## Transparent, flexible and highly conductive ion gels from ionic liquid compatible cyclic carbonate network<sup>†</sup>

Satyasankar Jana,\* Anbanandam Parthiban and Christina L. L. Chai\*

Received (in Cambridge, UK) 14th October 2009, Accepted 4th December 2009 First published as an Advance Article on the web 6th January 2010 DOI: 10.1039/b921517d

Transparent, flexible, self-standing and highly ion conductive ion gels have been synthesised from novel ionic liquid compatible cyclic carbonate (CC) network polymer. The use of dual functional cyclic carbonate methacrylate (CCMA) monomer for the synthesis has enabled versatile and operationally simple routes to such type of ion gels.

Combination of macromolecules with ionic liquids (ILs) offers new progress, challenges and opportunities in polymer science.<sup>1</sup> ILs are of much interest as green solvents for different kinds of polymerizations<sup>1,2</sup> mainly due to their non-flammable and non-volatile nature and are also used for solubilization of poorly soluble biopolymers.<sup>1</sup> The other unique properties of ILs such as high ionic conductivity, thermal and (electro)chemical stability and wide electrochemical window makes the polymer-IL combination useful as polymer electrolyte for various electrochemical devices.<sup>1,3</sup> One such material that is of interest for lithium batteries,<sup>3,4</sup> membranes,<sup>5</sup> chemical sensors,<sup>6</sup> thin film transistors<sup>7</sup> and solar cells<sup>8</sup> is the IL swelled polymer network, termed as ion gel.9 In general, ion gels are prepared either by physical assembly of (co)polymers $^{3b,7,10}$  or chemical crosslinking of monomers in an IL. Ion gels by the latter method is usually obtained either by the polymerization of vinyl monomers in the presence of a crosslinker<sup>9b,11</sup> or by the polyaddition reaction of (macro)monomers having multifunctional reactive groups.<sup>9a,12</sup> However (co)polymer networks used to synthesize all these types of ion gels reported to date are based on either poly(ethylene oxide) (PEO) or poly(methyl methacrylate) (PMMA) as the primary ionic liquid-solubilizing units.

Here we report the synthesis of ion gels based on a novel ionic liquid compatible side chain cyclic carbonate (CC) network polymer. Due to the dual functional nature of precursor cyclic carbonate methacrylate (CCMA) (Fig. 1), these ion gels were synthesized by both free radical polymerization (route A) and polyaddition reaction (route B) (Fig. 2). Additionally, the cyclic carbonate (CC) group present in these ion gels could potentially act as a coordinating unit for metal ions (*e.g.* Li<sup>+</sup>) as in the case of ethylene and propylene carbonates<sup>13</sup> and hence these ion gels are potential alternatives to these flammable solvents in lithium ion batteries.<sup>3a</sup>



**Fig. 1** Structure of ionic liquids used (a) [BMIM][PF<sub>6</sub>], (b) [EMIM][TFSI] and (c) dual functional cyclic carbonate methacrylate (CCMA) monomer.



Fig. 2 Photograph of transparent, flexible and self-standing disc shaped ion gels (a) IG5 and (b) IG6 after eight months of storage.

The CCMA monomer was synthesized using a N,N'-dicyclohexylcarbodiimide (DCC) mediated coupling reaction of glycerol 1,2-carbonate and methacrylic acid. Poly(cyclic carbonate methacrylate) (PCCMA), synthesised by free radical polymerisation, was only soluble in highly polar solvents like DMF and DMSO and insoluble in most common organic solvents presumably because of the presence of the rigid and highly polar CC pendant groups. Noteworthy is the observation that the linear PCCMA homopolymer is soluble in a wide range of ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF<sub>4</sub>]), 1-butyl-4-methylpyridinium tetrafluoroborate ([BMP][BF4]) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) etc. The ionic liquid [EMIM][TFSI] was synthesized using a modified method of Watanabe et al.9b

The compatibility of PCCMA in [EMIM][TFSI] was confirmed by polymerising CCMA monomer in [EMIM][TFSI] at 80 °C using benzoyl peroxide (BPO) initiator under nitrogen for 16 h. This gave a completely homogeneous and transparent viscous polymerization mixture. Upon addition to DCM, a fine white powder with >98% yield was collected and the resultant polymer was readily soluble in DMF and DMSO.

In contrast, polymerization of CCMA in ILs (*e.g.* [BMIM][PF<sub>6</sub>], [EMIM][TFSI]) in the presence of only 5 mol% of poly(ethylene glycol) dimethacrylate 550 (PEGDMA 550)

Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research (A\*STAR), 1 Pesek Road, Jurong Island, Singapore 627833. E-mail: satyasankar\_jana@ices.a-star.edu.sg, christina\_chai@ ices.a-star.edu.sg; Fax: (+65) 6316 6184; Tel: (+65) 67963918 (SJ), 67963902 (CLLC)

<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Details of monomer, IL, polymer, ion gel synthesis, impedance measurement/ spectra and other characterizations. See DOI: 10.1039/b921517d

Ion gel code	Composition		Electrolyte <sup>d</sup>	Ionic
	$\overline{\operatorname{CCMA}:\operatorname{IL}^b}$	LiTFSI	content (Wt%)	$conductivity^e$ (S cm <sup>-1</sup> )
IG1 <sup>a</sup>	5:5	No	57.1	$7.988 \times 10^{-6}$
$IG2^a$	3:7	No	75.6	$1.717 \times 10^{-4}$
IG3	7:3	No	43.9	$6.967 \times 10^{-6}$
IG4	5:5	No	64.7	$1.833 \times 10^{-4}$
IG5	4:6	No	73.3	$4.780 \times 10^{-4}$
IG6	3:7	No	81.0	$1.131 \times 10^{-3}$
IG7	7:3	Yes <sup>c</sup>	52.8	$1.009 \times 10^{-5}$
IG8	5:5	Yes <sup>c</sup>	68.4	$3.489 \times 10^{-4}$
IG9	4:6	Yes <sup>c</sup>	75.5	$8.996 \times 10^{-4}$
IG10	3:7	Yes <sup>c</sup>	82.2	$3.241 \times 10^{-3}$
<sup><i>a</i></sup> Prepared used; <sup><i>d</i></sup> IL	using [BMIM][F + LiTFSI; <sup>e</sup> Me	PF <sub>6</sub> ]; <sup>b</sup> Mol asured at 2	ar ratio, <sup><i>c</i></sup> 25 m 23 °C.	ol% of CCMA

using BPO initiator under a  $N_2$  atmosphere produced an insoluble, transparent, flexible and self-standing ion gels.

A number of ion gels were prepared with different ratios of CCMA to IL as shown in Table 1. All ion gels were highly transparent, flexible and did not leach IL upon storage (Fig. 2). The presence of absorption bands at 1354 cm<sup>-1</sup> (from [EMIM][TFSI]) and 1800 cm<sup>-1</sup> (CC carbonyl) in the FT-IR spectra of these gels confirms their composition (Fig. 3). The thermal stability of these ion gels increased with the increase in the IL content as is indicated by thermogravimetric analysis (Fig. 4). Unlike the linear homopolymer PCCMA, these ion gels were insoluble in DMF or DMSO due to the network structure prevailing in the latter. IL from these ion gels can be extracted quantitatively by solvent extraction using suitable solvents like acetone and DCM.



Fig. 3 FT-IR spectra of ion gels (a) IG3, (b) IG6 and (c) [EMIM][TFSI].



**Fig. 4** Thermogravimetric analysis of (a) [EMIM][TFSI], ion gels (b) IG6, (c) IG4, (d) IG3 and (e) sample after solvent extraction of IG4.

The first two ion gels prepared using  $[BMIM][PF_6]$  (IG1 and IG2 in Table 1) showed high ionic conductivity in the impedance measurement and the conductivity is directly proportional to the IL content, since conductivity is the result of the mobility of the cations and anions of the IL. Ion gels were also prepared using [EMIM][TFSI] (IG3 to IG10 in Table 1). It should be noted that this IL possess lower viscosity, higher ionic conductivity, higher thermal stability, better hydrophobicity as well as the potential for less toxic gas evolution as compared to the use of [BMIM][PF<sub>6</sub>] as the IL.<sup>14</sup> In this class of ion gels, ionic conductivity also increases with an increase in the ionic liquid composition from IG3 to IG6 (Table 1). The ion conductivity values are comparable to the values for ion gels obtained using other polymeric networks as reported in the literature.<sup>9b,12c</sup> Noteworthy is the observation that ion gel IG6 contains only 19% polymer and has the highest ion conductivity.

Similarly transparent, flexible and self-standing ion gels were prepared by mixing LiTFSI in a ratio of 1:4 to the respective CCMA monomer used (IG7 to IG10 in Table 1) *before* polymerisation. The ionic conductivity of these ion gels were higher than the respective ion gels without the lithium salt (*e.g.* IG10 *vs.* IG6) because of the contribution from the ions of LiTFSI.

In general, the incorporation of IL to the CCMA network not only dramatically improves the ionic conductivity but also introduces flexibility to the CCMA network. Films derived from the homopolymer PCCMA and samples produced after solvent extraction of ion gels based on CCMA network are highly brittle. Incorporation of IL also improves the thermal stability of the polymer as is observed from the TGA curves shown in Fig. 4.

The versatility of the use of cyclic carbonate methacrylate (CCMA) monomer in ion gel design is further demonstrated with the synthesis of ion gels using Route B (Scheme 1) where the reactivity of the CC group towards nucleophiles is exploited<sup>15</sup> (by route B in Scheme 1). For this purpose two PCCMA-*b*-PEG-*b*-PCCMA triblock copolymers with controlled structures were synthesized by ATRP using two low molecular weight difunctional poly(ethylene glycol) (PEG) macroinitiators (M.Wt. 598 and 898 Da, respectively) as reported by us.<sup>16</sup> Gelation of these block copolymers in [EMIM][TFSI] with



Scheme 1 Synthesis of ion gels in two different routes by exploiting the dual functionality of CCMA.

 Table 2
 Details of ion gels synthesized by route B

Ion gel code <sup>a</sup>	Copolymer used <sup>b</sup>	Diamine used <sup>c</sup>	Temp. (°C)	Ionic conductivity <sup><math>d</math></sup> (S cm <sup>-1</sup> )
IG11	P1	XDA	70	$6.249 \times 10^{-4}$
IG12	P2	HMD	RT	$7.734 \times 10^{-4}$
IG13	P2	DETA	RT	$9.288 \times 10^{-4}$
IG14	P2	XDA	70	$5.011 \times 10^{-4}$

<sup>*a*</sup> [EMIM][TFSI] content ~67.5%; <sup>*b*</sup> Copolymer P1: (CCMA)<sub>43</sub>-(EG)<sub>7</sub>-(CCMA)<sub>43</sub>; M<sub>n</sub> 16350 (calculated); Mn 20221 (GPC in DMF), PDI 1.18. copolymer P2: (CCMA)<sub>47</sub>-(EG)<sub>13</sub>-(CCMA)<sub>47</sub>; M<sub>n</sub> 18470 (calculated); M<sub>n</sub> 22460 (GPC in DMF), PDI 1.19; <sup>*c*</sup> 10 mol% relative to CC units of polymer is used; HMD = hexamethylenediamine, DETA = diethylenetriamine and XDA = p-xylylenediamine; <sup>*d*</sup> Measured at 23 °C.

various diamines produced transparent, flexible and self-standing ion gels with high ionic conductivity (Table 2 and see ESI).<sup>†</sup> Hexamethylenediamine (HMD) and diethylenetriamine (DETA) produced ion gels at room temperature whereas p-xylylenediamine (XDA) gave ion gels at 70 °C without the need for reactions under nitrogen. It was also observed that the homopolymer PCCMA can also yield ion gels using this method. This is one of the simplest ways to prepare stable ion gels.

The ionic liquid content of the ion gels synthesized by route B was about 67.5% (Table 2). In general, these ion gels possess higher ionic conductivity than the ion gels synthesized using route A with similar IL content (see IG4 and IG5 in Table 1). The higher ionic conductivity of ion gels synthesized by route B may be due to the higher mobility of ionic species caused by the presence of larger amounts of loosely bound IL in the crosslinked gel. Various other factors which may also contribute to this process *i.e.*: the more flexible nature of ion gels obtained by route B as a result of the ring opening of rigid cyclic carbonate units and the copolymeric nature of the ion gel, the presence of less uniform crosslinking sites, the ordering of IL induced by the physico-chemical interactions between the block copolymer and the IL before crosslinking and so on. Thermal stability of these gels is similar to the ion gels synthesized by route A as is demonstrated by thermogravimetric analysis (see ESI).†

In conclusion, we have synthesized a new class of flexible, self-standing and highly ion conductive ion gels using novel ionic liquid compatible cyclic carbonate network. Since cyclic carbonate network and ionic liquids are highly compatible, the gels formed were completely transparent and stable. Most importantly, the use of the dual functional cyclic carbonate methacrylate monomer for this purpose has enabled the synthesis of ion gels in two different routes. Incorporation of lithium salt to these ion gels dramatically improved the ionic conductivity. Due to this highly compatible nature, ionic liquids may be useful as plasticizer for CCMA based polymers which are otherwise very brittle and CCMA based polymers can be used as support materials for small molecules or catalysts, if required, for other reactions performed in IL.

This work was supported by the Science and Engineering Research council of A\*STAR (Agency for Science, Technology and Research), Singapore. We thank Mr H. Yu and Dr T. Zhiqun for their assistance during ion gel characterization.

## Notes and references

- 1 T. Ueki and M. Watanabe, *Macromolecules*, 2008, **41**, 3739, and references therein.
- 2 (a) N. Winterton, J. Mater. Chem., 2006, 16, 4281 and references therein; (b) B. Ochiai, Y. Satoh and T. Endo, J. Polym. Sci., Part A: Polym. Chem., 2009, 47, 4629.
- 3 (a) A. M. Christie, S. J. Lilley, E. Staunton, Y. G. Andreev and P. G. Bruce, *Nature*, 2005, **433**, 50; (b) Y. He and T. P. Lodge, *Macromolecules*, 2008, **41**, 167.
- 4 (a) J. H. Shin, W. A. Henderson and S. Passerini, *Electrochem. Commun.*, 2003, **5**, 1016; (b) H. Shobukawa, H. Tokuda, S. Tabata and M. Watanabe, *Electrochim. Acta*, 2004, **50**, 305; (c) J. H. Shin, W. A. Henderson and S. Passerini, *J. Electrochem. Soc.*, 2005, **152**, A978.
- 5 (a) J. Huang, A. Riisager, P. Wasserscheid and R. Fehrmann, *Chem. Commun.*, 2006, 4027; (b) J. B. Tang, H. D. Tang, W. L. Sun, H. Plancher, M. Radosz and Y. Q. Shen, *Chem. Commun.*, 2005, 3325.
- 6 P. G. Boswell, E. C. Lugert, J. Rabai, E. A. Amin and P. Buhlmann, J. Am. Chem. Soc., 2005, **127**, 16976.
- 7 (a) J. Lee, M. J. Panzer, Y. He, T. P. Lodge and C. D. Frisbie, J. Am. Chem. Soc., 2007, 129, 4532; (b) J. H. Cho, J. Lee, Y. He, B. Kim, T. P. Lodge and C. D. Frisbie, Adv. Mater., 2008, 20, 686; (c) J. H. Cho, J. Lee, Y. Xia, B. Kim, Y. He, J. M. Renn, T. P. Lodge and C. D. Frisbie, Nat. Mater., 2008, 11, 900.
- 8 (a) M. Watanabe and S. Yanagida, *Chem. Commun.*, 2005, 740;
  (b) R. Kawano and M. Watanabe, *Chem. Commun.*, 2005, 2107;
  (c) R. Kawano, M. K. Nazeeruddin, A. Sato, M. Gratzel and M. Watanabe, *Chem. Commun.*, 2005, 2107.
- 9 (a) M. A. Lligshirm, S. K. Spear, R. Subramanian, J. D. Holbrey, J. G. Huddleston and R. D. Rogers, *Chem. Mater.*, 2004, 16, 3091;
  (b) M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, 127, 4976; (c) K. Hanabusa, H. Fukui, M. Suzuki and H. Shirai, *Langmuir*, 2005, 21, 10383.
- (a) Y. He and T. P. Lodge, *Chem. Commun.*, 2007, 2732; (b) Y. He, P. G. Boswell, P. Buhlmann and T. P. Lodge, *J. Phys. Chem. B*, 2007, **111**, 4645; (c) A. Noro, Y. Matsushita and T. P. Lodge, *Macromolecules*, 2008, **41**, 5839.
   S. Seki, M. A. B. H. Susan, T. Kaneko, A. Noda and
- 11 S. Seki, M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, J. Phys. Chem., 2005, 109, 3886.
- 12 (a) M. A. Neouze, J. L. Bideau, P. Guveau, S. Bellayer and A. Vioux, *Chem. Mater.*, 2006, **18**, 3931; (b) K. Matsumoto and T. Endo, *Macromolecules*, 2008, **41**, 6981; (c) K. Matsumoto and T. Endo, *Macromolecules*, 2008, **42**, 4580.
- 13 (a) J. M. Tarascon and M. Armand, *Nature*, 2001, 414, 359;
  (b) F. B. Dias, L. Plomp and J. B. J. Veldhuis, *J. Power Sources*, 2000, 88, 169;
  (c) J. H. Golden, B. G. M. Chew, D. B. Zax, F. J. DiSalvo, J. M. J. Frechet and J. M. Tarascon, *Macromolecules*, 1995, 28, 3468;
  (d) J. Britz, W. H. Meyer and G. Wegner, *Macromolecules*, 2007, 40, 7558.
- 14 Z. Bai, Y. He and T. P. Lodge, Langmuir, 2008, 24, 5284.
- 15 (a) A. Steblynko, W. Choi, F. Sanda and T. Endo, J. Polym. Sci., Part A: Polym. Chem., 2000, 38, 2375; (b) D. C. Webster, Prog. Org. Coat., 2003, 47, 77.
- 16 S. Jana, H. Yu, A. Parthiban and C. L. L. Chai, manuscript submitted to J. Polym. Sci.: Part A: Polym. Chem.