

One-Step Synthesis of Thermosensitive Nanogels Based on Highly Cross-Linked Poly(ionic liquid)s**

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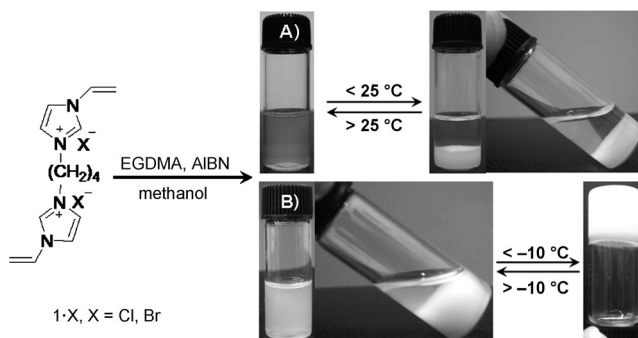
Ionic liquids (ILs) have attracted considerable attention in a wide variety of fields because of their excellent properties, such as immeasurably low volatility, non-flammability, high polarity, high ionic conductivity, and a wide window of electrochemical potential.^[1] In the past few years, the utilization of ILs for the design of advanced materials and polymer-based physical-chemical systems has been studied widely.^[2] In particular, ILs have been extensively utilized in the preparation of a new class of solid state electrolytes with high ionic conductivity known as ionic gels,^[3] which have found use in sensors, solar cells, capacitors, polymer light-emitting cells, CO₂ absorption, and other applications.^[4]

Currently, ILs are usually either gelled with polymers,^[5] incorporated with inorganic substances (silica nanoparticles and carbon nanotubes),^[6] or mixed with other ILs to prepare IL-based gels.^[7] The design and synthesis of low molar mass gelators are also effective methods.^[8] However, these methods and techniques for the preparation of IL-based gels present several limitations, ranging from expensive materials to complex synthetic procedures,^[9] which make them less attractive

Recently, we have demonstrated a facile one-step synthetic strategy for the preparation of IL-based cross-linked polymeric nanogels (CLPNs) by the conventional radical copolymerization of a phosphonium-based IL (PIL) and the cross-linkers ethylene glycol dimethacrylate (EGDMA) and divinylbenzene (DVB) in selective solvents.^[10] Nevertheless, when the imidazolium-based IL (ImIL), 1-vinyl-3-(ethoxycarbonyl)methyl imidazolium chloride was copolymerized with a cross-linker under the same conditions, the copolymers precipitated from the solvent, resulting in particles in the submicrometer range.^[11] Similar results were also reported by Han et al.^[12] The precipitation of ImIL-based cross-linked copolymers from the solvent during the polymerization process was due to the lower number of poly(ImIL) chains in the copolymer.^[11] This result was presumably caused by the

lower polymerization reactivity of ImIL monomers, as compared with the cross-linkers.

Herein, geminal dicationic, 1,4-butanediyl-3,3'-bis-1-vinylimidazolium halides ([BVIm]⁺X⁻ = **1**·X; X = Cl or Br), were developed to provide further insight into the mechanism of the one-step synthesis of CLPNs, and to prepare ImIL-based CLPNs through the copolymerization of **1**·X with cross-linkers in selective solvents. For comparison, 3-butyl-1-vinylimidazolium bromide ([C4VIm]Br) was also prepared. The results revealed that ImIL-based CLPNs can be easily prepared through the copolymerization of **1**·X with EGDMA and DVB in selective solvents. Stable, blue opalescent CLPN solutions can be prepared without any precipitation when the cross-linking copolymerization of **1**·X is conducted in methanol or ethanol (Supporting Information, Figure S1). However, the copolymers precipitated from the solvent when [C4VIm]Br was copolymerized with the cross-linkers under the same conditions. These results confirm the assumption that the polymer particles cannot be stable because of the low reactivity of ImIL monomers, as compared with the cross-linkers. In contrast, the polymer particles can be stabilized by introducing geminal ImIL monomers. More importantly, the ImIL-based CLPN is thermosensitive, and can reversibly transform to precipitate or macrogel in methanol with a change in temperature (Scheme 1). Herein,



Scheme 1. One-step synthesis of ImIL-based CLPN, with photographs showing the thermosensitive behavior of CLPN solutions. A) **1**·Br/EGDMA = 5:1 (mol/mol); B) **1**·Br/EGDMA = 10:1 (mol/mol).

a novel example of an ImIL-based thermosensitive nanogel prepared by one-step cross-linking copolymerization is presented.

The sizes of the ImIL-based CLPNs were measured using dynamic light scattering (DLS), the ζ -potential was also determined. As shown in Table 1, ImIL-based CLPNs with sizes of less than 100 nm can be prepared by the one-step

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Table 1: Properties of CLPNs prepared in methanol with different 1-X/cross-linker feed ratios.

Monomer	Feed ratio ^[a]	D_h	PDI	ζ -Potential
1-Br + EGDMA	5:1	100	0.21	16.5
1-Br + EGDMA	10:1	78	0.19	14.5
1-Br + EGDMA	15:1	67	0.22	13.9
1-Br + DVB	5:1	99	0.25	13.6
1-Br + DVB	10:1	69	0.30	16.5
1-Cl + EGDMA	5:1	88	0.24	13.8
1-Br + EGDMA ^[b]	5:1	42	0.32	11.3

[a] Molar ratio of 1-X/cross-linker. [b] Prepared in ethanol.
 D_h = hydrodynamic diameter, PDI = polydispersity index of CLPN.

synthesis, and the size decreases with the increase in 1-Br in the feed. This data is reasonable, because 1-Br acts as a stabilizer in the process. In agreement with PIL-based CLPNs, ImIL-based CLPNs prepared in ethanol were smaller than those prepared in methanol, which is probably because the solubility of ImIL is higher in ethanol than in methanol. Also, given that all CLPNs are positively charged, they are very stable in solution owing to mutual electrostatic repulsion. These results demonstrate that the one-step synthesis is an effective technique for the preparation of IL-based CLPNs.

The CLPN generated with a feed ratio of 5:1 1-Br/EGDMA was found to precipitate from methanol when the temperature decreased below 25°C, but a stable CLPN solution was immediately recovered at temperatures above 25°C (Scheme 1 A). This behavior indicates that 1-X-based CLPN is thermosensitive. Figure 2 shows the temperature dependence of the turbidity and diameter of CLPN (4.5 wt %) in methanol solution. The blue opalescent solution was translucent at temperatures above 28°C, and suddenly turned cloudy at temperatures below 25°C. The discrete transition, which occurred within a temperature difference of 3°C, indicates that 1-X-based CLPNs are thermosensitive and possess an upper critical solution temperature (UCST). The thermosensitive behavior was also supported by DLS. The hydrodynamic diameter (D_h) of CLPN increased rapidly from less than 100 nm to micrometer levels in the same temperature range. These results suggest that free CLPN was suddenly desolvated to form larger aggregates, leading to

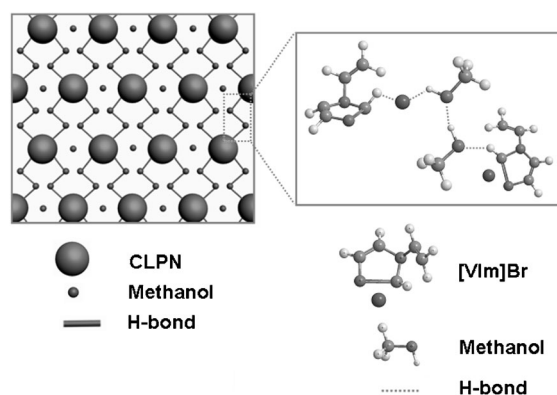


Figure 1. Proposed H-bond network between the imidazolium ring, Br^- , and methanol at lower temperatures.

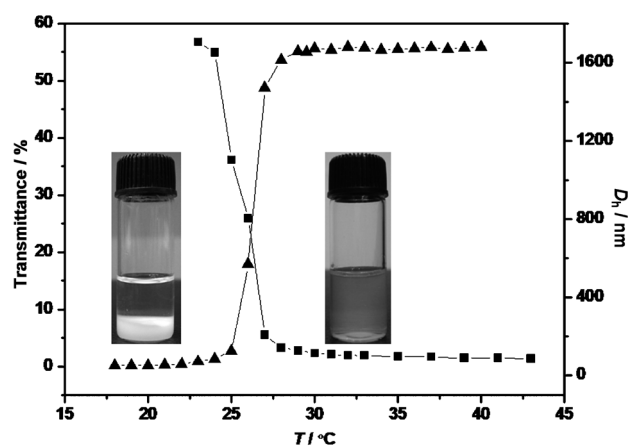


Figure 2. Temperature dependence of the transmittance at 500 nm (—▲—) and the hydrodynamic diameter (D_h ; —■—) for 4.5 wt % CLPN (1-Br/EGDMA = 5:1) in methanol.

precipitation from the solvent at temperatures below the UCST.

However, CLPNs (1-Br/EGDMA) with feed ratios of higher than 10:1 did not precipitate from the solvent when the temperature was below 25°C, not even at 4°C. Surprisingly, instead of precipitating, the CLPN solutions gelled when kept at temperatures below −10°C. As shown in Scheme 1 B, the reversible sol-gel transition of CLPN in methanol is driven by temperature change. A weak gel also formed when CLPN (1-Br/EGDMA = 5:1) completely precipitated from methanol (Scheme 1 A). The preliminary results showed that some interactions between CLPN and methanol exist, which can be enhanced by increasing the 1-Br content in the copolymers.

Dynamic rheological analysis is an effective technique for measuring the sol-gel transition behavior. The sol-gel transition point is indicated by the temperature at which the storage modulus (G') curve intersects the curve of the loss modulus (G''). Figure 3 shows the oscillatory temperature sweep profiles of 4.5 wt % CLPN solutions in methanol. When the temperature was above −7°C, both CLPN solutions exhibited a viscoelastic response, because CLPN was in the liquid state. When the temperature was below −7°C, both G' and G'' increased; however, G' increased more rapidly than G'' . The sol-gel transition occurred when G' was higher than G'' , at about −7°C for both CLPN solutions. The results obtained from the temperature-dependent oscillatory shear rheological measurements further confirmed the sol-gel transition behavior of CLPN solution in methanol with a 1-Br/cross-linker feed ratio above 10:1.

A variety of organo- and hydro-gelators that can immobilize organic fluids and/or water have been proposed in which various types of intermolecular interactions, such as hydrogen-bond, host-guest, π - π , cation- π , and electrostatics, play a significant role.^[13] In an effort to obtain evidence for the formation of a CLPN-based macrogel in methanol, ^1H NMR spectroscopy, IR spectroscopy, differential scanning calorimetry (DSC), and X-ray diffraction (XRD) were used to elucidate the nature of the interactions between methanol and ImIL-based CLPN.

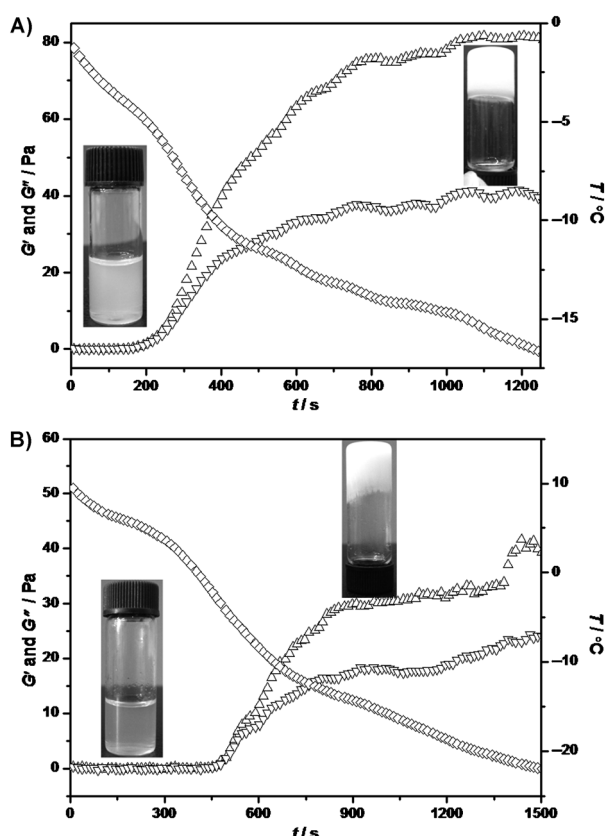


Figure 3. Shear storage modulus (G' ; Δ) and shear loss modulus (G'' ; ∇) for CLPN at a concentration of 4.5 wt% in methanol, as a function of temperature ($\diamond$). A) **1-Br**/EGDMA = 10:1 (mol/mol); B) **1-Br**/EGDMA = 15:1 (mol/mol). Photographs show the corresponding appearance of the sample.

First, the ^1H NMR spectra of **1-Br** in different deuterated solvents were obtained. As shown in Figure 4, all of the signals confirm the desired structure of **1-Br**. A prominent characteristic found in **1-Br** was the signal associated with the C2 proton of the imidazolium ring, which was not observed when the measurements were conducted in deuterated water or methanol. However, the signal emerged when the NMR

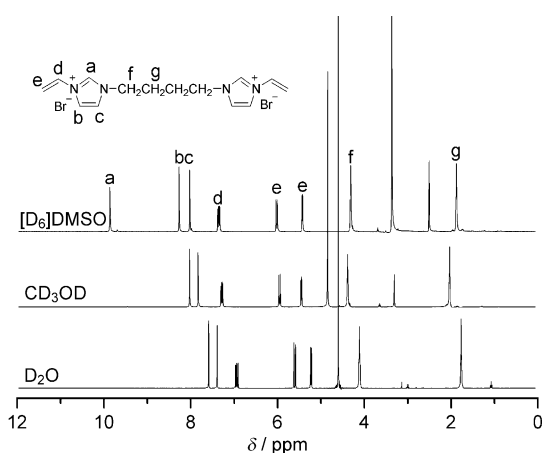


Figure 4. ^1H NMR spectra of **1-Br** in various deuterated solvents.

analysis was conducted in deuterated DMSO. Moreover, the addition of methanol into a **1-Br** solution in DMSO resulted in a significant decrease in the chemical shift and intensity of the signal of the C2 proton of imidazolium (Figure S2). The results indicate that the C2 proton of imidazolium can exchange with the protons of polar solvents such as water and methanol. Therefore, it is inferred that a strong H bond can form between **1-Br** and methanol.

IR spectroscopy is a powerful and effective technique for studying the interactions between ILs and solvents, as well as the formation/disruption of H bonds.^[14] It has been reported that the IR spectra of dried imidazolium-based ILs present a prominent absorption band at 3058 cm^{-1} , which is attributed to the C–H stretching vibration for $\text{C–H}\cdots\text{X}^-$. Upon uptake of water, the peaks associated with the aromatic C–H stretching vibration and the C–H stretching vibration of the $\text{C–H}\cdots\text{X}^-$ shift to higher wavenumbers.^[15] According to Pimentel and McClellan,^[16] the stretching mode of an A–H moiety shifts to lower frequencies upon H bond formation. Infrared spectra of ImIL-based CLPNs are shown in Figure S3. Based on the reports, the peaks at 3078 and 3137 cm^{-1} were attributed to the aromatic C–H stretching vibration and the C–H stretching vibration of $\text{C–H}\cdots\text{Br}^-$, respectively. The peaks were shifted to higher wavenumbers, as compared to the dried samples. This illustrates the disruption/diminution of the H bond between the imidazolium ring and Br^- , probably due to the presence of residual methanol or water.

To elucidate the interactions between CLPN and methanol, FTIR spectra of CLPN containing methanol were continuously collected in a temperature-controlled process (Figures S4–S8). As shown in Figure S9a, two prominent bands, which correspond to the vibrational region of the aromatic C–H stretching and the C–H stretching of $\text{C–H}\cdots\text{Br}^-$, were observed around 3125 and 3060 cm^{-1} , respectively. However, when methanol was added, both of the bands shifted to significantly higher wavenumbers, 3135 and 3087 cm^{-1} , respectively (Figure S9b). Compared with these shifts, most of the other bands of CLPN remained unchanged upon addition of methanol. The upward shift in the frequency of the C–H stretching was consistent with H bond disruption/diminution between the imidazolium ring and Br^- in the presence of methanol. Furthermore, the peaks again downshifted to lower wavenumbers when methanol was evaporated at higher temperature. This downshift is also indicative of H bond formation between the imidazolium ring and Br^- upon the evaporation of methanol. At the same time, the position of the O–H stretching band of methanol shifted from 3425 cm^{-1} to 3409 cm^{-1} , and the intensity decreased greatly. Therefore, the formation of a solution of CLPN in methanol involves the partial replacement of $\text{C–H}\cdots\text{Br}^-$ bonds with H bonds between the imidazolium ring and methanol. Considering these results, the formation of a thermo-reversible CLPN macrogel in methanol involved significant enhancement in the H bonds between the imidazolium ring, Br^- , and methanol at lower temperatures. The formation of a similar H-bond network was also observed in water.^[8c] Such a network could serve to enhance the enclosure of methanol, and ultimately formed a physical macrogel (Figure 1). When the temperature increased, the H-bond

network was destroyed, leading to the formation of a methanol solution of CLPN.

The morphology of CLPN was examined using electronic microscopy. Transmission electron microscopy (TEM) shows spherical nanoparticles with sizes of less than 50 nm (Figure 5A–C). The sizes observed are smaller than those from

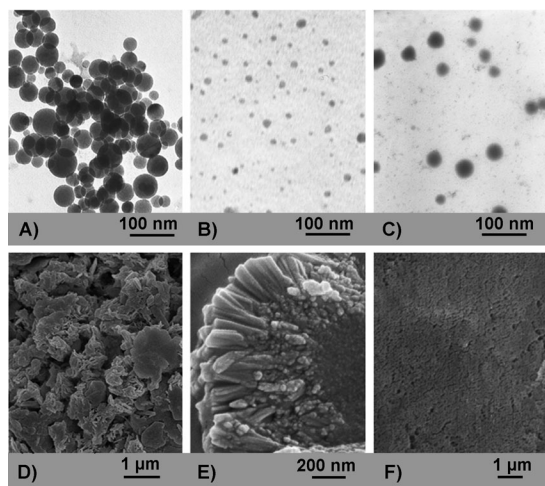


Figure 5. Representative TEM (A, B, and C) and SEM (D, E, and F) images of CLPN. A) **1-Br**/DVB = 10:1; B) CLPN prepared in ethanol; C) **1-Br**/EGDMA = 10:1; D) **1-Br**/DVB = 10:1; E) **1-Br**/EGDMA = 10:1; F) cryo-dried gel (**1-Br**/EGDMA = 10:1).

DLS measurements, because the particles were swollen in solution. Figures 5D and E show SEM images of CLPN obtained after precipitating the reaction solutions using diethyl ether. The CLPN aggregated and formed larger particles during the precipitation process. It can also be observed from Figure 5E that the aggregates are crystalline and consist of spherical CLPN particles. However, Figure 5F shows that cryo-dried CLPN gel has a regularly arranged structure. The crystal structure of ImIL-based CLPNs may result from poly(**1-Br**) chains on the CLPN surface. The crystal structure of ImIL-based CLPNs was also confirmed by XRD and DSC measurements (Figures S10 and S11).

ImIL-based CLPNs demonstrated excellent activity in the cycloaddition reaction of CO₂ with epoxides. As summarized in Tables S1 and S2, and in Figure S12, cyclic carbonates with high yield and selectivity were obtained. Also, CLPN could be easily separated and reused without detectable decrease in activity. Furthermore, a binary catalyst system combining an ImIL-based CLPN and K₂CO₃ was explored for the transesterification of a cyclic carbonate with methanol (Scheme S1). The results showed that the binary catalyst was effective in the reaction, and dimethyl carbonate was obtained in high yield (Table S3) and excellent selectivity. More importantly, CLPN could be readily separated by filtration after precipitation from methanol at temperatures below the UCST. As expected, ImIL-based CLPNs have much potential as both catalysts and novel catalyst supporters that can be readily recycled owing to their thermosensitive properties. More potential applications of thermosensitive

CLPNs, for example as gold nanoparticle supporters, are currently under investigation in our laboratory.

In summary, ImIL-based CLPNs were facily prepared by one-step cross-linking copolymerization of geminal dicationic monomers and cross-linkers in selective solvents. Stable CLPN solutions were obtained and the particle sizes could be fine-tuned by changing the **1-X**/cross-linker feed ratio. Therefore, the one-step synthesis herein presented is an efficient method for the preparation of IL-based CLPNs. Moreover, ImIL-based CLPNs are thermosensitive and display reversible, temperature-driven nanogel–macrogel transitions in methanol. ImIL-based CLPNs were also found to be effective catalysts for CO₂ cycloaddition reactions with epoxides, and could be readily separated by filtration, because of their thermosensitive properties. Such attributes make them a robust material platform suitable for a wide range of applications.

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