Insights into the thermal phase transition behavior of a gemini dicationic polyelectrolyte in aqueous solution†

Yingna Zhang, Hui Tang* and Peiyi Wu†

The thermal-induced phase transition behavior of a LCST-type poly(ionic liquid) (PIL) aqueous solution with gemini-cationic structure, poly[[8-octanediyl-bis(tri-n-butylphosphonium)4-styrene sulfonate]] (P[SS-P2]), was investigated in this paper. Based on the calorimetric measurements, a unique dependence of transition points on concentration was found in P[SS-P2] aqueous solution compared to its monocationic PIL and [SS-P2] aqueous solution. Optical microscopy showed that globular microscopic droplets were formed during the phase transition, suggesting that gemini dications and the possible dynamic ionic bonds may facilitate the liquid–liquid phase separation (LLPS) in P[SS-P2] aqueous solution. Temperature-variable 1H NMR and FT-IR investigations manifested that the dehydration of anionic chains instead of the dehydration of dications served as the driving force of the phase separation in the P[SS-P2] aqueous solution, implying that the polymerized anions tended to aggregate together first and lay in the core with dications distributed around the globules at the end of the transition process. Notably, considering that the SO3 groups in the gemini-cationic system tended to be distributed around the surface of collapsed anionic main chains rather than be wrapped into the aggregates, it is supposed that dynamic ionic bonding between dication and anionic backbones was distributed in the periphery of the globules and acted as the “cross-linkers”, which enhanced the stability of regular droplets after the phase transition in P[SS-P2] aqueous solution.

1. Introduction

Poly(ionic liquid)s (PILs), a novel class of polyelectrolytes, are commonly prepared from the polymerization of monomeric ionic liquids (ILs), presenting many unique properties such as durability, high ionic conductivity and excellent electrochemical stability. Notably, a series of PILs that undergo a reversible phase transition process in aqueous solution has attracted considerable attention recently, considering their potential applications as stimulis-responsive materials such as drug delivery, controlled bioseparation and sensing devices. Interestingly, when blending two different PILs without thermoresponsive behavior in aqueous media, the solution of the mixture may show LCST-type behavior, which is largely different from traditional thermosensitive polymers.

In recent years, various reports on the synthesis and aggregation properties of polyelectrolytes with thermal-induced phase transition behavior in aqueous solution have appeared, which revealed the key factors influencing the transition temperature of PILs. For instance, Ohno et al. investigated the thermoresponsive property of poly(tetrabutylphosphonium styrenesulfonate) [P4,4,4,4-tetra][SS] in aqueous solution and found that the PILs display different transition points when changing the alkyl chain length of the phosphonium cations. By changing polymer concentration or adding salts, Yuan et al. prepared cationic polyelectrolytes with tunable LCST-type phase separation temperatures and ascribed the influence of salt addition on the cloud point of the PIL to anion exchange and the salting out effect. Likewise, Aoshima et al. studied the effect of concentration on the separation temperature in alkylimidazolium-based cationic PILs and emphasized the interpolymer electrostatic interactions in the phase separation process.
Considerable efforts have been made to design and synthesize new thermoresponsive PILs, and it is noteworthy that most of the previously reported thermoresponsive PILs are monovalent ion polymers bearing various chemical structures. Recently, Yuan et al. prepared PILs with gemini-cationic structure, poly[(1,8-octanediyl-bis(tri-n-butylphosphonium)4-styrene sulfonate)] (P[SS-P$_2$]), which consist of two monomeric ILs connected via an alkyl chain. In comparison with its corresponding mono-cationic P[P$_{4,4,4,4}$][SS], the solution behavior of P[SS-P$_2$] was varied via the choice of salt additives and displayed a rather lower LCST and narrower hysteresis, demonstrating that the phase transition behavior is strongly influenced by the gemini-cationic structure. In particular, a homogeneous solution instead of a crosslinked gel via ionic interactions was produced in the polymerization of SS-P$_2$, which may be attributed to the low degree of polymerization and the dynamic ionic bonding between backbone and gemini-cations. Similarly, Gemini surfactants show unique aggregation properties compared with their corresponding monomer surfactants, such as lower critical micelle concentration (CMC) and unusual aggregation morphologies, suggesting that the gemini structure plays an important role in regulating the aggregation behavior.

Ionic bonds that formed via inter or intra chain interactions and served as dynamic crosslinkers in polyelectrolytes have been discussed in previous literature reports. By developing a charge balance, the performance of polyanhydolate (PA) physical hydrogel was improved by Cui et al. Luo et al. reported a series of polyion complex hydrogels that were synthesized by sequential homopolymerization of cationic and anionic monomers. They stressed that the weak ionic bonds serve as reversible crosslinkers, which endows the charged polyelectrolytes with self-healing properties. Considering that PILs with gemini-cationic structure may bring about the possibility of a dynamic crosslinking structure due to the ionic bonding between dications and anionic backbones, the unique phase transition process of P[SS-P$_2$] with gemini-cationic structure should be discussed in more detail.

Herein, temperature-dependent FT-IR spectra together with a two-dimensional correlation spectroscopy analysis method were employed to investigate the thermal-driven phase transition process of P[SS-P$_2$] solution. Several research works focused on the phase transition behavior of thermoresponsive PILs by tracking the interaction between polymers and water molecules via FT-IR spectroscopy. For instance, Li et al. traced the subtle changes of different chemical groups in P[P$_{4,4,4,4}$][SS] solution and revealed that the anionic chains collapsed into globules with SO$_3$ groups wrapped into aggregates during phase transition. Wang et al. studied thermal-responsive anionic PILs and assumed that an “urchin-like” structure was formed, resulting in the gradient distribution of water in PIL aggregates. This indicated that chemical environment together with hydration status variation of structural units could be traced by applying the temperature-dependent FT-IR method. In this, the effect of dynamic ionic bonding and gemini structure on the phase transition behavior of gemini dicaticionic PIL solutions together with the interaction between polymers and water molecules was explored.

2. Experimental section

2.1 Materials

Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol for purification. Tri-n-butylphosphine, 1,8-dibromooctane, sodium-4-vinylbenzenesulfonate (Na[SS]) and other chemicals were purchased from commercial suppliers and used as received.

2.2 Sample preparation

The IL monomer, 1,8-octanediyl-bis(tri-n-butylphosphonium) 4-styrene sulfonate ([SS-P$_2$]), and the corresponding PIL, P[SS-P$_2$], were synthesized according to the previous report. The chemical structure of P[SS-P$_2$] and synthesis route to P[SS-P$_2$] are shown in Scheme 1. The molecular parameters of P[SS-P$_2$] can be provided by GPC measurement ($M_n = 1.25 \times 10^4$ g mol$^{-1}$, PDI = 1.75).

2.3 Instruments and measurements

Calorimetric measurements of SS-P$_2$ and P[SS-P$_2$] solutions were carried out on a Mettler-Toledo differential scanning calorimetry (DSC) thermal analyzer with a scanning rate of 10 °C min$^{-1}$. Temperature-variable $^1$H NMR measurements of P[SS-P$_2$] in D$_2$O solutions (10 wt%) were carried out on a Bruker AV (500 MHz) spectrometer with an increment of 2.0 °C. Optical microscopy observations of P[SS-P$_2$] and SS-P$_2$ aqueous solution (10 wt%) were performed via a Leica DM2500P polarizing microscope equipped with a Linkam THMS600 hot stage.

Samples of P[SS-P$_2$] and SS-P$_2$ D$_2$O solution (10 wt%) were well sealed between zinc sulfide (ZnS) tablets for FT-IR measurements. The temperature-dependent FTIR spectra were recorded on a Nicolet Nexus 6700 spectrometer equipped with a DTGS detector at a resolution of 4 cm$^{-1}$ and 32 scans. Temperatures were under procedural control at a heating rate of 0.3 °C min$^{-1}$ by using an electronic cell holder with an increment of 1.0 °C.

Perturbation correlation moving window (PCMW) analysis was conducted with an appropriate window size ($2m + 1 = 11$), and two-dimensional correlation spectroscopy analysis (2DoCs) was performed with the software 2D Shige. ver. 1.3 (Shigeki Morita, Kwansei-Gakuin University, Japan, 2004–2005). Relevant spectrograms were plotted into contour maps by using the Origin program ver. 8.0 with warm colors (red and yellow) indicating positive intensities while cool color (blue) regions indicate negative ones.

![Scheme 1](image-url)
3. Results and discussion

3.1 Calorimetric measurements

To better understand the thermo-responsive phase transition behavior of the gemini-dicationic solution, calorimetric measurements of P[SS-P₂] and [SS-P₂] aqueous solutions during the heating process were made, as shown in Fig. 1. The temperature corresponding to the highest point of the endothermic peak was regarded as the transition temperature. Considering that the long chains of polymerized anions may respond as a whole to the temperature variation, the transition point of P[SS-P₂] aqueous solution was higher than that of [SS-P₂] aqueous solution at the same concentration. With increasing the concentration of the gemini-dicationic aqueous solution, the transition temperatures decreased due to the hydrophobic interaction among solutes. In particular, the endothermic peak of P[SS-P₂] was much weaker at lower concentrations. Since the enthalpy change reflects the energy that stems from the disruption of the solute–water interaction, such as hydrogen bonds, the weaker endothermic peak of P[SS-P₂] at lower concentrations indicated that less water was eliminated from the aggregates during the dehydration process.

A concentration-dependent phase transition temperature diagram is shown in Fig. 2. Yuan et al. investigated the concentration-dependent LCST of mono-cationic PIL aqueous solutions and revealed that the concentration has an obvious effect on the transition behavior of PILs. They supposed that a polymer chain demixes more easily at high concentrations, which might be explained by a lower relative degree of dissociation at higher concentration due to the ion product rule. However, it is worth noting that the phase transition of the gemini-dicationic P[SS-P₂] aqueous solution was not as sensitive to variable concentrations as its monomer solution. A similar phenomenon was reported in microgels that possess a cross-linking structure. Due to the electrostatic interaction between the main chains of polymerized anions and dications in P[SS-P₂] aqueous solution, dynamic ionic bonding and the gemini structure played a dominant role in the phase transition of P[SS-P₂]. As a result, the polymer chains may be crosslinked in partial regions and the mobility of chains was restricted by the physical crosslinking structure.

3.2 Optical microscopy

In this study, optical microscopy was employed to determine the phase transition directly, and the photographs are displayed in Fig. 3. Globular microscopic droplets emerged from the homogeneous P[SS-P₂] aqueous solution above the transition temperature (38 °C). According to the previous study on the poly(2-isopropyl-2-oxazoline) (PIPOZ) aqueous solution system, the bridging hydrogen bonds C=O···D–O···O=C among polymer chains served as “cross-linking points” and facilitated the emergence of liquid–liquid phase separation (LLPS). Interestingly, Wang et al. investigated the liquid–liquid phase separation of a cationic gemini surfactant with N-benzoylglutamic acid and found that the two hydrophobic chains of gemini surfactants are possibly located in different aggregates as a bridge of the aggregates. Similarly, gemini dications in the present system also play bridging roles, connecting anionic main chains, and facilitate the LLPS morphology in the gemini-cationic system. In addition, due to the electrostatic interaction between anions and dications, dynamic ionic bonds may act as “linkages” and have an important effect on the aggregate structure of P[SS-P₂] after phase transition. Therefore, stable regular droplets were formed in the P[SS-P₂] aqueous solution. As for the [SS-P₂] aqueous solution (Fig. S1, ESI†), irregular and fragmented droplets were observed when increasing temperature above 19 °C, which was largely different from the morphology in the P[SS-P₂] aqueous solution.

3.3 Temperature-variable ¹H NMR analysis

Since information on the chemical environment together with hydration status variation of structural units during the transition process can be obtained by NMR spectroscopy, temperature-variable ¹H NMR measurements of P[SS-P₂] in D₂O (10 wt%) from 30 to 50 °C were carried out to quantitatively analyze the phase transition degree and the hydration variation, as shown in Fig. 4. The signals of the protons shifted towards lower fields with increasing temperature and the intensities attenuated gradually upon heating and decreased drastically around the transition point, which was similar to the variation tendency of PNIPAM and POEGMA. Especially, hydration status for different protons during the heating process was also displayed. The intensity of Hₐ (CH₃) and H_d,e protons (CH₃ in dications) decreased as temperature increased, indicating that the dications were partially dehydrated during the phase transition process. In contrast, the signals of H_m protons (anions in PIL) exhibited an obvious intensity decrement.
It is helpful to understand the responding behaviors of anions and dications by quantitatively tracing the variations of the dehydration process of different parts in P[SS-P2]. Herein, the phase separation fraction \( p \) was employed and defined as

\[
p = 1 - \frac{I}{I_0}
\]

where \( I_0 \) is the integrated intensity of a selected proton peak at the starting temperature (30 °C) and \( I \) is the integrated intensity of the same peak at various temperatures. We selected proton \( H_m \) to represent hydration variations of anions and proton \( H_a \) together with \( H_{d,e} \) to analyze the hydration variations of dications.

It was revealed that the response of the dications lagged behind that of the polymerized anions and the phase transition of P[SS-P2] aqueous solution was induced and dominated by the polymerized anions. The final \( p \) value of \( H_m \) was nearly 0.8 while the final \( p \) value of \( H_a \) was around 0.6, demonstrating that the polymerized anions tended to assemble together and lay in the hydrophobic core at the end of the transition process with dications distributed around the aggregates. Compared with the typical “S” shaped trend of \( H_m \) displayed in the \( p \)-temperature variation curves shown in Fig. 4c, the \( p \) value for \( H_a \) exhibited a sharp increase at the transition point. The dications underwent a relatively sharp transition with a transition temperature region (\(-5 \) °C). In contrast, a gradual dehydration process (\(-8 \) °C) was observed in the polymerized anions, which can be attributed to the stereo-hindrance effect of the covalently linked anions or the electrostatic repulsion effect of the anions.

### 3.4 Conventional IR analysis

Temperature-variable FT-IR spectral analysis of P[SS-P2] and [SS-P2] in D\(_2\)O (10 wt%) was performed to obtain quantitative information on the phase transition including frequency variations of different parts, and changes of hydrogen bonding and hydration status (Fig. 5a–d). To avoid the overlap of the broad \( \delta(OH) \) of H\(_2\)O (3300 cm\(^{-1}\)) with the C–H stretching region, D\(_2\)O was employed as the solvent instead of H\(_2\)O to monitor the variations of C–H groups in dications. Meanwhile, symmetric stretching bands of the sulfonate group at 1100–1010 cm\(^{-1}\) were chosen to trace the changes of SO\(_3\) in anions considering that the asymmetric stretching bands of the sulfonate group at 1350–1200 cm\(^{-1}\) overlapped with the absorption of D\(_2\)O at around 1200 cm\(^{-1}\). Two spectral regions including C–H stretching bands (3010–2840 cm\(^{-1}\)) and S≡O bands (1138–1117 cm\(^{-1}\)) were investigated to provide detailed information on the hydration variations of the dications and anions.

Obvious variations upon heating were identified in the C–H and S≡O stretching bands of P[SS-P2] and [SS-P2] aqueous solutions, indicating that the hydration status and hydrogen bond interaction in the systems changed. Notably, the C–H stretching bands showed a red shift with increasing temperature. Considering that higher vibrational frequency represents more water molecules surrounding the C–H moieties, this indicated that...
water molecules were divorced from the C–H moieties upon heating. As for the bands of the S=O groups, a shift to a lower vibrational frequency was observed, suggesting that hydrogen bonds between S=O groups and water molecules were disrupted. Nevertheless, hydrogen bonds between S=O groups and water molecules still existed at the end of the phase transition due to the strong hydrophilic nature of the S=O groups. For clarity, second derivative spectra are presented in Fig. 5e–h. It is noteworthy that a band around 2860 cm⁻¹ corresponding to the stretching band of the alkyl CH₂ chain between dications was identified. Compared with other C–H stretching bands, the band around 2860 cm⁻¹ shifted to a higher frequency with temperature increment, implying an unusual over-hydration behavior.

Temperature-dependent frequency variations of ν(C–H) and ν(S=O) were quantitatively analyzed to determine detailed information of the hydration degree of different chemical groups in P(SS-P₂) and [SS-P₂] solutions during the transition process, as shown in Fig. 6. It can be observed that the frequency of bands shifted to lower wavenumbers during the heating process, suggesting that the SO₃ and C–H groups experienced dehydration process. In the previous study, absorption in the C–H regions at around 2968, 2937, and 2876 cm⁻¹ represented νₐs(CH₃), νₐs(CH₂) and νₛ(CH₂), respectively. Based on the discussion above, absorption at around 1126 cm⁻¹ represented the stretching vibration band of νₛ(S=O). Herein, the frequency variations of the CH₃ and SO₃ groups were selected to represent the hydration variation of dications and anions, respectively. Notably, a practically linear variation of frequency shift for the SO₃ groups was identified compared with the anti-sigmoid shaped change for CH₃ groups, indicating that the SO₃ groups underwent a more gradual dehydration process due to the strong hydration ability.

Especially, distinctions between P(SS-P₂) and [SS-P₂] monomer in the frequency variation were also detected. For the C–H stretching vibration bands, the initial frequency of P(SS-P₂) was lower than that of [SS-P₂], implying weaker hydrated interactions of C–H groups in P(SS-P₂) than those in [SS-P₂]. The frequency shifts of P(SS-P₂) were also lower than that of [SS-P₂], demonstrating that dications of P(SS-P₂) underwent a lower degree of dehydration than that of [SS-P₂]. The frequency shifts of νₛ(CH₃) were calculated to quantitatively analyze the hydration variations of the dications and the shifts were 5.1 cm⁻¹ for P(SS-P₂) and 6.4 cm⁻¹ for [SS-P₂], respectively. In addition, the final frequency of νₛ(CH₃) in P(SS-P₂) was much higher than that in [SS-P₂], which suggested that dications in [SS-P₂] were likely to be wrapped into the globules and had less chance to contact with water molecules while dications in P(SS-P₂) tended to be distributed around the globules.

As for the SO₃ groups, the initial frequency for P(SS-P₂) was higher than that for [SS-P₂], indicating that more water molecules surrounded SO₃ groups in P(SS-P₂). Interestingly, the frequency shift of SO₃ groups in P(SS-P₂) (0.9 cm⁻¹) was much lower than that of SO₃ groups in [SS-P₂] (1.7 cm⁻¹) or the monocationic PIL (1.5 cm⁻¹), indicating that the SO₃ groups in P(SS-P₂) experienced a low degree of dehydration and were still strongly hydrated after the phase transition process. It can be
assumed that SO₃ groups were distributed around the surface of globules rather than being wrapped into the globules, which was largely different from the mono-cationic PIL. Considering that SO₃ groups were inclined to interact with dications via dynamic ionic bonds, an ionic crossing linkage structure may be formed with dications in P[SS-P₂] distributed around the surface of the globules.

3.5 Perturbation correlation moving window (PCMW)

In order to discern precise transition points and transition temperature regions of various chemical groups in the gradual phase transition process, the perturbation correlation moving window (PCMW) method was employed in the present study and the spectra of P[SS-P₂] and [SS-P₂] solutions are plotted in Fig. S2 (ESI†). Generally, the intense spectral variation points in the PCMW synchronous map represent transition points of each band, while in the PCMW asynchronous map, the initial and final temperatures of the transition process could be indentified, which can be regarded as the phase transition range.⁴⁹⁻⁵¹

The transition points of chemical groups can be recognized from the synchronous spectra and detailed information on the transition temperature regions could be derived by analyzing the asynchronous spectra. With regard to the P[SS-P₂] solution, the transition points of the C–H and SO₃ groups were 39 and 37 °C based on the synchronous spectra, indicating that the dehydration of anions occurred prior to that of the dications and the SO₃ groups served as the driving force of the thermally induced phase transition. Accordingly, anionic main chains collapsed into globules and lay in the hydrophobic core with dications distributed around the surface of the aggregates. Thus, the aggregate structure can be described as globules with hydrophobic cores and surface-crosslinkages, which was facilitated by dynamic ionic bonds. As for the [SS-P₂] solution, the strongest intensity variations of the C–H and SO₃ groups occurred at 19 °C, illustrating that the C–H and SO₃ groups displayed synergetic change. According to the 2Dcos analysis (Fig. S3, ESI†), it is the dications rather than anions that serve as the driving force of the phase transition. That is, the dications that possess alkyl chains provide the hydrophobic interactions needed for the LCST-type phase transition and are wrapped into droplets with anions distributing around the surface of the droplets. However, owing to the lack of stable structures after the phase transition, the size of these droplets is irregular and inhomogeneous.

According to the asynchronous spectra analysis, the SO₃ groups underwent the transition process at 34–40 °C whereas the transition region of the C–H groups was 36–41 °C in the P[SS-P₂] aqueous solution, showing that the transition temperature range was nearly 6 °C. It is worth noting that the transition range of P[SS-P₂] aqueous solution was broader than that of the [SS-P₂] aqueous solution, which can be ascribed to the stereo-hindrance effect. Considering covalently linked anions in P[SS-P₂] and the electrostatic repulsion effect, the polymerized anions underwent a gradual transition with a broad transition temperature region. Different from the [SS-P₂] aqueous solution, the phase transition process of P[SS-P₂] aqueous solution was dominated by the polymerized anions, and thus the transition range of P[SS-P₂] was broad.

3.6 Two-dimensional correlation analysis (2Dcos)

Here, the 2Dcos method proposed by Noda et al was applied to deduce the accurate responding sequence of various chemical groups during the phase transition process.³⁷ It is worth mentioning that the improved spectral resolution in 2Dcos is helpful to indentify the overlapped IR bands,⁴⁹ which means that more useful information about the interaction variations and conformational changes upon heating in the polymer solution could be obtained.⁵³ The 2Dcos maps of P[SS-P₂] and [SS-P₂] are shown in Fig. S3 and S4 (ESI†) and the tentative assignments of bands are shown in Table 1.

According to the Noda rule and the 2Dcos spectra, the sequence order of different chemical groups in P[SS-P₂] as temperature increases can be displayed as follows (”>” means earlier than or prior to): 1122 > 1129 > 2974 > 2883 > 2957 > 2872 > 2860 > 2944 cm⁻¹ or ν₂(SO₃...(m−n)D₂O in anion) > ν₃(SO₃...·mD₂O in anion) > ν₉(hydrated CH₃ in dication) > ν₃(hydrated CH₂ in dication) > ν₉(alkyl CH₂ chain between dication) > ν₉(alcohol CH₂ in dication).

Leaving alone the differences in stretching modes, the sequence can be displayed as: SO₃ > CH₃ > CH₂ or SO₃ > C–H groups. The sequence indicated that the dehydration of SO₃ groups occurred before the dehydration of C–H groups, which corresponded well with the results from the PCMW analysis. That is, the driving force of phase transition stemmed from the abruption of hydrogen bonds between SO₃ groups and water molecules. Therefore, it was the polymerized anions rather than dications that drove the dehydration preferentially through the hydrophobic interaction. Thus, the polymerized anions played a dominant role in the self-aggregation process in the P[SS-P₂] solution.

Compared with the mono-cationic PIL, the responding order of SO₃ groups in P[SS-P₂] was different. For the mono-cationic PIL, the hydrated SO₃ groups responded earlier than the dehydrated SO₃ groups, which means that the dehydration of SO₃ groups occurred prior to the conformational changes of the SO₃ groups.³⁶ In addition, the SO₃ groups were wrapped into globules during the phase transition process in mono-cationic PIL. Specifically, for P[SS-P₂], the dehydrated SO₃ groups responded

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Tentative assignments</th>
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<tbody>
<tr>
<td>2974</td>
<td>ν₉(alkyl CH₂ chain between dication)</td>
</tr>
<tr>
<td>2957</td>
<td>ν₉(hydrated CH₂ in dication)</td>
</tr>
<tr>
<td>2883</td>
<td>ν₉(alcohol CH₂ in dication)</td>
</tr>
<tr>
<td>2860</td>
<td>ν₉(alkyl CH₂ chain between dication)</td>
</tr>
<tr>
<td>1122</td>
<td>ν₉(SO₃...(m−n)D₂O in anion)</td>
</tr>
</tbody>
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earlier than the hydrated SO₃ groups, demonstrating that the dehydration of SO₃ groups occurred lagging behind the conformational changes of SO₃ groups. It is likely that SO₃ groups escaped from the hydrophobic core during the conformational changes and were distributed on the surface of the globules instead of being wrapped into globules. Moreover, compared with the mono-cationic PIL, a new band around 2860 cm⁻¹ was observed in the asynchronous spectra, which can be assigned to the stretching band of alkyl CH₂ chains between dications. The long alkyl chains underwent an over-hydration process during heating, demonstrating that dications were stretched due to the attraction by different anionic chains. Here, we assumed that dynamic ionic bonding between SO₃ groups and diphosphonium cations was formed around the surface of the hydrophobic core. Consequently, due to the gemini structure, the ionic cross-linkages were formed in the periphery of the globules, facilitating the stable formation of microscopic droplets. Meanwhile, the distribution of SO₃ groups reduced the surface tension of water and enhanced the stability of the globules.

Based on the analysis above, a schematic illustration of the phase transition process mechanism of P[SS-P₂] aqueous solution is presented in Scheme 2. For P[SS-P₂] solution, on account of the hydrophobic covalently linked anions, polymerized anions first respond to temperature and begin to collapse into globules above the LCST. In particular, SO₃ groups are distributed around the surface of the hydrophobic core and are exposed to water molecules, which reduces the surface tension of water and enhances the stability of globules. In addition, dications tend to be distributed in the periphery of globules via electrostatic attraction. Owing to the fact that the long alkyl chains in dications experience an over-hydration process upon heating, dications are likely to be stretched and play roles of bridging between different anionic chains. Therefore, it is likely that dynamic ionic bonds serve as ionic cross-linkers around the surface of collapsed aggregates. The ionic surface-crosslinking structure results in the stable formation of microscopic droplets after phase transition in P[SS-P₂] aqueous solution.

4. Conclusions

The phase separation behavior of P[SS-P₂] aqueous solution with gemini-cationic structure was investigated in the present study. Ascribed to the dynamic ionic bonding in P[SS-P₂], the solution showed a unique dependence of transition points on concentrations compared with its mono-cationic PIL and [SS-P₂] aqueous solution. Stable globular droplets were observed in the P[SS-P₂] aqueous solution above the transition temperature, suggesting an LLPS morphology in the gemini-cationic system. Based on the temperature-variable ¹H NMR spectra and temperature-dependent FTIR analysis, the response of the dications lagged behind that of the polymerized anions and the phase transition of P[SS-P₂] aqueous solution was induced by the polymerized anions. In particular, the polymerized anions tended to assemble together and lie in the hydrophobic core at the end of the transition process with dications distributed around the aggregates. It can be assumed that the SO₃ groups were distributed around the surface of globules rather than being wrapped into the globules, which was largely different from the mono-cationic PIL. In addition, since long alkyl chains in the dications exhibited an over-hydration behavior upon heating, dications were likely to be stretched and played bridging roles connecting anionic main chains. Therefore, it is likely that dynamic ionic bonds acted as the “cross-linkers” in the periphery of globules and exerted influence on the aggregate structure in P[SS-P₂] aqueous solution after the phase transition, resulting in the formation of stable regular droplets in the P[SS-P₂] aqueous solution.

Conflicts of interest

There are no conflicts to declare.
Acknowledgements

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Notes and references