ in the anions of the IL, $H_{g,h}$ in the cations of the IL, $H_l$, and $H_m$ in PNIPAM and $H_n$ in PVCL were chosen for analysis.
Temperature dependence of the phase separation fraction $p$ for different protons in $[\text{P}4,4,4,6]\text{[MC3S]}$ is presented in Fig. 4(d). After a slight decrease, $p$ rises gradually at ca. $37^\circ C$, which is in good agreement with the DSC result. The phenomenon that $p$ undergoes a decrease before LCST is inconspicuous (minimum degree of dehydration $p_{\text{min}} = -0.1$) and it has also been found in other LCST-type ILs. Additionally, we find that $[\text{P}4,4,4,6]\text{[MC3S]}$ experiences a relatively facile transition with a long temperature span (more than $10^\circ C$) and the final phase separation fraction $p_{\text{max}}$ is merely ca. 0.5. It reveals that $[\text{P}4,4,4,6]\text{[MC3S]}$ cannot accomplish a thorough LCST transition and $[\text{P}4,4,4,6]\text{[MC3S]}$ is still surrounded by many water molecules after the phase transition, which is different from other thermoresponsive polymers or gels.

By the way, careful observation shows that the $p_{\text{max}}$ of cations is lower than that of anions, which indicates that anions are more close to the hydrophobic cores. This phenomenon occurs not only in IL solution (Fig. 4(d)) but also in IL-included ternary systems (Fig. 4(e) and (f)).

Fig. 4(e) shows the temperature dependence of $p$ for $\text{D}_2\text{O}$ solution of $[\text{P}4,4,4,6]\text{[MC3S]}$-PNIPAM. Obviously, the addition of PNIPAM has changed the phase transition behavior of the IL greatly and the variations of the protons in PNIPAM and IL are quite different. $[\text{P}4,4,4,6]\text{[MC3S]}$ has an unusual over-hydration behavior before dehydration while PNIPAM experiences a two-step transition process in $[\text{P}4,4,4,6]\text{[MC3S]}$-PNIPAM solution, which has never been reported before. In a certain temperature range ($15-25^\circ C$), both the IL and PNIPAM are well dissolved and their $p$ values almost overlapped and close to zero. When the temperature was increased to $25^\circ C$, the curve diverges into two. Specifically, PNIPAM begins to dehydrate, which is in good agreement with the DSC and optical microscopy results. Meanwhile, an unusual over-hydration behavior occurs in the IL. This result confirms the surmise that PNIPAM dominates the phase separation of PNIPAM-involved IL solution to some extent. We believe that the competitive process for water between the IL and PNIPAM was captured by $^1\text{H}$ NMR. PNIPAM begins to lose complexed water at $25^\circ C$. At the same time, the IL has to form hydrogen bonds with more water, which promotes the hydration degree of IL. Between 25 and $32^\circ C$, the $p$ of IL continues to decrease until reaching $p_{\text{min}} = -0.38$, which is much lower than the pure IL solution ($p_{\text{min}} = -0.1$). On the other hand, due to the drag effect of over-hydrated IL, the dehydration degree of PNIPAM is low. At $32^\circ C$, both the IL and PNIPAM dehydrate sharply and drastically (less than 5 $^\circ C$). However, the $p_{\text{max}}$ of IL is about 0.3, which is less than the pure IL solution (ca. 0.5). A weaker dehydration process happens in the IL after the addition of PNIPAM.

Through the observation of Fig. 4(f), we can find that the addition of PVCL has little effect on the temperature dependence of $p$ for the IL, including a higher LCST and a sharper dehydration process. The $p_{\text{min}}$ is ca. 0.08 and the $p_{\text{max}}$ is ca. 0.57, which are in close proximity to the aforementioned pure IL solution. Only one dehydration process of $[\text{P}4,4,4,6]\text{[MC3S]}$-PVCL solution occurs at $39^\circ C$, which is in accordance with the DSC and optical microscopy results. Hence, the different roles of PVCL and PNIPAM in the phase transition behavior of IL solution are obvious and tempting. However, we have to say, the final dehydration degree of PVCL and PNIPAM is much higher than that of the IL, which reveals that the dehydration processes of these two thermoresponsive polymers are more complete than that of the IL. Although temperature-variable $^1\text{H}$ NMR spectroscopy provides the convenience for the study of different protons and elucidates much irreplaceable information with regard to the phase transition behavior, it is arduous for $^1\text{H}$ NMR to trace the changes in other non-proton

![Fig. 4](https://example.com/fig4.png)

Normalized temperature-variable $^1\text{H}$ NMR spectra of (a) $[\text{P}4,4,4,6]\text{[MC3S]}$, (b) $[\text{P}4,4,4,6]\text{[MC3S]}$-PNIPAM and (c) $[\text{P}4,4,4,6]\text{[MC3S]}$-PVCL in $\text{D}_2\text{O}$ ($[\text{P}4,4,4,6]\text{[MC3S]}/\text{D}_2\text{O} = 20\%$ (w/v), polymers/$[\text{P}4,4,4,6]\text{[MC3S]} = 20$ wt%) and (bottom) their temperature dependence of the phase separated fraction $p$ for different protons, respectively.
chemical groups, such as the ester group. In this case, we need to take advantage of FT-IR measurements.

**Conventional FT-IR analysis**

Vibrational spectroscopy has been proved to be very sensitive to subtle conformational changes, especially for the thermoresponsive behavior. Here, temperature-variable FT-IR spectroscopy has been performed to study the changes in C–O groups during phase transition, as shown in Fig. 5. It should be noted that D$_2$O was utilized as the solvent instead of H$_2$O to eliminate the overlap of the δ(O–H) band at around 1640 cm$^{-1}$ with ν(C–O). Obviously, there exists two kinds of distinguishable C–O groups in the IL-included ternary systems, one is the ester group in [P$_{4,4,4,6}$][MC3S] (1740–1670 cm$^{-1}$), the other is the amide groups in thermoresponsive polymers (1670–1580 cm$^{-1}$ for PNIPAM and 1650–1570 cm$^{-1}$ for PVCL). The C–O stretching bands shift to lower wavenumbers with temperature increase, which should represent the dehydration process during the phase transition. Similar changes can also be found in other thermoresponsive ILs and polymers that under dehydrated conditions. However, the change in ester groups is smaller than that in amide groups. Besides, the peak forms of amide groups are complicated, which reflects the corresponding microscopic structures. It is noted that there exists an isosbestic point in Fig. 5(a) at 1638 cm$^{-1}$. Generally, an isosbestic point appears only when one species is quantitatively converted to another single species. In the case of [P$_{4,4,4,6}$][MC3S]–PNIPAM solution, it indicates that the changes in the amide groups in PNIPAM take place between two single states without apparent intermediate conformations. As for [P$_{4,4,4,6}$][MC3S]–PVCL solution, the amide groups of PVCL have two strong bands at 1608 and 1631 cm$^{-1}$, which are much different from the pure PVCL solution and the PVCL solutions with conventional ILs. The changes in the peak form in amide groups are distinct and could reflect the water environment of the IL indirectly. To show the changes in the frequency and peak form clearly, we plotted the second derivative curves of amide C=O stretching bands, as presented in Fig. 6. The minima in the second derivative curves correspond to the actual peaks in the original absorption spectra. At 15 °C (below LCST) in Fig. 6(a), the pure PNIPAM and IL-PNIPAM solutions have only one strong band at around 1625 cm$^{-1}$, which can be attributed to the vibration of C–O ⋅⋅⋅D–O–D hydrogen bonds in PNIPAM. When the temperature rises to 40 °C (above LCST), a new band at 1650 cm$^{-1}$ is formed, which is assigned to the strong intra-/inter-molecular hydrogen bond C–O ⋅⋅⋅D–N (PNIPAM). Compared with pure PNIPAM solution, IL-PNIPAM experiences a mild phase transition process, especially for the formation of C–O ⋅⋅⋅D–N bonds. This phenomenon manifests that after phase transition, there are still plenty of water surrounding the PNIPAM to hinder the formation of high-density intra-/inter-molecular hydrogen bonds C–O ⋅⋅⋅D–N. In other words, PNIPAM captures water more easily than the IL to “break” the water structure of the IL.

As for IL-PVCL in Fig. 6(b), the situation is much different. Actually, there exist three peaks corresponding to three kinds of lactam groups with distinct water environments. The peak at 1592 cm$^{-1}$ is due to fully hydrated C=O bands (lactam groups hydrogen-bonded to two water molecules); the peak at 1608 cm$^{-1}$ is attributed to hydrated C=O bands ν(C–O ⋅⋅⋅D–O–D) (lactam groups hydrogen-bonded to one water molecule), while the 1631 cm$^{-1}$ one corresponds to polymer–water–polymer hydrogen bonds ν(C–O ⋅⋅⋅D–O–D–O=C) (two lactam groups hydrogen-bonded to one water molecule). At 25 °C (below LCST), fully hydrated and hydrated C=O bands exist at the same time in pure PVCL solution. After phase transition, the intensity of the fully hydrated band decreases, revealing the dehydrated process of lactam groups. While for IL-PVCL solution, the peak at 1592 cm$^{-1}$ disappears and the peak at 1631 cm$^{-1}$ appears at 25 °C (below LCST), indicating that the PVCL in IL-included solution cannot fully hydrate and the relatively dehydrated polymer–water–polymer hydrogen bonds have been formed already before LCST. When the temperature reaches 50 °C (above LCST), the number of polymer–water–polymer hydrogen bonds increase with a decrease of hydrated C=O bands. Obviously, the PVCL in IL-included solution experiences a relatively thorough dehydrated process in comparison to pure PVCL solution. That is to say, PVCL loses water to “make” the water structure around the IL. Last but not least, the formation of polymer–water–polymer hydrogen bonds found in IL-PVCL solution is a spectroscopic sign of the LLPS.

**Fig. 5** Temperature-dependent FT-IR spectra of (a) [P$_{4,4,4,6}$][MC3S]–PNIPAM and (b) [P$_{4,4,4,6}$][MC3S]–PVCL in D$_2$O (IP$_{4,4,4,6}$)[MC3S]/D$_2$O = 20% (w/v), polymers/IP$_{4,4,4,6}$[MC3S] = 20 wt%) in the region of 1740–1570 cm$^{-1}$ during heating between 15 °C and 40 °C and 25 °C and 50 °C, respectively. The temperature increment interval is 1 °C with an increasing rate of 0.5 °C min$^{-1}$.

**Fig. 6** FT-IR spectra and the corresponding second-derivative spectra of (a) [P$_{4,4,4,6}$][MC3S]–PNIPAM–D$_2$O and PNIPAM–D$_2$O solutions and (b) [P$_{4,4,4,6}$][MC3S]–PVCL–D$_2$O and PVCL–D$_2$O solutions at different temperatures during heating.
phenomenon. This provides a microscopic explanation for the different morphologies shown in the optical micrographs above.

**Perturbation correlation moving window**

To obtain clear phase transition points and phase transition temperature regions of distinct C—O groups in IL-included ternary systems, PCWM analysis was carried out. PCWM is a burgeoning technique, whose basic principles can be traced to the conventional moving window proposed by Thomas. In 2006, this technique was improved by Morita to expand the application by introducing the perturbation variable into the correlation equation. Not only does PCWM have the original ability in determining the transition points as the conventional moving window did, but also it can monitor complicated spectral variations along the perturbation direction, which is difficult to detect using other conventional methods. For the convenience of discussion, tentative band assignments of [P4,4,4,6][MC3S]–PNIPAM–D2O and [P4,4,4,6][MC3S]–PVCL–D2O solutions are listed in Table 1.

Fig. 7 presents PCMW synchronous and asynchronous spectra of [P4,4,4,6][MC3S]–PNIPAM and [P4,4,4,6][MC3S]–PVCL solutions during the phase transition process. There are two pairs of bands in the ν(C—O) region of 1740–1570 cm⁻¹. Notably, in Fig. 7(a), the signal intensity of ester C—O (1740–1670 cm⁻¹) is weaker than that of amide C—O (1670–1580 cm⁻¹), which indicates that the amide groups in PNIPAM experience a more drastic transition process than the ester groups in the IL. This conclusion is in conformity with the DSC and temperature-variable ¹H NMR results that PNIPAM dominates the phase separation of PNIPAM-involved IL solution. As far as [P4,4,4,6][MC3S]–PVCL is concerned, the almost equal intensities of ester C—O (1740–1670 cm⁻¹) and amide C—O (1650–1570 cm⁻¹) reveal the synergetic variations of the IL and PVCL during the transition process.

PCMW synchronous spectra can help us find the transition point whereas asynchronous spectra are useful to confirm the transition temperature region by peaks with the strongest intensities. For convenience, we plotted all the points and regions read from PCMW synchronous and asynchronous spectra in Fig. 8. With regard to the [P4,4,4,6][MC3S]–PNIPAM solution (violet dotted line), the transition point of ν(C—O···D–N) in PNIPAM is located at 23 °C, which is lower than ν(C—O···D–O–D) in PNIPAM (24 °C), ν(Dehydrated C—O) in the IL (24 °C) and ν(Hydrated C—O) in the IL (26 °C), indicating that the formation of a strong intra-/inter-molecular hydrogen bond C—O···D–N is the driving force for the LCST behavior. In consideration of [P4,4,4,6][MC3S]–PVCL solution (orange dotted line), the transition point of ν(Hydrated C—O) in the IL is the lowest one, which means the dehydration of ester C—O in the IL dominates the phase separation behavior of [P4,4,4,6][MC3S]–PVCL solution. Additionally, we can find that the dehydrated ester C—O responds earlier than the hydrated one in [P4,4,4,6][MC3S]–PNIPAM, while the sequence is opposite in the [P4,4,4,6][MC3S]–PVCL solution. In other words, the ester C—O in the IL would not start to dehydrate until its conformational changes were completed in [P4,4,4,6][MC3S]–PNIPAM. Taking [P4,4,4,6][MC3S]–PVCL into account, the ester C—O is dominant for the LCST process, so it is not difficult to understand that ester C—O shows a conventional dehydration order, a hydrated ester C—O responds earlier than the dehydrated one.

![Fig. 7](image1.png)

**Fig. 7** PCMW synchronous and asynchronous spectra of (a) PNIPAM/[P4,4,4,6][MC3S] solution between 15 °C and 40 °C and (b) PVCL/[P4,4,4,6][MC3S] solution between 25 °C and 50 °C during heating ([P4,4,4,6][MC3S]/D2O = 20% (w/v), polymers/[P4,4,4,6][MC3S] = 20 wt%). Herein, warm colors (red and yellow) denoted positive intensities, whereas cool colors (blue) denoted the negative ones.

![Fig. 8](image2.png)

**Fig. 8** The corresponding transition temperatures and transition temperature regions of PNIPAM/[P4,4,4,6][MC3S] (violet) and PVCL/[P4,4,4,6][MC3S] (orange) solutions ([P4,4,4,6][MC3S]/D2O = 20% (w/v) and polymers/[P4,4,4,6][MC3S] = 20 wt%) during the heating process as read from PCMW synchronous and asynchronous spectra.

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Tentative assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1713</td>
<td>ν(Dehydrated C—O) for [P4,4,4,6][MC3S]</td>
</tr>
<tr>
<td>1690</td>
<td>ν(Hydrated C—O) for [P4,4,4,6][MC3S]</td>
</tr>
<tr>
<td>1650</td>
<td>ν(C—O···D–N) for PNIPAM</td>
</tr>
<tr>
<td>1625</td>
<td>ν(C—O···D–O–D) for PNIPAM</td>
</tr>
<tr>
<td>1631</td>
<td>ν(C—O···D–O···O—C) for PVCL</td>
</tr>
<tr>
<td>1608</td>
<td>ν(C—O···D–O–D) for PVCL</td>
</tr>
</tbody>
</table>
Proposed phase transition dynamic mechanisms of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM and \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL solutions

Based on the above analysis, we can understand the impact of different thermoresponsive polymers (PNIPAM and PVCL) on the phase transition behavior of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) solution. The schematic illustration is shown in Fig. 9.

In general, PNIPAM can “break” the water structure of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) to decrease the transition temperature, while PVCL can “make” the water structure to increase it. For \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM solution, there exists two phase transition steps during the heating process and it is PNIPAM that dominates the phase transition. When temperature reaches 25 °C, the amide C–O in PNIPAM and the ester C–O in the IL begin to dehydrate. At the same time, the C–H of the IL has to form hydrogen bonds with more water to promote its degree of hydration. Above 32 °C, C–H groups in the IL and PNIPAM dehydrate together to complete the phase transition. In the case of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL solution, the relatively dehydrated polymer–water–polymer hydrogen bond C–O : : D–O–D : : O–C has been formed already before the LCST due to the competition for water. Moreover, the phase separation behavior of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL occurs at 39 °C, which is dominated by \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) with a LLPS phenomenon.

Conclusions

In this paper, DSC, optical microscopy, and temperature-variable \(^1\)H NMR and FT-IR spectroscopy in combination with the PCMW technique are utilized to explore the influence of different thermoresponsive polymers (PNIPAM and PVCL) on the phase transition behavior of a thermoresponsive ionic liquid \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) solution. It is interesting to note that PNIPAM can drastically decrease the LCST of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) to 25 °C, while PVCL can slightly increase it to 39 °C. This is attributed to the effect that PNIPAM can “break” the water structure to decrease the LCST of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\), while PVCL can “make” the water structure to increase it. What is more, the morphologies of the phase transition in \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM and \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL solutions are different. The LLPS phenomenon occurs in the \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL solution, while it does not happen in the \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM one. According to temperature-variable \(^1\)H NMR analysis, we successfully traced a two-step transition behavior in \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM solution: one is for PNIPAM units (ca. 25 °C), the other is for the corporate dehydration of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) and PNIPAM (ca. 32 °C). In the first step, \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) experiences an unusual over-hydration process due to the competition for water between the IL and PNIPAM. For \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL, there is only one transition process at ca. 39 °C. FT-IR spectra demonstrated the changes in ester and amide C–O groups during phase transition. Unexpectedly, the relatively dehydrated polymer–water–polymer hydrogen bond C–O : : D–O–D : : O–C has been formed already before LCST in \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL. Finally, PCMW was employed to illuminate the phase transition dynamic mechanisms of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM and \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PVCL solutions. The formation of strong intra/inter-molecular hydrogen bonds C–O : : D–N in PNIPAM is the driving force for the LCST phenomenon of \([\text{P}_{4,4,4,6}]\text{[MC3S]}\)–PNIPAM solution, while it is the \([\text{P}_{4,4,4,6}]\text{[MC3S]}\) that dominates the phase separation of...
[P4,4,4,6][MC3S]–PVCL solution. Additionally, the formation of polymer–water–polymer hydrogen bonds $\text{C-O-D-O-C}$ is a microscopic explanation for the macroscopic LLPS phenomenon. Thus, the phase transition dynamic mechanisms of [P4,4,4,6][MC3S]–PNIPAM and [P4,4,4,6][MC3S]–PVCL are clarified, which could be helpful to understand the versatile and complex interactions between ILs and polymers.

Acknowledgements

We gratefully acknowledge the financial support from the National Science Foundation of China (NSFC) (No. 21274030 and 51473038).

Notes and references


