Hydrogen bonding induced UCST phase transition of poly(ionic liquid)-based nanogels

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Abstract

In this study, novel thermo-responsive nanogels were facilely fabricated via ternary cross-linking copolymerization of ionic liquid (IL)-based monomers and cross-linker in methanol. To achieve the thermo-responsive performance of nanogels, monomers with hydroxyl or carboxyl group which can contribute to hydrogen (H)-bonding interaction is the key point of this strategy. The thermo-responsive behavior of poly(ionic liquid)s (PIL)-based nanogels were tested using dynamic light scattering (DLS), turbidimetric method, and differential scanning calorimetry (DSC) measurements. The results demonstrated that these novel nanogels presented reversible upper critical solution temperature (UCST) phase transition with the temperature changing. And their UCSTs could be tuned via the feed ratio of IL-based monomers and cross-linker. The nanogels were also measured using scanning electronic microscopy (SEM), thermo-gravimetric analyses (TGA) and Fourier transform infrared spectroscopy (FT-IR) techniques. In addition, a possible mechanism of thermo-responsive performance was suggested based on the above results. As a result, our findings provide an efficient and applicable platform for the fabrication of thermo-responsive polymeric nanomaterials.

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1. Introduction

Stimuli-responsive polymers (SRPs) that are capable of responses to external or internal stimuli, such as temperature, light, pH, magnetic fields, electric fields, redox, etc., [1–5], represent one of the most exciting and emerging fields of scientific interests. These SRPs materials are playing an increasingly important role in a diverse range of applications, including drug delivery, diagnostics, tissue engineering and smart optical systems, biosensors, as well as microelectromechanical systems [6–10]. Among the varieties of SRPs, thermo-responsive polymers have attracted significant attention owing to their technical feasibility and practical advantages [11–14]. The most widely studied thermo-responsive polymers are N-alkyl-substituted acrylamide-based polymers [15–17]. Currently, a popular and efficient technique to fabricate thermo-responsive polymers is through the polymerization of specific monomers whose structures or properties can change reversibly in response to temperature after the polymerization [18]. However, there are still many exciting challenges facing this field, especially in design, synthesis, and engineering of SRPs through those monomers without the feature mentioned above [19].

In recent years, ionic liquids (ILs), which is promoted as a subclass of electrolyte, has attracted considerable attention because of their excellent chemical stability, non-flammability, low volatility, high ionic conductivity and wide electrochemical window [20–28]. Due to their highly tunable virtues, ILs has been found to be of great potential in stimuli-responsive systems, especially thermo-responsive behavior in both water and organic solvents. Presently, the fabrication of ILs and PILs with thermo-responsive phase behavior can be achieved through IL/molecule liquid mixture, polymer/IL mixture, and homo-/copolymerization of IL-based monomers. H. Ohno and J. Yuan have summarized the recent progress on the design of ILs/poly (ionic liquid)s (PILs) with thermo-responsive phase behaviors in water and organic solvents [29–35]. In brief, the thermo-responsive phase behavior of ILs/PILs was inherently derived from the non-covalent interactions between IL and solvents. Given the structural diversity of ILs, there are still...
many promising PIL materials that have great potential to present the thermo-responsive phase behavior. Moreover, these thermo-responsive PIL materials will provide the opportunity for discovering unprecedented phenomena and applications not previously realized for the classical neutral thermo-responsive polymers [21,36].

In the past several decades, polymer-based nanomaterials have garnered tremendous attractions due to their versatile virtues and applications [37–39]. In the previous studies, we have demonstrated a facile one-step synthesis of highly cross-linked polymeric nanogels through conventional free radical copolymerization of IL-based monomers and the cross-linkers ethylene glycol dimethacrylate (EGDMA) and divinylbenzene (DVB) in methanol without any stabilizers or surfactants [40,41]. More interestingly, novel thermo-responsive nanogels could be prepared via copolymerization of biimidazolium-based monomers and the cross-linkers above under the identical conditions [42]. We also found that reversible additional fragment transfer (RAFT) copolymerization was a universal tactics to obtain thermo-responsive nanogels for those common IL-based monomers [43]. As a result, it can be summarized that introducing H-bonding interaction is an efficient technique to fabricate novel thermo-responsive polymeric nanomaterials based on PIL. On the other side, hydroxyl, amino, and carboxyl are the most-used groups to construct H-bonding systems. Herein, hydroxyl- and carboxyl-containing ILs, 1-vinyl-3-hydroxyethylimidazolium bromide ([VHEIm]Br) and 1-vinyl-3-carboxyl methylimidazolium chloride ([VCMIm]Cl) (as shown in Scheme 1a), were prepared and copolymerized with cross-linkers in methanol. Owing to H-bonding interaction between hydroxyl (carboxyl) groups, the as-prepared nanogels are capable of reversible thermo-responsive performance. Thereby, our findings testified that IL-based thermo-responsive polymers can be conveniently fabricated through introducing H-bonding interaction (Scheme 1b).

2. Experimental section

2.1. Materials

Azobisisobutyronitrile (AIBN) was purchased from Shanghai Chemical Reagent Company and recrystallized from methanol before use. Ethylene glycol dimethacrylate (EGDMA, 98%), 1-vinylimidazole (VIm, 98%) and 4-vinylbenzyl chloride were bought from Aladdin Reagent Company. The inhibitors in EGDMA and VIm were removed through distillation on vacuum. Other reagents, such as chloroacetic acid, 2-bromoethanol, triphenylphosphine, methanol, acetone, diethyl ether, dichloromethane, tetrahydrofuran (THF) were A.R. grade and commercially available. All these reagents were used as received without further treatment.

2.2. Characterization

Proton and carbon nuclear magnetic resonance (1H NMR and 13C NMR) spectra were recorded on a Brucker AM 400 MHz spectrometer at 25 °C. Fourier transform infrared (FT-IR) spectra were conducted on a DIGIL FTS3000 spectrophotometer using KBr tablets. Variable temperature FT-IR were measured using a Specac FTIR accessory (GS20502). Thermo-gravimetric analyses (TGA) were

Scheme 1. Chemical structures of IL-based monomers and as-prepared nanogels (a) and schematical illustration of the preparation of PIL-based nanogels and their thermo-responsive behaviors (b).
measured on a Perkin Elmer TG/TGA 6300 at a heating rate of 10 °C min⁻¹. The morphology of the as-prepared nanogels was observed by scanning electron microscopy (SEM, JSM 6700F, Japan). Dynamic light scattering (DLS) measurements were performed at 25 °C and a scattering angle of 90° on a commercial laser light scattering (ALV/SP-125) equipped with an ALV-5000 multi-r digital time correlator and ADLAS DPY425 solid-state laser (output power = 22 mW at λ = 632.8 nm). The upper critical solution temperature (UCST) of thermo-responsive nanogel solutions was measured by turbidimetry at 500 nm using a spectrophotometer (UV–Vis Spectrometer, TU-1901). Differential scanning calorimetry (DSC) measurements were performed using a NETZSCH DSC 204HP apparatus at a scanning rate of 2 °C min⁻¹. Dynamic rheology measurements were performed by oscillatory temperature sweeps (stress-controlled) at the oscillation frequency of 1 Hz and the deformation of 0.1. The rheological behaviors of the samples were measured by an Advanced Rheology Expanded System (ARES, TA), fitted with a parallel plate (diameter of 50 mm) and circulating environmental system for temperature control. The gap distance between the two parallel plates was fixed at 0.2 mm. The gel formation process was investigated by decreasing the temperature at a rate of about 10 °C h⁻¹.

2.3. Synthesis of ionic liquid monomers

2.3.1. Synthesis of 1-vinyl-3-hydroxyethyl imidazolium bromide ([VHEIm]Br) [44].

2-Bromoethanol (2.01 g, 16.09 mmol), 1-vinylimidazole (1.41 g, 14.98 mmol) and methanol (50 mL) were introduced into a clean round-bottom flask with a magnetic stirrer. Subsequently, the mixture was stirred at 70 °C for 48 h under nitrogen atmosphere. After then, the reaction mixture was precipitated from diethyl ether, and washed using diethyl ether for several times. A white solid powder was obtained by filtration, and dried under vacuum at room temperature overnight. (Yield: 77%). ¹H NMR (DMSO-d₆, 400 MHz, d ppm): 9.55 (s, 1H), 8.26 (s, 1H), 7.93 (s, 1H), 7.40–7.32 (dd, 1H), 6.03–5.99 (dd, 1H), 5.45–5.42 (dd, 1H), 5.33–5.02 (s, 1H), 4.29–4.26 (m, 2H), 3.77–3.75 (m, 2H). ¹H NMR (D₂O, 400 MHz, d ppm): 7.68–7.67 (d, 1H), 7.44–7.43 (d, 1H), 7.04–6.98 (t, 1H), 5.70–5.66 (dd, 1H), 5.32–5.29 (dd, 1H), 5.05 (s, 2H), 3.66 (s, 3H). ¹³C NMR (DMSO-d₆, 100 MHz, d ppm): 136.02, 129.21, 124.05, 119.30, 109.04, 59.46, 52.44. m.p. 46–50 °C.

2.3.2. Synthesis of 1-vinyl-3-carboxylmethylimidazolium chloride ([VCMIm]Cl) [45].

1-Chloroacetic acid (5.03 g, 53.23 mmol), 1-vinylimidazole (5.19 g, 55.15 mmol) and dichloromethane (50 mL) were introduced into a clean dried round-bottom flask with a magnetic stirrer. Subsequently, the mixture was stirred at 70 °C for 48 h under nitrogen atmosphere. The reaction mixture was precipitated from diethyl ether, and washed by diethyl ether for several times. The white solid was obtained by filtration and dried under vacuum at room temperature overnight. (Yield: 85%). ¹H NMR (D₂O, 400 MHz, d ppm): 7.41–7.63 (m, 3H), 7.3–7.4 (m, 12H), 6.9 (d, 2H), 6.68 (d, 2H), 3.94–4.51 (m, 1H), 5.18 (d, 2H), 4.35 (d, 2H); ¹³C NMR (D₂O, 100 MHz, d ppm): 137.7, 135.7, 134.1, 131.4, 130.1, 126.6, 117.6, 116.7, 115.4, 77.9. m.p. 121.9 °C.

2.3.4. Synthesis of 3-(4-vinylbenzen)-1-vinylimidazolium chloride ([VBVIm]Cl) [43].

4-Vinylbenzyl chloride (3.05 g, 19.98 mmol), 1-vinylimidazole (2.26 g, 24.01 mmol) and methanol (50 mL) were introduced into a clean dried round-bottom flask with a magnetic stirrer. After then, the mixture solution was stirred at 70 °C for 48 h under nitrogen atmosphere. The reaction mixture was precipitated in diethyl ether for several times. The yellow oil liquid was obtained and dried under vacuum at room temperature overnight. (Yield: 88%). ¹H NMR (DMSO-d₆, 400 MHz, d ppm): 10.34 (s, 1H), 8.45 (s, 1H), 8.15 (s, 1H), 7.52–7.50 (d, 2H), 7.41–7.39 (d, 2H), 6.64–6.62 (dd, 1H), 6.50–6.06 (d, 1H), 5.78–5.74 (d, 1H), 5.55 (s, 2H), 5.32–5.30 (d, 1H), 5.19–5.16 (d, 1H), 3.77 (s, 3H). ¹³C NMR (DMSO-d₆, 100 MHz, d ppm): 137.62, 136.01, 135.61, 134.22, 132.6, 129.16, 128.91, 126.65, 123.26, 119.80, 115.99, 115.31, 108.95, 51.75, 48.52.

2.4. Preparation of poly(ionic liquid)-based nanogels

Nanogels composed of different ionic liquidic were prepared according to our previous method [40–43]. The following example describes the typical synthesis of PIL-based nanogels using 300 mol % EGDMA based on [VCMIm]Cl. This protocol is representative of all nanogel syntheses. [VCMIm]Cl (0.20 g, 1.06 mmol), [VBVIm]Cl (0.25 g, 1.01 mmol), EGDMA (0.60 g, 3.03 mmol) and AIBN (0.0065 g, 0.04 mmol) were dissolved in methanol (30 mL) and the mixture was stirred at 70 °C for 20 h. After then, the reaction solution was precipitated from diethyl ether and the crude product was washed using THF and diethyl ether, respectively. Then the product was dried under vacuum at 50 °C overnight (Yield: 80%).

3. Results and discussion

3.1. Preparation and characterization of PIL-based nanogels

As demonstrated in our previous studies, H-bonding interaction plays a considerable role for the thermo-responsive behavior of PIL-based nanogels [42]. Hence, ILs containing hydroxyl and carboxyl groups are promising candidates to achieve thermo-responsive nanogels based PILs. Functional ILs, [VHEIm]Br and [VCMIm]Cl were synthesized according to the references, and characterized in detail using MS, ¹H and ¹³C NMR measurements. However, it was found that the particles in the micrometer range precipitated from the solvent when the above monomers were copolymerized with the cross-linkers under the same conditions reported [40]. It is possibly because the lower reaction ratio of these as-prepared monomers compared with the cross-linkers [41]. To obtained the stable nanogel solutions in solution, two common IL-based monomers, 4-vinylbenzyl-triphenylphosphorous chloride (VBP-Ph) and 3-(4-vinylbenzene)-1-vinylimidazolium chloride ([VBVIm]Cl), were synthesized, and copolymerized with [VHEIm]Br and [VCMIm]Cl under the identical conditions. As illustrated in Fig. S1, stable and blue opalescent nanogel solutions could be obtained when VBP-Ph and [VBVIm]Cl were used as the comonomers. In the previous works, it has been testified that VBP-Ph and [VBVIm]Cl are more active monomers and can stable the nanogels.
in methanol. Therefore, ternary copolymerization is an efficient approach to prepared stable nanogels with hydroxyl and carboxyl groups.

The sizes of PIL-based nanogels were measured using dynamic light scattering (DLS). As summarized in Table 1, PIL-based nanogels with sizes of less than 200 nm (except NG5) can be prepared via ternary copolymerization in methanol. As far as [VHEIm][Br]-based nanogel is concerned, hydrodynamic diameter (D_h) increases with the increase of [VHEIm][Br] in feed when the ratio of VBP-Ph and [VBVIm][Cl] to EGDMA is invariable. Meanwhile, the size of nanogels based on [VHEIm][Br] increased significantly with increasing EGDMA in the feed. The result is presumably reasonable because IL-based monomers and EGDMA play the roles of stabilizer and nuclei in the polymerization process, respectively. When there are more IL-based monomers, the PIL-based nanogels can be more stable and grow larger. On the other side, when there are more EGDMA in the feed, the particles grow quickly due to the higher reaction ratio of EGDMA. However, these particles can be stabilized efficiently due to fewer stabilizers and get larger quickly (NG5 in Table 1). They will precipitate from the solution in the presence of IL-based monomers and EGDMA play the roles of stabilizer and nuclei in the polymerization process, respectively. When there are more IL-based monomers, the PIL-based nanogels can be more stable and grow larger. On the other side, when there are more EGDMA in the feed, the particles grow quickly due to the higher reaction ratio of EGDMA. However, these particles can’t be stabilized efficiently due to fewer stabilizers and get larger quickly (NG5 in Table 1). They will precipitate from the solution in the presence of too many EGDMA (NG6 in Table 1). Likewise, D_h of [VCMIm][Cl]-based nanogels increase when the feed ratio of VBP-Ph to cross-linker is 1:3. However, the sizes of [VCMIm][Cl]-containted nanogel decreased with the increase of [VCMIm][Cl] in the feed when the feed ratio of VBP-Ph to EGDMA is 1:2, which is opposite to that of [VHEIm][Br]-based nanogel. It is probably due to the higher reaction ratio and better solvophilicity of [VCMIm][Cl]. Although PIL-based nanogels are in wide size dispersion, there is only one peak in DLS curves (as indicated in Fig. S3). All the nanogels are positively charged, which is benefited to the stability of nanogels resulting from the electrostatic repulsion interactions. Nevertheless, [VHEIm][Br]-based nanogel presented higher ζ-potential than [VCMIm][Cl]-containted nanogel. It should be because of the partial ionization of carboxyl groups of [VCMIm][Cl] in the solution.

The morphologies of PIL-based nanogels with different feed ratio of IL monomers and EGDMA were examined by scanning electronic microscopy (SEM). Fig. 1 represents the typical SEM images of PIL-based nanogels. According to these images, spherical nanoparticles with the average diameter less than 200 nm were obtained via ternary cross-linking copolymerization in methanol. The particles presented in the SEM images were smaller than the results measured by DLS (see Table 1). This was probably because the latter were highly swollen in methanol.

In addition, PIL-based nanogels were characterized using FT-IR spectroscopy. As illustrated in Fig. 2, some typical peaks attributed to imidazolium IL and EGDMA copolymer can be clearly recognized, such as aromatic benzene ring (1646, 1500 cm⁻¹, stretching vibration), aromatic imidazolium ring (1454, 1180 cm⁻¹ stretching vibration), carbonyl group (1720–1730 cm⁻¹, stretching vibration), C=N in imidazole ring (1554 cm⁻¹, stretching vibration), hydroxyl (3300–3500 cm⁻¹, stretching vibration), etc. At the same time, the peak ascribed to the carbon–carbon double bond (1582 cm⁻¹, stretching vibration) in the vinyl group of the monomers disappeared. These results demonstrate the formation of imidazolium IL and EGDMA copolymers. Furthermore, thermostabilities of the as-prepared nanogels were also checked using thermogravimetric analyses (TGA). As indicated in Fig. 3, these PIL-based nanogels are stable below 250 °C, which may be due to their highly cross-linked structure. The weight loss below 150 °C is probably because of the evaporation of absorbed water or solvent. In addition, the onset decomposition temperature (T_{dec}) of [VHEIm][Br]-based nanogels (about 260 °C) are lower than those of [VCMIm][Cl]-based nanogels (about 280 °C). Thus, the as-prepared nanogels containing hydroxyl and carboxyl groups are highly potential catalysts for cycloaddition reaction of CO₂ with epoxides [46,47].

3.2. Thermo-responsive behavior of PIL-based nanogels

Owing to hydrogen-bonding interaction between hydroxyl or carboxyl groups, the as-prepared nanogels are promising to be thermo-responsive. As showed in Fig. S2, all the nanogel solutions are blue opalescent and translucent at higher temperatures. They suddenly turned cloudy at lower temperatures. To specify the transition behaviors with the temperature changing, the behavior of PIL-based nanogel solution was monitored using turbidimetric method. As summarized in Fig. 4a, the transmittance of PIL-based nanogel solution is above 70% except for NG18, which is of lower transmittance due to its higher concentration and larger size. With the temperature decreasing, a sharply decrease in transmittance could be observed. The discrete transition induced by the temperature indicates that PIL-based nanogels are thermo-responsive and are of upper critical solution temperature (UCST) transition performances. NG10 and NG12 presented a sharp transition compared with others. It is possibly because that the concentrations of

<table>
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<th>Entry</th>
<th>Monomers</th>
<th>Feed ratio (molar ratio)</th>
<th>D_h (nm)</th>
<th>PDI</th>
<th>ζ (mV)</th>
</tr>
</thead>
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<td>NG1</td>
<td>[VHEIm][Br], VBP-Ph</td>
<td>1:1:2</td>
<td>22.0</td>
<td>0.49</td>
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<td>[VHEIm][Br], VBP-Ph</td>
<td>3:1:2</td>
<td>27.9</td>
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<td>NG3</td>
<td>[VHEIm][Br], VBP-Ph</td>
<td>5:1:2</td>
<td>48.6</td>
<td>0.36</td>
<td>14.2</td>
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<td>NG4</td>
<td>[VHEIm][Br], VBP-Ph</td>
<td>8:1:2</td>
<td>59.7</td>
<td>0.27</td>
<td>15.8</td>
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<tr>
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<td>[VHEIm][Br], VBP-Ph</td>
<td>5:1:6</td>
<td>239</td>
<td>0.30</td>
<td>11.8</td>
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<tr>
<td>NG6</td>
<td>[VHEIm][Br], VBP-Ph</td>
<td>5:1:8</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>NG7</td>
<td>[VHEIm][Br], [VBVIm][Cl]</td>
<td>2:1:2</td>
<td>88.5</td>
<td>0.29</td>
<td>13.1</td>
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<tr>
<td>NG8</td>
<td>[VHEIm][Br], [VBVIm][Cl]</td>
<td>4:1:2</td>
<td>141</td>
<td>0.28</td>
<td>14.0</td>
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<td>NG9</td>
<td>[VHEIm][Br], VBP-Ph</td>
<td>10:1:2</td>
<td>173</td>
<td>0.27</td>
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<td>NG10</td>
<td>[VCMIm][Cl], VBP-Ph</td>
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<td>59.3</td>
<td>0.20</td>
<td>3.74</td>
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<tr>
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<td>[VCMIm][Cl], VBP-Ph</td>
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<td>[VCMIm][Cl], VBP-Ph</td>
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<td>[VCMIm][Cl], [VBVIm][Cl]</td>
<td>2:1:3</td>
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<td>NG18</td>
<td>[VCMIm][Cl], [VBVIm][Cl]</td>
<td>4:1:3</td>
<td>110</td>
<td>0.27</td>
<td>3.37</td>
</tr>
</tbody>
</table>

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*Polymerization conditions: [EGDMA]·[monomers]·[ABN] = 100:1, methanol (50 mL), 70 °C. Molar ratio of [VHEIm][Br·[VCMIm][Cl], VBP-Ph·[VBVIm][Cl] and EGDMA. Particles precipitated, no data; D_h: the average hydrodynamic diameter; PDI: polydispersion index.*
nanogels are different and the temperature was not automatically controlled. Additionally, UCST of the as-prepared nanogels were measured by DSC. As illustrated in Fig. S4, the UCST is highly dependent on the composition of PIL-based nanogel. For example, UCST of NG4 (32.5 °C) is much higher than that of NG2 (13.3 °C), and UCST of NG16 (18 °C) is lower than that of NG18 (23.2 °C). Combining the data in Table 1, it can be found that the more functional IL monomers ([VHEIm]Br and [VCMIm]Cl) in the feed ratio will enhance UCST of as-prepared nanogels. The result can be reasonably attributed to the hydrogen bonding interaction coming from [VHEIm]Br and [VCMIm]Cl. The more [VHEIm]Br and [VCMIm]Cl were fed in the ternary copolymerization, the more hydrogen bonding interactions will produce. Therefore, higher UCST could be achieved. When the feed ratio of [VCMIm]Cl, VBP-Ph and EGDMA is 10:1:2 (NG13), the nanogel solution can transform to macrogel at the temperature below 20 °C. As demonstrated in Fig. 4b, both shear storage modulus (G’) and shear loss modulus (G”) are very low and in the same range when the temperature is above 20 °C, which demonstrates that the nanogel solution

![Representative SEM images of PIL-based nanogels (a NG3; b NG7; c NG9; d NG17). All the scale bars are 1 μm.](image1)

![FT-IR spectra of cross-linked polymers (a poly (VBPPh-co-EGDMA); b NG2; c NG10; d poly ([VBMIm][Cl-co-EGDMA]; e NG7; f NG17).](image2)

![TG curves of PIL-based nanogels with different monomers and feed ratio.](image3)
exhibited a viscoelastic response. When the temperature decreases, both $G'_0$ and $G''_0$ increased; however, $G'_0$ increased much more rapidly than $G''_0$. The sol-gel transition occurred when $G'_0$ was higher than $G''_0$ at around 20 °C. The results obtained from the temperature-dependent oscillatory shear rheological measurements confirmed the sol-gel transition behavior of [VCMIm]Cl-based nanogel solution in methanol. Moreover, all these temperature-induced transitions are reversible.

To testify H-bonding interactions between PIL-based nanogels, FT-IR spectra of PIL-based nanogels containing methanol were continuously collected during a temperature-controlled process. According to Pimentel and McClellan [48], the stretching mode of an A–H moiety shifts to lower frequencies upon hydrogen bond formation in IR spectra. As depicted in Fig. 5, a characteristic band centered on 3360 cm$^{-1}$, corresponding to the stretching vibration of O–H in hydroxyl groups, could be observed clearly. When temperature decreased from 40 °C to 15 °C, the band shifted obviously to lower wavenumbers (about 3320 cm$^{-1}$), which was attributed to the diminution of hydrogen bonding between methanol and nanogels and the formation of hydrogen bonding between nanogels. Compared with these shifts, most of the other bands of PIL-based nanogels remained unchanged upon the temperature changing. Considering these results, the formation of thermo-reversible PIL-based nanogels in methanol involved significant enhancement of H-bonds between hydroxyl and carboxyl groups in nanogel at lower temperatures. The formation of similar H-bonded network was also observed in water [49]. Such a network can serve to enhance the enclosure of methanol, and formed a physical macrogel ultimately (as illustrated in Scheme 1b). As a consequence, the reversible nanogel-macrogel transition can be triggered by exchanging of the two kinds of H-bonding systems.

4. Conclusion

In summary, IL monomers with hydroxyl and carboxyl groups were prepared and utilized to fabricate thermo-responsive nanogels based-PIL. These novel nanogels could be obtained through ternary copolymerization of IL monomers and cross-linker in methanol. The results showed that stable nanogel solutions could be prepared in a wide range of monomer feed ratio, and the particle sizes could be finely tuned via the feed ratio of IL monomers and cross-linker. Additionally, PIL-based nanogels are thermo-responsive and display reversible solution-precipitation and solution-macrogel transitions with the temperature changing. DSC measurement revealed that UCST of PIL-based nanogels could be tuned from −1 to 40 °C via the different feed ratio. Therefore, our findings further testify that introducing H-bonding interaction to IL monomers is an efficient approach to achieve thermo-responsive PIL-based nanogels. Our studies thus provide a new platform for the fabrication of thermo-responsive nanomaterials, as well as explore the potential applications of ILs in smart polymers.

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Fig. 4. Thermo-responsive behavior of PIL-based nanogel. (a) Temperature dependence of the transmittance (at 500 nm) curves of as-prepared nanogel solution with different feed ratio; (b) Shear storage modulus ($G'$) and shear loss modulus ($G''$) for NG9 in methanol solutions (12.5 wt%) as a function of temperature.

Fig. 5. FT-IR curves of PIL-based nanogels with 2.0 wt% methanol in the ν(C–H) region of 3800–2600 cm$^{-1}$ during the temperature increasing from 15 to 40 °C.
Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2016.06.048

References

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