Toward the two-step microdynamic phase transition mechanism of an oligo(ethylene glycol)methacrylate-based copolymer with a LCST-type poly(ionic liquid) block†

Yalan Dai and Peiyi Wu

A new LCST-type thermoresponsive polyelectrolyte P[P₄,₄,₄,₄][SS], poly(tetraethyl phosphonium styrene sulfonate), was introduced to PMEO₂MA (poly[2-(2-methoxyethoxy)ethyl methacrylate]) via RAFT polymerization, in order to explore the transition behavior of the block copolymer PMEO₂MA-b-P[P₄,₄,₄,₄][SS] with two distinct LCST-type segments. A relatively sharp LCST-type phase transition with only one transition point is observed in the turbidity curves, while the whole phase transition is completely different from the micro perspective. The phase transition temperature range is relatively broad, according to the unsynchronized changes of different protons of the two blocks in the temperature-variable ¹H NMR analysis. From PCMW analysis, it is found that there exists an obvious two-step phase transition behavior, especially in the region of the C–H groups. Accordingly, we divided the whole transition process into two subregions: 20–40 °C and 40–55 °C in 2Dcos analysis. At the first stage of 20–40 °C, the CH₃ groups mainly belonging to the backbones of PMEO₂MA blocks have the earliest response to the heating and drive the first step of the dehydration process of PMEO₂MA-b-P[P₄,₄,₄,₄][SS], resulting in the formation of an intermediate micelle state composed of the collapsed PMEO₂MA core and hydrophilic P[P₄,₄,₄,₄][SS] corona. In particular, the conformational changes and the more compact structures due to the interaction between the C–O groups and P[P₄,₄,₄,₄][SS] segments (ν(C=O–D₂O–PILs)) were observed using IR analysis. With the continual increase of the temperature, when the second temperature range of 40–55 °C is reached, the P[P₄,₄,₄,₄][SS] segments start to collapse and expel the water molecules, driven by the anions of the poly(ionic liquid)s, with the phosphonium cations being distributed over the relatively hydrophilic outside.

1. Introduction

Considerable attention has been paid to thermoresponsive polymers over the past few decades owing to their potential applications as “smart materials”, especially in tissue engineering,¹ bioconjugates,² chemical sensors,³⁻⁵ drug delivery,⁶,⁷ molecular actuators,⁸ separation technology,⁹ DNA transfection,¹⁰ etc. Among the various thermoresponsive polymers, polymers with a lower critical solution temperature (LCST), above which they separate from aqueous solution, have been extensively studied. These LCST-type polymers, such as poly(N-isopropylacrylamide) (PNIPAM),¹¹⁻¹³ poly(N-vinylcaprolactam) (PVCL),¹⁴,¹⁵ poly(oligo(ethylene glycol)-methacrylate) (POEGMA),¹⁶⁻¹⁸ poly(2-isopropyl-2-oxazoline) (PIP0Z),¹⁹,²⁰ poly(N,N-dimethylaminoethyl methacrylate) (PDMAEMA),²¹,²² etc., undergo a coil-to-globule phase transition in water during the heating process, and the transition temperature can be shifted to human body temperature by copolymerization with hydrophilic monomers, making it suitable for biomedical applications. It should be pointed out that these typical polymers are non-ionic, completely neutral or weakly charged when dissolved in aqueous solution.

Meanwhile, strong polyelectrolytes exhibiting a LCST-type phase transition are comparably less investigated. Ritter et al. reported that a poly(t-butyl-3-vinylimidazolium bis(trifluoro-methane sulfonyl)imide) (poly[bvim][Tf₂N]) aqueous solution displayed a pseudo-LCST effect with the presence of cyclodextrin (CD). They found that the cyclodextrins form complexes with the large hydrophobic anion at low temperature and slips off upon heating, resulting in the soluble-to-insoluble transition in water.²³ In recent years, a new class of strong polyelectrolyte...
system with LCST-type transition properties has attracted more and more researchers’ attention, i.e. thermo-responsive LCST-type poly(ionic liquid)s (PILs). Ohno et al. first reported that poly(4-tetraethylphosphonium styrenesulfonate) ([P4,4,4,4][SS]) showed a LCST-type phase transition in aqueous solution. Additionally, with the change of the alkyl chain length of the phosphonium cations, the polyelectrolytes exhibit different phase transition temperatures.24 Later on, they observed a sharp and reversible LCST-type phase transition of another poly(ionic liquid), poly(tributylphosphonium 3-sulfopropylmethacrylate) ([P4,4,4,4][C3S]), in pure water.25 Besides, Yuan et al. first reported the LCST-type phase transition of a cationic polyelectrolyte based on the styrenic liquid tributyl-4-vinylbenzylphosphonium pentanesulfonate (poly(TVBP-CrS)), and the phase transition temperature can be flexibly adjusted via anion exchange and salting out effects.26

With the development of controlled living radical polymerizations (CLRP)s and the special demands of drug release, block copolymers possessing dual thermo-responsive properties have been synthesized using polymer design. Sugihara et al. reported the four different viscoelastic stages of a LCST–LCST-based block copolymer poly(2-(2-ethoxy)ethoxyethyl vinyl ether)-b-poly(2-methoxyethyl vinyl ether) (poly(EEOVE)-b-poly(MOVE)) upon heating: a clear liquid (sol, < 40 °C), transparent gel (42–55 °C), hot clear liquid (sol, 57–63 °C), and an opaque mixture (> 63 °C). Furthermore the gel formation was strongly dependent on the Mn/Mw.27,28 Laschewsky et al. used reversible addition–fragmentation chain transfer polymerizations (RAFT) to prepare a double thermo-responsive diblock copolymer poly(N-n-propylacrylamide)-b-poly(N-ethylacrylamide) (PNPAM-b-PNEM); the copolymer displayed thermally induced two-step self-assembly behavior in aqueous solution due to the different LCST phase transitions of PNIPAM (around 20 °C) and PNEAM (around 70 °C).29,30 Liu et al. investigated a dendritic macromolecule, H40-poly(N-isopropylacrylamide)-poly(2-(dimethylamino)ethyl methacrylate) (H40-PNIPAM-PDMA), synthesized via a fractionated fourth-generation hyperbranched polyester (Bolton H40) based macroRAFT agent. The two-stage thermally induced collapse was observed using laser light scattering measurements during the heating process.31 Also, our group once explored the thermally induced phase transition of poly(N-isopropylacrylamide)-b-poly(N-vinylcaprolactam) (PNIPAM-b-PVCL) containing two distinct LCST-type thermosensitive segments via 2Dcos analysis. It is interesting to note that only one transition was observed by us, and there exists a cooperative aggregation of PNIPAM and PVCL segments upon heating.32

However, to the best of our knowledge, most of the studies have only focused on the traditional non-ionic LCST-type polymers, a combination of traditional LCST polymers and wholly charged LCST-type PILs has been rarely studied. On the one hand, the introduction of charges can lead to changes of the hydrophilic–hydrophobic balance, and the thermal transition behavior and self-assembly of traditional polymers might be affected in the presence of poly(ionic liquid)s. On the other hand, the LCST-type phase transition property of PILs also could be modulated by the interactions among different groups in the solution. Recently, the thermo-responsive phase behaviors of a PNIPAM/[P4,4,4,4][SS] mixture and a PNIPAM-[P4,4,4,4][SS] statistical copolymer have been compared by our group. It was found that PNIPAM-[P4,4,4,4][SS] showed a linear and mild phase transition process.33 Due to the huge difference between the LCST–LCST block copolymer and random copolymers in many aspects, such as the structure, solution properties, and self-assembly behavior, the thermal phase behaviors and microdynamics of the dual block systems composed of components with different thermo-sensitive properties have attracted our attention.

In this work, we attempt to elucidate the thermally induced aggregation process of the PMEO2MA-b-[P4,4,4,4][SS] copolymer containing a non-ionic LCST-type block and a LCST-type poly(ionic liquid) segment, involving the respective contributions of hydrogen bonding and hydrophobic interactions in the heating. Turbidity and DLS measurements as well as temperature-variable 1H NMR are utilized to examine the transition points, in order to provide an overall view of the transition process. Fourier transform infrared spectroscopy (FTIR), a useful technique to probe conformational variations in the hydration states or molecular motion of specific chemical groups, is employed to depict the microscopic changes with regard to the dynamic aggregation process of PMEO2MA-b-[P4,4,4,4][SS] and uncover the underlying diverse molecular interactions. Moreover, 2D correlation spectroscopy (2Dcos) analysis is applied in order to illustrate the dynamic phase transition behavior of the copolymer upon heating. In this way, the corresponding phase transition mechanisms of PMEO2MA-b-[P4,4,4,4][SS] in its aggregation process can be distinguished. Additional information on the specific order of chain conformation changes taking place during the whole transition could be extracted. This study provides an in-depth understanding of the molecular motion of different chemical groups among PMEO2MA and [P4,4,4,4][SS] segments in aqueous solution during the heating process, which may be of benefit for future smart materials design with a wide range of applications.

2. Experimental section

2.1 Materials

2-(Methoxyethoxy)ethyl methacrylate(MEO2MA) (Mn = 188 g mol⁻¹, 95%) was purchased from Sigma-Aldrich and purified by passing through a column filled with neutral alumina prior to use. Tetraethylphosphonium bromide ([P4,4,4,4][Br]) and sodium-4-vinylbenzenesulfonate ([Na][SS]) were purchased from Aladdin Reagent Co. 4-Cyano-4-(thiobenzoylthio) pentanoic acid (CTA) was obtained from Sigma-Aldrich and used as received. 2,2’-Azobisiso-butylonitrile (AIBN, Aladdin reagent Co.) was purified through recrystallization from methanol. N,N-Dimethylformamide (DMF, Aladdin reagent Co.) was dried with CaH₂ for 24 h and distilled under vacuum.

2.2 Sample preparation

Firstly, the [P4,4,4,4][SS] monomer was synthesized via the ion exchange reaction of [Na][SS] and [P4,4,4,4][Br] in distilled water for 12 h according to previous reports.24,34 The block copolymer
PMEO2MA-b-P[P_4,4,4,4][SS] explored in our work was synthesized via RAFT polymerization. Typically, the precursor PMEO2MA was first synthesized as macro-CTA. Polymerization of [P_4,4,4,4][SS] from the macro-CTA was as follows. Macro-CTA (0.102 g), [P_4,4,4,4][SS] (0.912 g), and AIBN (1.4 mg) were added into a reaction tube with 3 mL DMF. The solution was degassed using three freeze–evacuate–thaw cycles and placed in a preheated oil bath maintained at 70 °C for 3 h, and then quenched by rapidly exposing it to liquid nitrogen. The product was purified via dialysis against distilled water (MWCO 3500) and then freeze-dried. Details of NMR spectra and GPC traces of the copolymer are provided in Fig. S1 (ESI†). The molecular structure of the copolymer in the investigation is shown in Scheme 1. Additionally, for better comparison, we also tried to synthesize the P[P_4,4,4,4][SS] homopolymer and PMEO2MA-b-P[P_4,4,4,4][SS] mixture (1:1), and the details are provided in the ESI.†

2.3 Instruments and measurements

Turbidity measurements were conducted at 550 nm on a Lambda 35 UV-vis spectrometer with deionized water as a reference (100% transmittance). The transmittance was recorded while heating the samples at a rate of 1.0 °C min⁻¹ from 20 to 50 °C with an interval of 1.0 °C. Each temperature point was held for 2 min before measurement to ensure thermal equilibrium. DLS measurements were performed on a Malvern Zetasizer Nano ZS instrument (scattering angle: 173°) at a heating rate of 1 °C min⁻¹ with an interval of 1.0 °C and each temperature point was held for 2 min before measurement. Temperature-variable ¹H NMR spectra were recorded on a Varian Mercury plus (500 MHz) spectrometer using D₂O as the solvent (20 wt%) with an interval of 1 °C.

For FTIR measurements, the solution of PMEO2MA-b-P[P_4,4,4,4][SS] (20 wt% in D₂O) was sealed between two ZnS tablets. All FTIR spectra were collected on a Nicolet Nexus 6700 spectrometer equipped with a DTGS detector. 32 scans at a resolution of 4 cm⁻¹ were accumulated to achieve an appropriate signal-to-noise ratio. The temperatures were controlled using an electronic cell holder at a rate of ca. 0.3 °C min⁻¹ with an increment of 1 °C (accuracy 0.1 °C). The collected spectra in specific wavenumber ranges were selected to perform perturbation correlation moving window (PCMW) and 2D correlation analysis utilizing the software 2D Shige ver. 1.3 (Shigeaki Morita, Kwansei Gakuin University, Japan, 2004–2005), and were further plotted into the contour maps using Origin ver. 8.6, with warm colors (red and yellow) defined as positive intensities and cool colors (blue) as negative ones.

3. Results and discussion

3.1 Turbidity measurements

To illustrate the influence of the introduction of the polyelectrolyte block on the thermoresponsive properties of the PMEO2MA precursor, turbidity measurements of PMEO2MA-b-P[P_4,4,4,4][SS] and PMEO2MA aqueous solutions at 10 wt% concentration are firstly employed to give a direct view of the solubility changes upon heating from 20 to 50 °C, as shown in Fig. 1. Herein, we take the initial temperature point where the transmittance increases more than or drops below 50% as the cloud point (T_cm). During the heating process, the PMEO2MA precursor exhibits a LCST-type phase transition with a transition point of 28 °C, while the introduction of the poly[ionic liquid] segment leads to a higher transition temperature (T_cm = 33 °C) of PMEO2MA-b-P[P_4,4,4,4][SS]. This phenomenon indicates that the introduction of the P[P_4,4,4,4][SS] block has increased the hydrophilic properties of the solution, resulting in the improvement of T_cm. We can only find one transition point and a relatively narrow transition temperature range of PMEO2MA-b-P[P_4,4,4,4][SS] in the turbidity curves, and this will be further discussed using results from other analysis methods.

3.2 DLS measurements

To complement the results found from the turbidity curves, the phase transition behavior of PMEO2MA-b-P[P_4,4,4,4][SS] was further confirmed using the DLS measurement, from a microscopic perspective (Fig. 2). As expected, for the PMEO2MA solution the hydrodynamic diameters (D_h) undergo an abrupt increase at ca. 25 °C, suggesting the beginning of the collapse process of the polymer chains. At high temperatures, it is observed that the D_h goes through a sharp decrease at around 40 °C which may result from the collapse of the aggregates due to removing more water molecules and the formation of more compact and regular structures. Additionally, this is also an important reason for precipitation occurring gradually, due to the large

![Fig. 1 Transmittance vs. temperature for PMEO2MA-b-P[P_4,4,4,4][SS] and PMEO2MA aqueous solution (10 wt%) at the wavelength of 550 nm. The heating rate is 1 °C min⁻¹.](image-url)
aggregate sizes and the formation of more aggregates. In contrast to the narrow transition region in the turbidity curves, PMEO₂MA shows a relatively wide temperature range, about 15 K (approximately from 25 to 40 °C), for the entire aggregation process in the DLS curves, which parallels well with the phase transition behavior of the OEGMA-based polymers. Similarly, the $D_h$ of the PMEO₂MA-b-P[P₄,₄,₄,₄][SS] copolymer shows a drastic increase at ca. 31 °C, revealing the collapse of the copolymer chains. Finally, the aggregate size is maintained at around 10 000 nm at 50 °C. It is elucidated that the whole phase transition process of PMEO₂MA-b-P[P₄,₄,₄,₄][SS] is relatively slow and continuous during the heating process. In addition, it is noted that the PMEO₂MA-b-P[P₄,₄,₄,₄][SS] copolymer shows a hydrodynamic diameter of ca. 350 nm in water at low temperature. For clarity, the $D_h$ z-average size distributions of the copolymer at 25 and 45 °C are portrayed in Fig. S2 (ESI†). It is found that single polymer chains and a very small number of loose aggregates (the scattering intensity is strongly dependent on the radius of the particle (~$R^6$ for spherical particles)) might exist, which are derived from chain entanglement in the solution with a relatively high concentration at low temperature.

3.3 Temperature-variable ¹H NMR analysis

To monitor the micro-structural variation of PMEO₂MA-b-P[P₄,₄,₄,₄][SS] in solution upon heating, temperature-variable ¹H NMR measurements were employed to quantitatively describe the phase transition degree, thanks to the unavoidable attenuation of proton resonance signals upon desolvation in response to external stimuli. Fig. 3(a) presents the ¹H NMR spectra of the PMEO₂MA-b-P[P₄,₄,₄,₄][SS] copolymer in D₂O (20 wt%), recorded from 20 to 55 °C with the assignment of various protons labeled. For clarity, the comparison of ¹H NMR results in D₂O at low and high temperatures is plotted in Fig. S3 (ESI†). Furthermore, the temperature-dependent ¹H NMR spectra of the PMEO₂MA precursor are compared in Fig. S4 (ESI†). Almost all of the proton signals gradually shift toward a higher chemical shift along with changing intensity during heating. It can be obviously found that the proton intensities of the copolymer undergo a gradual decrease from 20 to 55 °C, suggesting that the PMEO₂MA-b-P[P₄,₄,₄,₄][SS] chains collapse with the increment of temperature. Notably, however, there are differences in the degree of decrease in intensities of different parts of PMEO₂MA-b-P[P₄,₄,₄,₄][SS].

We performed the normalization of integral areas according to the solvent HDO peak. For further clarification of the different microdynamic responses of the PMEO₂MA and P[P₄,₄,₄,₄][SS] segments in the copolymer during the whole heating process, we employed the phase separation fraction $p$ to quantitatively estimate the degrees of dehydration in the phase transition of PMEO₂MA-b-P[P₄,₄,₄,₄][SS]. Here, $p$ is defined as:

$$p = 1 - \frac{I}{I_0}$$  

where $I$ is the integrated intensity of the selected resonance peak in the ¹H NMR spectra and $I_0$ is the integrated intensity of this peak when no phase separation occurs. In this work, we take the integrated intensity obtained from the initially dissolved temperature (20 °C) as $I_0$. The temperature dependence of the phase separation fraction $p$ for proton signals (Hₐ, Hₐ', Hₐ, Hₐ', and H₂) belonging to the P[P₄,₄,₄,₄][SS] segment and peaks (Hₐ, Hₐ, and H₂) belonging to the PMEO₂MA block in D₂O is presented in Fig. 3(b). For the PMEO₂MA block, the phase separation fraction of the proton signal Hₐ close to the C—O groups appears to increase dramatically at ca. 30 °C, and has a value of ca. 0.7 at high temperature. Peak Hₐ, which is attributed to the aliphatic side chains of the PMEO₂MA segment, shows a relatively slower phase separation degree change at ca. 30 °C, revealing that the collapse of the PMEO₂MA block occurs drastically at ca. 30 °C and the side chains of the PMEO₂MA segments contribute to gradually squeezing water molecules out.

![Fig. 2](image1.png)

**Fig. 2** DLS measurements of PMEO₂MA-b-P[P₄,₄,₄,₄][SS] and PMEO₂MA aqueous solutions at a concentration of 10 wt% during heating with a heating rate of 1.0 °C min⁻¹.

![Fig. 3](image2.png)

**Fig. 3** (a) Normalized temperature-variable ¹H NMR spectra of PMEO₂MA-b-P[P₄,₄,₄,₄][SS] in D₂O (20 wt%), (b) temperature dependence of the phase separated fraction $p$ for different protons in the PMEO₂MA-b-P[P₄,₄,₄,₄][SS] copolymer.
Meanwhile, the $p$ values of the protons derived from the end CH$_3$ group exhibit a linear increase with a smaller degree upon heating. For the $\text{P[P}_{4,4,4,4}\text{][SS]}$ segments, it is observed that the $p$ values of the resonant signals corresponding to the anions of the PIL backbones (H$_a$) undergo a sharp increase until the temperature reaches ca. 40 °C, indicating the beginning of the drastic dehydration change of the $\text{P[P}_{4,4,4,4}\text{][SS]}$ backbones. Notably, the temperature is higher than that of the PMEO$_2$MA segments, providing the information that the two blocks expel water molecules asynchronously. However, the $p$ values of the signals H$_{b,d}$, mainly belonging to the aliphatic chains of $\text{P[P}_{4,4,4,4}\text{][SS]}^+$ cations, display a slight, linear increase from the low temperature, revealing the small dehydration degrees of the phosphonium cations during the heating process. On the whole, comparing the two different blocks, we can find that the $p$ values of protons H$_{a,a'}$ at 50 °C ($\sim 0.3$) are smaller than that of proton H$_e$ ($\sim 0.7$), demonstrating that the PMEO$_2$MA segments carry out a dramatic dehydration process with a larger phase separation degree. It could be concluded that the PMEO$_2$MA segments dehydrate more drastically and earlier than the PIL blocks, and that core–shell assembly structures exist with relatively dehydrated PMEO$_2$MA segments wrapped inside. Sequentially, the $\text{P[P}_{4,4,4,4}\text{][SS]}$ chains start to collapse, responding to the increment of temperature with the cations spreading over the relatively hydrophilic outside.

3.4 Conventional FTIR analysis

To further understand the structural changes and elucidate the dynamic mechanism of the thermoresponsive behaviors, temperature-resolved FTIR measurements of PMEO$_2$MA-b-$\text{P[P}_{4,4,4,4}\text{][SS]}$ in D$_2$O (20 wt%) were performed, as shown in Fig. 4. Additionally, we recorded temperature-variable FTIR spectra of pure PMEO$_2$MA solutions for comparison, as shown in Fig. S5 (ESI†). Notably, D$_2$O is utilized as the solvent here instead of H$_2$O in order to eliminate the overlap of the broad $\nu$(O–H) band of H$_2$O at around 3300 cm$^{-1}$ with the $\nu$(C–H) bands, as well as that of the $\delta$(O–H) band of H$_2$O at around 1640 cm$^{-1}$ with the $\nu$(C=O) bands of PMEO$_2$MA-b-$\text{P[P}_{4,4,4,4}\text{][SS]}$. This is a direct way to observe the motions of different segments by monitoring the characteristic peaks of different chemical groups. Therefore, in this work, three main spectral regions, C–H stretching (3010–2840 cm$^{-1}$), C=O stretching (1751–1679 cm$^{-1}$), and SO$_3^-$ symmetric stretching (1049–1022 cm$^{-1}$), are traced in the following discussion. As presented in Fig. 4, it is observed that both the C–H and SO$_3^-$ stretching bands shift towards lower wavenumbers with the increase of temperature, while the frequencies of the C–O groups shift to higher wavenumbers, demonstrating the variation of the hydration interaction and the destruction of hydrogen bonding. It is well known that the hydrophobic moieties of water-soluble polymers are surrounded by well-ordered water clathrates, resulting in a higher vibrational frequency.$^{31,42}$ Hence, the red shift of the C–H bands indicates that the aliphatic groups in the copolymers undergo a dehydration process upon heating. Besides, the blue shift of the C=O groups also reveals the dehydration of hydrophobic ester linkages and water. For the hydrophilic sulfonate groups, the frequencies of $\nu$(SO$_3^-$) perform a slight red shift, which corresponds to the breaking of hydrogen bonds between hydrophilic sulfonate groups and H$_2$O.

3.5 Perturbation correlation moving window (PCMW) analysis

Due to the advantages of the PCMW technique for determining the specific transition points and transition temperature regions of various chemical groups (an in-depth introduction of PCMW analysis is covered in the ESI†), the synchronous and asynchronous spectral maps of the PCMW are plotted for deeper exploration of the phase transition of PMEO$_2$MA-b-$\text{P[P}_{4,4,4,4}\text{][SS]}$ (20–55 °C) in D$_2$O upon heating, as shown in Fig. 5. Obviously, it is observed that two transition points exist at ca. 36 and 44 °C in the synchronous spectral maps, and this is significantly different from the one transition point in Fig. 1. Specifically, the phase transition temperature of the C–H groups at 2958, 2927, and 2871 cm$^{-1}$ and the C=O groups at 1710 cm$^{-1}$ is determined to be about 36 °C, while the peaks at 2975, 2942, and 1039 cm$^{-1}$ show a transition point of around 44 °C. In other words, there exists an interval of approximately 8 °C of the two transition points exhibited in the PCMW results. In addition, from the asynchronous spectrum diagram, it is found that the phase transition temperature range can be divided into two subregions according to the PCMW analysis: 20–40 °C and 40–55 °C. We will explain the two-step transition behavior in different temperature ranges using 2Dcos analysis subsequently. In addition, the same PCMW analysis of PMEO$_2$MA precursor was also carried out, and results are shown in Fig. S6 (ESI†) for comparison.

![Fig. 4](image-url) Temperature-dependent FTIR spectra of PMEO$_2$MA-b-$\text{P[P}_{4,4,4,4}\text{][SS]}$ (20–55 °C) in D$_2$O (20 wt%) with an interval of 1 °C in the regions of 3010–2840 cm$^{-1}$, 1751–1679 cm$^{-1}$, and 1049–1022 cm$^{-1}$.
3.6 Two-dimensional correlation spectroscopy (2Dcos)

As a new mathematical method proposed by Noda in 1986, 2Dcos has been widely applied to investigate spectroscopic intensity fluctuations under different external perturbations, including temperature, concentration, pressure, time, electromagnetic fields, etc.43,44 By spreading the original spectra along a second dimension, spectral resolution can be greatly enhanced and the information not readily visible in conventional analysis can be extracted. In addition, 2Dcos can be applied to deduce the specific sequence order of different chemical groups under a certain chemical or physical change, and help to demonstrate the microdynamic mechanisms during the process. Based on the PCMW analysis results, we divided the heating process into two subregions (20–40 and 40–55 °C) to generate the 2Dcos spectra. The synchronous and asynchronous spectra are individually obtained from the specific FTIR spectra in the two regions, as shown in Fig. 6.

Temperature region I: 20–40 °C. Initially, the transition process in temperature region I between 20 and 40 °C was analyzed in detail on heating. In Fig. 6, many subtle bands that cannot be easily observed in the 1D raw spectra, such as some overlapping peaks and hydrated and dehydrated states of C–H groups, have been identified, revealing the diversities of those specific groups. For clarity, all bands detected in the asynchronous spectra and their corresponding tentative assignments are presented in Table 1.

Based on Noda’s rule with a relatively simplified method (see Table S1, ESI†),46 the specific sequence order for the first phase transition stage in temperature region I is described as (→ means earlier than or prior to): 2971 → 1041 → 1729 → 2898 → 2956 → 2927 → 2871 → 1716 → 2881 → 2939 cm⁻¹, or νas(hydrated CH₃) → νs(hydrated SO₃) → νas(dehydrated C=O) → νs(CH) → νas(dehydrated CH₃) → νas(dehydrated CH₂) → νs(dehydrated CH₂) → νs(dehydrated SO₃) → νs(hydrated C=O) → νas(hydrated CH₂) → νs(hydrated CH₂).

Fig. 6 2D synchronous and asynchronous spectra of PMEO₂MA-b-P[P₄,₄,₄,₄]₄SS in D₂O (20 wt%) during heating between 20 and 40 °C. Warm colors (red and yellow) are defined as positive intensities, while cool colors (blue) are defined as negative intensities.
Without considering the differences in stretching modes of the chemical groups of PEO2MA-b-P[P4,4,4,4][SS], the specific order can be displayed as follows: CH3 → SO3− → C−O → CH2. Obviously, in temperature region I, the hydrophobic CH3 and sulfonate groups have an earlier response to the temperature increment than the C−O groups and CH2 groups. In other words, the dehydration interaction among the C−H end groups should be the driving force for the beginning of the collapse behavior of the copolymer. In combination with the temperature-variable 1H NMR analysis, the backbones of the PEO2MA segments are more sensitive to the rise of the temperature during this period. Under the drag of the dehydration of the CH3 segments, the hydrophobic CH3 groups might make conformational changes before their dehydration process. This phenomenon is also reflected in other ionic liquid based phase transition systems.45 In summary, during the first stage, it is indicated that the PEO2MA blocks of the copolymer first begin to expel the water molecules, with an obvious associated conformational collapse, resulting in the formation of the hydrophobic center.

**Temperature region II: 40−55 °C.** Temperature region II, between 40 and 55 °C, was analyzed to deeply understand the second-step transition mechanism of PEO2MA-b-P[P4,4,4,4][SS] on heating. For clarity, all of the bands recognized from the 2D asynchronous maps and their tentative assignments are presented in Table 2. Obviously, compared with the peaks of 1729 and 1716 cm−1 observed in the asynchronous spectra of the temperature region I, we found another cross peak at 1710 cm−1 in the ester C=O region. Due to the conformational changes during the first-step collapse of the copolymer, compared with the relatively dispersed states at low temperature, parts of the carbonyl groups in the PEO2MA segments, which suggests the formation of more compact structures, with the formation of some new interactions. According to previous literature reports,47,48 it is concluded that the peaks of 1710 cm−1 can be attributed to the interaction between the P[P4,4,4,4][SS] blocks and the carbonyl groups of the PEO2MA segments, which suggests the formation of an intermediate state with the new interaction. This phenomenon also indicates that segregation dominates for the

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**Table 2** Tentative band assignments of PEO2MA-b-P[P4,4,4,4][SS] in D2O (40−55 °C) according to the 2Dcos results.

Without considering the differences in stretching modes of the chemical groups of PEO2MA-b-P[P4,4,4,4][SS], the specific order can be displayed as follows: CH3 → SO3− → C−O → CH2. Obviously, in temperature region I, the hydrophobic CH3 and sulfonate groups have an earlier response to the temperature increment than the C−O groups and CH2 groups. In other words, the dehydration interaction among the C−H end groups should be the driving force for the beginning of the collapse behavior of the copolymer. In combination with the temperature-variable 1H NMR analysis, the backbones of the PEO2MA segments are more sensitive to the rise of the temperature during this period. Under the drag of the dehydration of the CH3 segments, the hydrophobic CH3 groups might make conformational changes before their dehydration process. This phenomenon is also reflected in other ionic liquid based phase transition systems.45 In summary, during the first stage, it is indicated that the PEO2MA blocks of the copolymer first begin to expel the water molecules, with an obvious associated conformational collapse, resulting in the formation of the hydrophobic center.

**Temperature region II: 40−55 °C.** Temperature region II, between 40 and 55 °C, was analyzed to deeply understand the second-step transition mechanism of PEO2MA-b-P[P4,4,4,4][SS] on heating. For clarity, all of the bands recognized from the 2D asynchronous maps and their tentative assignments are presented in Table 2. Obviously, compared with the peaks of 1729 and 1716 cm−1 observed in the asynchronous spectra of the temperature region I, we found another cross peak at 1710 cm−1 in the ester C=O region. Due to the conformational changes during the first-step collapse of the copolymer, compared with the relatively dispersed states at low temperature, parts of the carbonyl groups in the PEO2MA segments, which suggests the formation of more compact structures, with the formation of some new interactions. According to previous literature reports,47,48 it is concluded that the peaks of 1710 cm−1 can be attributed to the interaction between the P[P4,4,4,4][SS] blocks and the carbonyl groups of the PEO2MA segments, which suggests the formation of an intermediate state with the new interaction. This phenomenon also indicates that segregation dominates for the

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Tentative assignment</th>
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<tbody>
<tr>
<td>2973</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>2960/2958</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>2940</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>2931/2929/2927</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>2898</td>
<td>ν(CH)</td>
</tr>
<tr>
<td>2883</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>2869</td>
<td>νas(hydrated CH3)</td>
</tr>
<tr>
<td>1729</td>
<td>ν(dehydred C−O)</td>
</tr>
<tr>
<td>1710</td>
<td>ν(dehydred C−O)</td>
</tr>
<tr>
<td>1039</td>
<td>ν(dehydred SO3−)</td>
</tr>
<tr>
<td>1031</td>
<td>ν(dehydred SO3−)</td>
</tr>
</tbody>
</table>
diblock copolymers in solution, breaking the balance of segregation and complexation of the two blocks.49

Based on the same method utilized in temperature region I, we can deduce the final sequence order in temperature region II of the block copolymer in D2O to be: 2940 → 1710 → 1039 → 2883 → 2973 → 1729 → 2898 → 2958 → 2869 → 2929 → 1031 cm⁻¹, or ν\text{as}(hydrated CH_3) → ν(C=O⋅D_2O-PILs) → ν(hydrated SO_3⁻) → ν\text{as}(hydrated CH_2) → ν\text{as}(dehydrated CH_3) → ν\text{as}(dehydrated C=O) → ν(CH) → ν\text{as}(hydrated CH_2) → ν\text{as}(dehydrated CH_3) → ν\text{as}(hydrated CH_2) → ν\text{as}(dehydrated CH_3) → ν\text{as}(dehydrated CH_2). Ignoring the differences of vibrational modes, the specific order can be deduced as follows: CH_2 → C−O⋅D_2O-PILs → SO_3⁻ → CH_2 → C=O, revealing that the dehydration of the hydrophobic C–H groups occurs first and the ν(C=O⋅D_2O-PILs) breaks subsequently during the heating process in temperature region II. Hence, it is reasonable to believe that the C–H groups in the copolymer play a vital role in the aggregation process. With the further dehydration of the anionic SO_3⁻ groups, the poly(ionic liquid) segments squeeze the water molecules out gradually, leading to the more dehydrated aggregates in the copolymer solution.

On the basis of the above analysis upon heating, a two-step transition mechanism of PMEO2MA-b-P[P4,4,4,4][SS] copolymer in D2O solution upon heating could be proposed, as depicted in Scheme 2.

In the first stage, the PMEO2MA-b-P[P4,4,4,4][SS] copolymer chains dissolve sufficiently in the aqueous solution at the initial temperature. As the temperature rises, the CH_3 end groups mainly belonging to the backbones of PMEO2MA blocks respond first and drive the collapse of the PMEO2MA segments. This is accompanied by the collaborative and weak dehydration of anions derived from the P[P4,4,4,4][SS] main chains, and a new intermediate micelle state forms with the collapsed PMEO2MA center and related extended P[P4,4,4,4][SS] corona. The phosphonium cations, which are insensitive to the increment of temperature, locate around the outside. Particularly, it is worth noting that parts of the carbonyl groups can interact with the PIL segments (ν(C=O⋅D_2O-PILs)) due to the adjustment of molecular conformation. When the temperature continues to rise to temperature range II, the P[P4,4,4,4][SS] blocks begin to collapse and expel water molecules, driven by the dehydration of hydrophobic CH_2 groups. Accompanied by the destruction of the interaction between the C=O groups and poly(ionic liquid) block, further dehydration of the P[P4,4,4,4][SS] segment happens, especially in the region of anions, resulting in a more hydrophobic environment. Finally, the more compact aggregates collapse, with the [P4,4,4,4]⁺ cations spread over the relatively hydrophilic periphery.

4. Conclusions

In this work, the thermal phase behavior, assembly process, and microdynamics of the PMEO2MA-b-P[P4,4,4,4][SS] copolymer containing a non-ionic LCST-type block and a LCST-type poly(ionic liquid) segment were studied using various methods including turbidity, DLS, temperature-variable ¹H NMR and FTIR spectroscopy in combination with 2Dcos methods, etc. It is found that a sharp LCST-type phase transition with only one transition point is observed in the turbidity curves, while the phenomenon is different from the microscopic angle. ¹H NMR analysis indicates that the responses to the rise of temperature are asynchronous for different protons of the two different LCST-type blocks, and it shows a wide temperature region for the whole phase transition. Notably, it is indicated, through a deep investigation using the PCMW method, that the LCST transition behavior of the PMEO2MA-b-P[P4,4,4,4][SS] copolymer consists of two steps, and the transition temperature range can be divided into two subregions, 20–40 °C and 40–55 °C.

2Dcos analysis was employed to elucidate the dynamic dehydration mechanism by tracing the characteristic peaks of the C–H, C=O, and SO_3⁻ groups. In the first aggregation stage of 20–40 °C, the CH_3 end groups mainly belonging to the PMEO2MA backbones have the earliest response to the increment of temperature, driving the dehydration process of the PMEO2MA blocks. A new intermediate conformation is formed with the collapsed PMEO2MA segments acting as the core and the relatively stretched P[P4,4,4,4][SS] as the corona. The interaction between the C=O groups and PIL segments (ν(C=O⋅D_2O-PILs)) was found from the spectral analysis. With the help of the dehydration of anions and the destruction of ν(C=O⋅D_2O-PILs), the second-step collapse is completed with the phosphonium cations scattered over the hydrophilic outside.
Acknowledgements

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Notes and references