A thermoreversible ion gel by triblock copolymer self-assembly in an ionic liquid†

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A new thermoreversible ion gel with high ionic conductivity was developed through the self-assembly of a triblock copolymer, by choosing appropriate associating end-blocks for the ionic liquid.

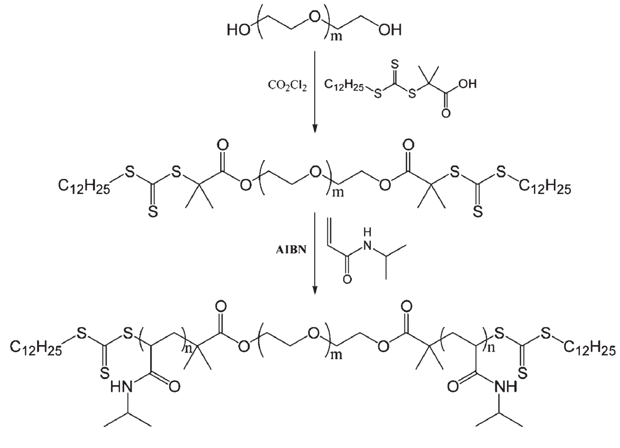
Polymer gel electrolytes are currently of great interest as prospective alternatives to liquid electrolytes, especially in terms of achieving comparable ionic conductivities (σ). Among these ion gels is a new class of soft solids, polymeric networks swollen with significant loadings of ionic liquids and/or other functional components.[1–3] They overcome the leakage and flammability issues of organic solvent-based electrolytes. Compared to more traditional solid polymer electrolytes obtainable by polymerization of ionic liquids[4] or doping polymers with ionic liquids,[5] ion gels require significantly less polymer and offer improved ionic conductivity.[2,3] Although initial work on these solid polymer electrolytes has mainly concentrated on lithium ion conducting gels due to their use in lithium batteries,[6] applications are now expanding into other devices including chemical sensors,[7] organic thin film transistors,[8] electromechanical actuators,[9] polymer light-emitting electrochemical cells,[10] and gas separation membranes.[11]

Ionic liquids have recently been widely explored as functional materials,[12] not just as "green solvents", because of their unique combination of physicochemical properties.[13] These properties, especially the high ionic conductivity and wide electrochemical window, make ionic liquids attractive electrolytes for electrochemical devices.[14] In addition, the large variety of cations and anions affords more flexibility for different applications.[15]

In contrast to more traditional solid polymer electrolytes, there has been relatively little investigation into ion gels. Rogers and coworkers have prepared an ion gel by the cross-linking reaction of disuccinimidylpropyl poly(ethylene glycol) (PEG) monomers with four-arm tetraamine PEG cross-linkers.[1] Watanabe and coworkers have successfully produced pyridinium and imidazolium salt-based ion gels by *in situ* polymerization of vinyl monomers in ionic liquids.[2]

Recently we have reported a new way of developing ion gels through the self-assembly of **ABA** triblock copolymers,[3] where the **A** blocks are insoluble and the **B** block is compatible with the chosen ionic liquid. Transparent gels were achieved with as little as 4 wt% triblock copolymer, and the ionic conductivity was only several percent below the pure ionic liquid. Furthermore, the use of triblock copolymers provides more flexibility in controlling the gel structure and physical properties through variation of the copolymer block lengths, architecture, or identities. However, for solvent-free processing it is desirable to design thermoreversible ion gels. In such physical gels, the cross-linking is reversible upon changing temperature, whereby the material can be processed in its liquid state, and used in its solid state. This goal can be achieved through judicious selection of block copolymer and ionic liquid. In this work, we synthesized a poly(*N*-isopropyl acrylamide-*b*-ethylene oxide-*b*-*N*-isopropyl acrylamide) (PNIPAm–PEO–PNIPAm) triblock copolymer, and characterized the temperature sensitive ion gel formed by self-assembly in the room-temperature ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide ([EMIM][TFSI]). The thermo-responsiveness is due to the recently reported upper critical solution temperature (UCST) phase behavior of PNIPAm/[EMIM][TFSI] mixtures.[16] Of particular interest are the thermo-responsiveness, ionic conductivity, and rheological properties of the ion gel.

A PNIPAm–PEO–PNIPAm triblock copolymer was synthesized by reversible addition–fragmentation chain transfer (RAFT) polymerization (Scheme 1) from a telechelic PEO precursor. The hydroxyl end-groups of PEO were coupled to the chain transfer agent (CTA), *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate, *via* an acid chloride intermediate. CTA end-capped PEO was subsequently used to grow PNIPAm blocks by RAFT polymerization. Each step of the reaction was followed by ^{1}H NMR spectroscopy and the product was characterized by size exclusion chromatography (SEC). The final product has an overall molecular weight of M_n = 29 kg mol^{-1} and a polydispersity of



Scheme 1 Synthesis of PNIPAm–PEO–PNIPAm triblock copolymer.

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M_w/M_n = 1.16. The two PNIPAm end-blocks have molecular weights of M_n = 2.8 kg mol^{-1}, and the fraction of diblocks (*i.e.*, polymers with only one PNIPAm block) is less than 10%.

The [EMIM][TFSI] ionic liquid was prepared following a synthesis protocol reported previously.[2] 1-Ethyl-3-methylimidazolium bromide ($EMIM^+Br^-$) was first prepared by the quaternization reaction of 1-methylimidazole with ethyl bromide, followed by repeated recrystallization. Then the anion exchange reaction between $EMIM^+Br^-$ and Li^+TFSI^- in water yields a hydrophobic ionic liquid phase. The obtained [EMIM][TFSI] was repeatedly washed with distilled water, vacuum dried, and identified by NMR.

The polymer electrolyte was prepared by directly dissolving 10 wt% PNIPAm–PEO–PNIPAm in [EMIM][TFSI]. At room temperature the sample is a viscous liquid, which solidifies after cooling and becomes a transparent ion gel. Upon heating to room temperature it becomes a liquid again, and in subsequent cooling–heating cycles we found the gel transition to be reversible.

Dynamic shear measurements were performed on the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel over the temperature range of 5–50 °C. Representative data at 5, 20, and 50 °C are shown in Fig. 1. At 50 °C the sample is a liquid. Its dynamic storage modulus (G') is significantly smaller than the loss modulus (G''), and both moduli exhibit different power law dependences on the angular frequency (ω) in the low-frequency window ($\omega\tau \ll 1$, where τ is the longest relaxation time of the polymer): $G' \sim \omega^2$ and $G'' \sim \omega$. This is the typical rheological behavior of a viscous fluid.[17] At 5 °C the sample is an optically transparent gel (see inset to Fig. 2). G' is larger than G'' and is nearly frequency independent – a characteristic of solid-like behavior. At a temperature of 20 °C, the sample shows intermediate behavior: over the entire frequency range of experiments we observed similar values and power law dependences for G' and G'': $G' \approx G'' \sim \omega^{0.5}$. This is the signature of the transition between liquid-like and solid-like behavior, and closely approximates the gel point.[18] Intermediate power law dependences were observed for other temperatures between 5 and 50 °C. These data are not included in Fig. 1 for the sake of clarity.

A further manifestation of the thermoresponsive gel transition is presented in Fig. 2, in which the temperature dependences of G' and G'' were measured at a frequency of 0.1 rad s^{-1} during a temperature ramp from −4 to 26 °C at a heating rate of 0.5 °C min^{-1}. Fig. 2 clearly shows that there is a transition for both G' and G'' as a function of temperature, with the change in G' approaching four orders of magnitude. The gel transition temperature is around 17 °C, consistent with the results in Fig. 1.

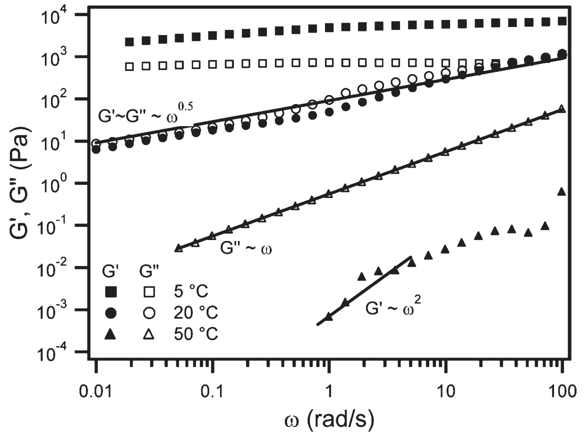

Fig. 1 Dynamic storage and loss moduli of the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel at three representative temperatures.

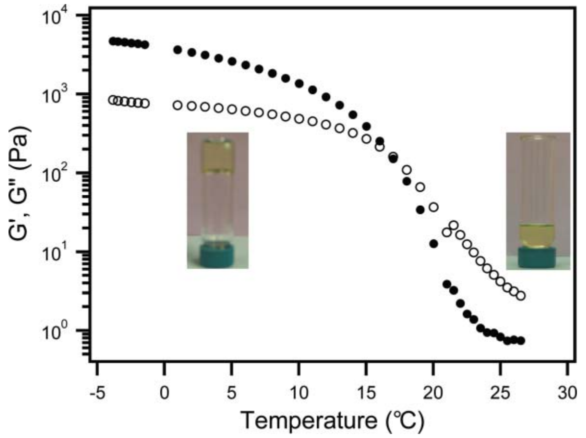

Fig. 2 Variation of dynamic storage (solid symbols) and loss (open symbols) moduli of the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel as a function of temperature at a frequency of ω = 0.1 rad s^{-1} and a strain amplitude of γ = 5%. The insets are photographs of the ion gel at corresponding temperatures.

The gelation arises from the noncovalent association of PNIPAm end-blocks undergoing the UCST, bridged by the ionic liquid compatible PEO mid-block. In previous work we reported the self-assembly of amphiphilic block copolymers in an ionic liquid and demonstrated the feasibility of structuring ionic liquids through micellization, microemulsion, or gelation of block copolymers.[19] This work is an extension of the idea. The gel transition temperature of the ion gel (*ca.* 20 °C) is consistent with reported phase-separation temperatures of the PNIPAm/[EMIM][TFSI] system,[16] taking into account the molecular weight effect. There are at least two possible ways to increase the gel transition temperature: (1) by increasing the molecular weight of PNIPAm end-blocks, (2) by copolymerizing NIPAm monomer with a solvatophobic comonomer, as was reported for some lower critical solution temperature (LCST) polymer–ionic liquid systems.[20]

A key property of the ion gel is its ionic conductivity σ. The σ of neat [EMIM][TFSI] and the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel were measured over the temperature range of 10–90 °C by AC impedance measurements. The results are plotted in Fig. 3 along with the reciprocal of the viscosity (η) of neat [EMIM][TFSI] as measured in our laboratory. The temperature dependence of σ varies very little upon gelation. Over the investigated temperature range, the σ of the ion gel was found to be reduced by only about a factor of two from the pure solvent. At room temperature, σ reaches *ca.* 5 mS cm^{-1}, which is much higher than the ion gel we have reported before,[3] and also higher than the values of conventional polymer electrolytes. The high ionic conductivity of similar ion gels (formed by triblock copolymer self-assembly) has recently been shown to significantly improve the performance of organic thin film transistors.[8]

For both the neat [EMIM][TFSI] and the ion gel, the temperature dependences of σ nearly track the temperature dependence of the inverse η of neat [EMIM][TFSI]. The

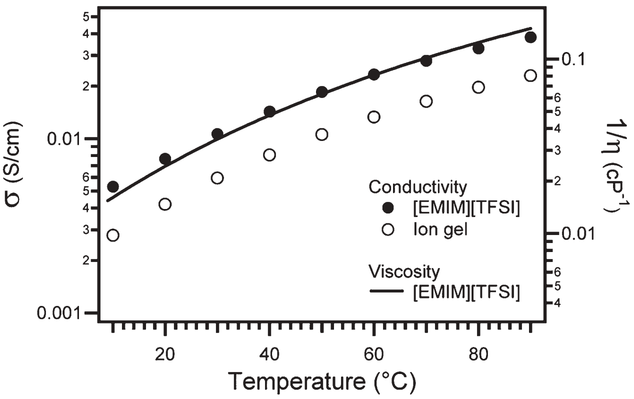

Fig. 3 Temperature dependence of the ionic conductivity for neat [EMIM][TFSI] and the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel. (left axis) The reciprocal of the viscosity of neat [EMIM][TFSI] is plotted *versus* right axis. There is an arbitrary vertical shift between the left and right axes to compare the temperature dependence of the ionic conductivity and the viscosity.

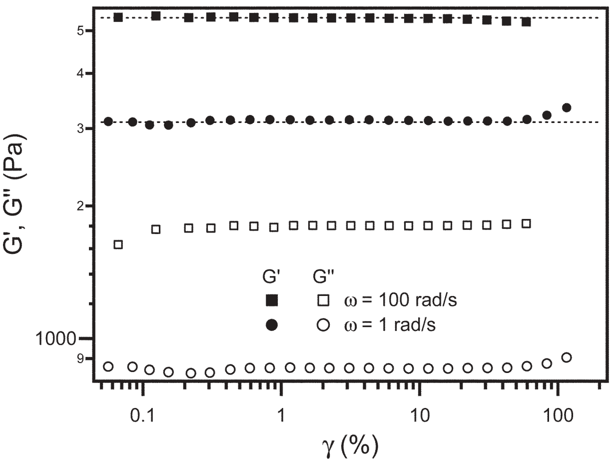

Fig. 4 Dynamic strain sweep of the PNIPAm–PEO–PNIPAm/[EMIM][TFSI] ion gel at two selected frequencies.

proportionality between σ and $1/\eta$ (Walden's rule[21]) has been observed for a number of ionic liquids.[22] Thus, the viscosity is a good indicator of ionic conductivity and provides an easy way to estimate its temperature dependence. The slight mismatch between the temperature dependences of σ and $1/\eta$ is common in many ionic liquids, and is generally attributed to ion pairing or clustering.[14]

We also investigated the rheological response of the ion gel under large strains. Dynamic strain sweep experiments were conducted on the ion gel over a wide range of strains γ (up to the instrument limit). Representative results measured at two frequencies are provided in Fig. 4. The linear viscoelastic regime is defined as the regime below the critical value γ_c where G' remains invariant with respect to strain. This ion gel has a large γ_c value ($> 70\%$), indicating a very strong gel. Even at 100% strain, there is no evidence of break up of the gel microstructure.

In summary, we have designed a new thermoreversible ion gel through the gelation of PNIPAm–PEO–PNIPAm in an ionic liquid, [EMIM][TFSI]. The ion gel is highly conductive and possesses sufficient mechanical strength even under large strains. More importantly, this thermoreversible ion gel offers the advantage of solvent-free processing in practical applications. Possible ways of controlling the gel transition temperature were also discussed.

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Notes and references

1 M. A. Klingshirn, S. K. Spear, R. Subramanian, J. D. Holbrey, J. G. Huddleston and R. D. Rogers, *Chem. Mater.*, 2004, **16**, 3091.
2 M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, **127**, 4976.
3 Y. He, P. G. Boswell, P. Buhlmann and T. P. Lodge, *J. Phys. Chem. B*, 2007, DOI: 10.1021/jp064574n.
4 H. Ohno, M. Yoshizawa and W. Ogihara, *Electrochim. Acta*, 2004, **50**, 255; H. D. Tang, J. B. Tang, S. J. Ding, M. Radosz and Y. Q. Shen, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 1432; S. J. Ding, H. D. Tang, M. Radosz and Y. Q. Shen, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 5794.
5 B. Singh and S. S. Sekhon, *J. Phys. Chem. B*, 2005, **109**, 16539; A. Lewandowski and A. Swiderska, *Solid State Ionics*, 2004, **169**, 21.
6 H. Shobukawa, H. Tokuda, S. Tabata and M. Watanabe, *Electrochim. Acta*, 2004, **50**, 305; J. H. Shin, W. A. Henderson and S. Passerini, *J. Electrochem. Soc.*, 2005, **152**, A978; J. H. Shin, W. A. Henderson and S. Passerini, *Electrochem. Commun.*, 2003, **5**, 1016; A. M. Christie, S. J. Lilley, E. Staunton, Y. G. Andreev and P. G. Bruce, *Nature*, 2005, **433**, 50.
7 P. G. Boswell, E. C. Lugert, J. Rabai, E. A. Amin and P. Buhlmann, *J. Am. Chem. Soc.*, 2005, **127**, 16976.
8 J. Lee, M. J. Panzer, Y. He, T. P. Lodge and C. D. Frisbie, *J. Am. Chem. Soc.*, 2007, **129**, 4532.
9 T. Fukushima, A. Kosaka, Y. Yamamoto, T. Aimiya, S. Notazawa, T. Takigawa, T. Inabe and T. Aida, *Small*, 2006, **2**, 554; D. Z. Zhou, G. M. Spinks, G. G. Wallace, C. Tiyapiboonchaiya, D. R. MacFarlane, M. Forsyth and J. Z. Sun, *Electrochim. Acta*, 2003, **48**, 2355; B. J. Akle, M. D. Bennett and D. J. Leo, *Sens. Actuators, A*, 2006, **126**, 173.
10 Y. Shao, G. C. Bazan and A. J. Heeger, *Adv. Mater.*, 2007, **19**, 365.
11 J. Huang, A. Riisager, P. Wasserscheid and R. Fehrmann, *Chem. Commun.*, 2006, 4027; J. B. Tang, H. D. Tang, W. L. Sun, H. Plancher, M. Radosz and Y. Q. Shen, *Chem. Commun.*, 2005, 3325.
12 S. G. Lee, *Chem. Commun.*, 2006, 1049.
13 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. . Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
14 M. Galinski, A. Lewandowski and I. Stepniak, *Electrochim. Acta*, 2006, **51**, 5567.
15 M. A. Neouze, J. Le Bideau, F. Leroux and A. Vioux, *Chem. Commun.*, 2005, 1082; A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2003, **107**, 4024; R. Kawano and M. Watanabe, *Chem. Commun.*, 2005, 2107; C. Coll, R. H. Labrador, R. M. Manez, J. Soto, F. Sancenon and M. J. Segui, *Chem. Commun.*, 2005, 3033; M. A. B. H. Susan, A. Noda, S. Mitsushima and M. Watanabe, *Chem. Commun.*, 2003, 938.
16 T. Ueki and M. Watanabe, *Chem. Lett.*, 2006, **35**, 964.
17 R. G. Larson, *The Structure and Rheology of Complex Fluids*, Oxford University Press, New York, 1999.
18 H. H. Winter and F. Chambon, *J. Rheol.*, 1986, **30**, 367; F. Chambon, Z. S. Petrovic, W. J. MacKnight and H. H. Winter, *Macromolecules*, 1986, **19**, 2146.
19 Y. He, Z. Li, P. Simone and T. P. Lodge, *J. Am. Chem. Soc.*, 2006, **128**, 2745.
20 T. Ueki and M. Watanabe, *Langmuir*, 2007, **23**, 988; Y. G. Takei, T. Aoki, K. Sanui, N. Ogata, T. Okano and Y. Sakurai, *Bioconjugate Chem.*, 1993, **4**, 341.
21 P. Walden, *Z. Phys. Chem., Abt. A*, 1931, **157**, 389.
22 R. Hagiwara, K. Matsumoto, Y. Nakamori, T. Tsuda, Y. Ito, H. Matsumoto and K. Momota, *J. Electrochem. Soc.*, 2003, **150**, D195; R. Hagiwara and Y. Ito, *J. Fluorine Chem.*, 2000, **105**, 221.