

Transparent, flexible and highly conductive ion gels from ionic liquid compatible cyclic carbonate network†

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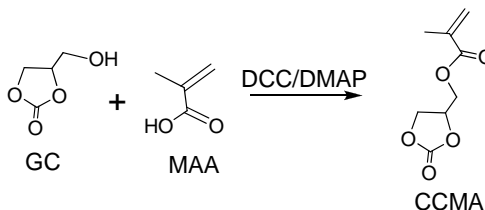
i) Materials

Methacrylic acid (MAA, 99 %), 4-dimethylaminopyridine (DMAP, 99 %), 1-methylimidazole, redistilled (> 99 %) ethylene glycol dimethacrylate (EGDMA), hexamethylenediamine (HMDA, 98 %), and poly(ethylene glycol) dimethacrylate 550 (PEGDMA 550) samples were supplied by Aldrich. CuBr (98 %) was obtained from Acros. Glycerol 1,2-carbonate (GC, >93 %) was supplied by TCI. *N,N'*-dicyclohexylcarbodiimide (DCC, 99+ %), 1-butyl-4-methylpyridinium tetrafluoroborate ([BMP][BF₄], >97%) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄], 98%) were purchased from Fluka. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 98 %), diethylenetriamine (DETA, 99 %), 1-n-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆], 98 %), benzoyl peroxide (97 %) and p-xylylenediamine (XDA, 97 %) were bought from Alfa Aesar. Bromoethane (> 99 %) was bought from Merck. DMF and DCM (HPLC grade) were purified by passing through a solvent purification system (Glass Contour) and used without any further purification.

ii) Instrumentation

¹H NMR and ¹³C NMR spectra were recorded on 400 MHz and 100 MHz Bruker UltraShield AVANCE 400SB spectrometer respectively. Residual solvent peaks were used as internal standard. A Digilab Excalibur Series FTS3000 infra-red spectrometer was used to collect Fourier Transform Infra-red (FT-IR) spectra. Elemental microanalysis was performed using Eurovector E300 elemental analyzer. High resolution mass spectra were recorded on Agilent 6210 TOF/LCMS. Thermogravimetric analysis (TGA) was carried out under N₂ atmosphere at a heating rate of 10 °C/ min using SDT-2960T TA Instruments. The DMF run Size Exclusion Chromatography (SEC) system was equipped with a Viscotek GPCmax Pump module, a Viscotek TDA 302 refractive index detector unit, fitted with TOSOH H_{HR} Guard Column and one TOSOH GMH_{HR}-M mixed bed column (5 μm, ID 7.8 mm × 300 mm). The eluent flow rate was 1.0 mL/min, and the columns were maintained at 60 °C. Impedance spectroscopy of polymer electrolytes was recorded in an Autolab PGSTAT 302 electrochemical test system (Eco Chemie, Netherland). AC signal of 10mv amplitude was applied over the frequency range of 1.5×10⁵ Hz to 1Hz at 23°C.

iii) Synthesis of cyclic carbonate methacrylate (CCMA) monomer

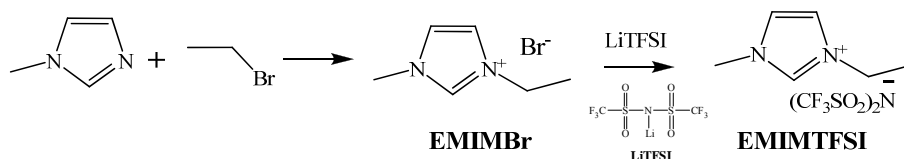


Scheme S1 Synthesis of CCMA monomer.

DCC (12.231 g, 59.28 mmol), glycerol carbonate (GC, 7.0 g, 59.28 mmol) and 4-dimethylaminopyridine (DMAP, 72 mg, 0.593 mmol) were dissolved in dry DCM (75 mL) and the solution was cooled in an ice bath for 30 min. DCM solution (25 mL) of methacrylic acid (MAA, 5.103 g, 59.28 mmol) was added dropwise to the previous solution over a period of 30 min and the stirring was continued for another 30 min on ice bath. The mixture was then brought to room temperature and stirred for further 2½ h. The white precipitated dicyclohexylurea byproduct was filtered off and the clear product solution was concentrated to 75 mL. The reaction mixture solution was washed with water (3 × 75 mL), dried over MgSO₄ and then concentrated to 20 mL in a rotary evaporator to produce a white colored viscous liquid. This was cooled in a freezer for 40 h and then passed through a cotton plug to remove more urea byproduct (because of the highly polar nature of CCMA monomer, the urea byproduct was found to be soluble in the liquid monomer). The product was finally purified by column chromatography using 9:1 ether/ hexane mixture to produce colourless viscous liquid (yield 7.58 g, 67 %). Found C, 51.41; H, 5.62 %; calculated for C₈H₁₀O₅; C, 51.61; H, 5.41 %. Mass m/z found [M+Na]⁺ = 209.04229; Calculated for C₈H₁₀O₅ 209.04204. δ_H(400 MHz; CDCl₃): 1.95 (3H, s, CH₃), 4.33 (2H, m, CH₂), 4.44 (1H, m, CH₂), 4.58 (1H, t, CH₂), 4.98 (1H, m, CH), 5.66 (1H, s, methacrylate CH₂), 6.15 (1H, s, methacrylate CH₂). δ_C(100 MHz; CDCl₃): 18.16, 63.44, 66.07, 73.8, 127.35, 135.12, 154.44, 166.65.

iv) Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)

imide ([EMIM][TFSI])



Scheme S2 Synthesis of [EMIM][TFSI].

The ionic liquid [EMIM][TFSI] was synthesized in two steps by a slightly modified procedure reported by Watanabe et al.¹

Step I (synthesis of EMIMBr): Bromoethane (19.91 g, 1.5 × 0.1218 mol) was added dropwise to a mixture of 1-methylimidazole (10 g, 0.1218 mol) in cyclohexane (50 ml) and stirred at room temperature for 1 h and refluxed at 80 °C for another 23 h. The mixture was cooled to room temperature and two separate layers were obtained. The upper cyclohexane layer was decanted off and the lower layer was concentrated in a rotary evaporator to yield a white solid. The solid was then dissolved in acetonitrile (25 ml) and precipitated from ethyl acetate (150 ml). The solvent was decanted off and the white crystalline product was dried in a vacuum oven at 40 °C overnight. Yield 22.7 g (97.5%). The product was very hygroscopic and was characterized by ¹H and ¹³C NMR spectroscopy. δ_H(400 MHz; CDCl₃): 1.445 (3H, t, CH₃), 3.896 (3H, s, NCH₃), 4.253 (2H, q, NCH₂CH₃), 7.779 and 7.87 (each 1H, s, CH), 9.291 (1H, s, CH). δ_C(100 MHz; CDCl₃): 15.13, 35.69, 44.06, 121.93, 123.5, 136.22.

Step II (synthesis of [EMIM][TFSI]): Aqueous solution (40 ml) EMIMBr (11.64 g, 60.89 mmol) was added slowly to the aqueous solution (50 ml) of LiTFSI (17.48 g, 60.89 mmol) at room temperature and stirred for 20 h. Initially the mixture was cloudy and after a few minutes then a clear ionic liquid layer separated out at the bottom. The top aqueous phase was decanted off and the organic layer was washed with water (4 × 50 ml). The colorless IL was concentrated in a high vacuum rotary evaporator (1.5 h at 65 °C) followed by drying in a vacuum oven at 100 °C for 24 h and another 120 °C for another 24 h. The final product was stored in dry box/ glove box. Yield 21.02 g (88 %). δ_H(400 MHz; CDCl₃): 1.447 (3H, t, CH₃), 3.877 (3H, s, NCH₃),

4.23 (2H, q, NCH₂CH₃), 7.726 and 7.811 (each 1H, s, CH), 9.14 (1H, s, CH). δ_c (100 MHz; CDCl₃): 15.05, 35.65, 44.08, 121.93, 123.54, 136.18. ESI-MS Found [M]⁺ = 111.09144; calculated for EMIM⁺ 111.09167 and [M]⁻ 279.91723; calculated for TFSI⁻ 279.91784.

v) Synthesis of poly (cyclic carbonate methacrylate) (PCCMA) in [EMIM][TFSI]

Cyclic carbonate methacrylate (CCMA, 0.25 g, 1.343 mmol) and benzoyl peroxide (BPO, 6.5 mg, 0.065 mmol, 2 mol % relative to CCMA) were dissolved in [EMIM][TFSI] (1 g) at room temperature and then purged with N₂ for 30 min. The mixture was then heated at 80 °C for 16h under N₂ to produce a highly viscous homogeneous transparent solution. The mixture was then diluted by DMF (~ 4 ml) and the polymer was precipitated from excess DCM (~100 ml). The product was repeatedly washed with acetone and then dried in vacuum oven at 80 °C for 24 h to produce fine white powder (0.245 g, 98 %). The polymer was soluble in DMF, DMSO, [BMIM][PF₆], [EMIM][BF₄], [EMIM][TFSI], [BMP][BF₄] and insoluble in other common organic solvents. The polymer was characterized by ¹HNMR spectroscopy, SEC (DMF) and TGA. Mn (GPC in DMF) 102498, PDI 3.217.

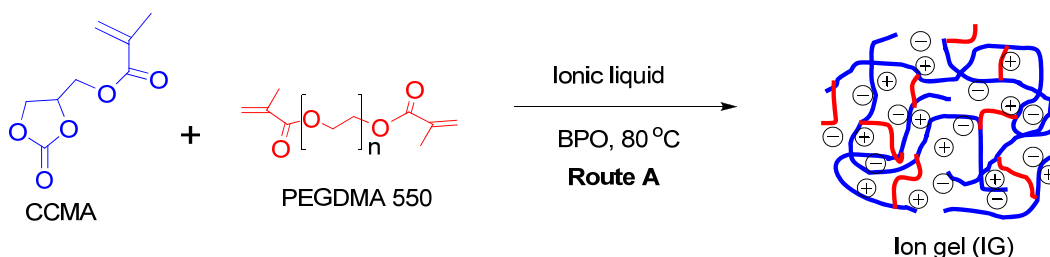
vi) Details of CCMA based triblock copolymer structure

PCCMA-*b*-PEG-*b*-PCCMA triblock copolymers were synthesised by ATRP using dibromo PEG macroinitiators. The experimental details and all characterizations are discussed elsewhere.²

Copolymer **P1**: (CCMA)₄₃-(EG)₇-(CCMA)₄₃; M_n 16350 (calculated); observed Mn 17900 (NMR), 20221(GPC in DMF), PDI 1.18.

Copolymer **P2**: (CCMA)₄₇-(EG)₁₃-(CCMA)₄₇; M_n 18470 (calculated); M_n 20980 (NMR), 22460 (GPC in DMF), PDI 1.19.

vii) Typical preparation of ion gel (IG) based on CCMA network in [EMIM][TFSI] by route A.

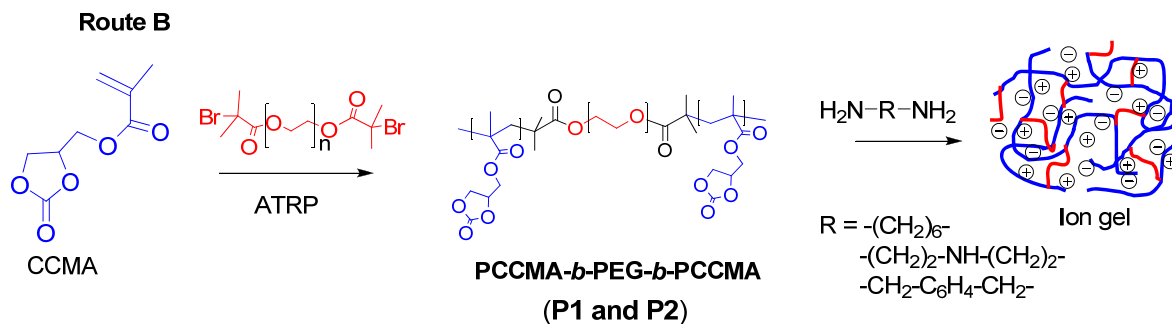


Scheme S3 Preparation of ion gels by route A.

Ion gel, IG6: CCMA (60 mg, 0.3223 mmol), PEGDMA 550 (8.9 mg, 0.01612 mmol, 5 mol% relative to CCMA), initiator BPO (1.72 mg, 0.0709 mmol, 2 mol% of total vinyl content) and ionic liquid [EMIM][TFSI] (294 mg, 0.752 mmol) were mixed and stirred for an hour at room temperature under N_2 to ensure a homogenous solution. The mixture was then injected (0.07 ml) by syringe to a glass or teflon mould with circular cut Teflon spacer (12 mm diameter and ~ 0.5 mm thick) and then heated at $80\text{ }^\circ\text{C}$ for 24 h in an oven under N_2 atmosphere. The sample was cooled to room temperature and a clear self standing disc shaped gel sample was peeled off from the mould. It was observed that clarity of the ion gel produced in glass mould (with Teflon spacer) is better than that produced using a teflon mould (with Teflon spacer). Usually ion gels produced using teflon mould were used for impedance measurement. Thickness of the ion gel film was measured after impedance measurement using micrometer.

Ion gel, IG10: This sample was prepared by the procedure similar to **IG6** but with the addition of LiTFSI (23.1 mg, 0.0857 mmol; 25 mol % relative to CCMA) before polymerisation.

**viii) Typical preparation of ion gel (IG) based on CCMA network in [EMIM][TFSI]
route B**



Scheme S4 Preparation of ion gels by route B.

At first a stock solution of p-xylylenediamine (XDA, 50 mg) in 100 mg of [EMIM][TFSI] was prepared by mixing at ~ 50 °C. Then copolymer P1 ((CCMA)₄₃-(EG)₇-(CCMA)₄₃; 60 mg, 0.3223 mmol w.r.t. CCMA unit) was dissolved in 0.1 ml DMF and mixed with [EMIM][TFSI] (125 mg). DMF was removed in high vacuum oven at 70-80 °C for > 4h (checked by weight difference) to produce transparent and viscous solution. Then the stock solution of p-xylylenediamine (13 mg, XDA content 4.3 mg, 0.03223 mmol; ~ 10 % w.r.t. CCMA unit content in polymer) was carefully added to the polymer solution and mixed well. The viscous mixture was then transferred to the teflon mould as described before. The sample was then cured at 70 °C for 24 h (It was observed that while curing this mixture at RT, gel was formed but did not produce a self-standing film). A transparent flexible disc was collected from the mould after cooling to room temperature. Usual polymer content of these gels was ~ 32.47 %. Thickness of the film was measured after impedance measurement using micrometer.

Ion gels using hexamethylenediamine (HMDA) or diethylenetriamine (DETA) were prepared in same manner but cured at room temperature.

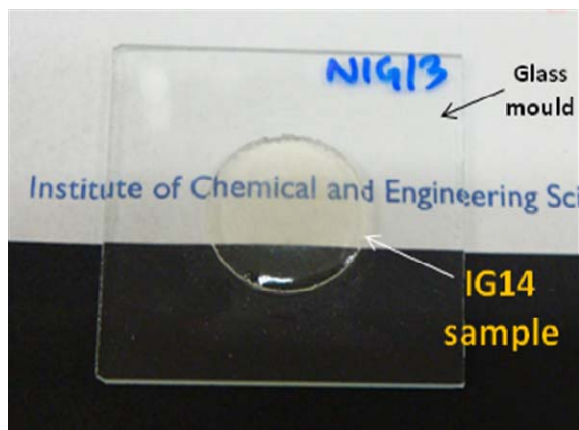


Fig. S1 Photograph of ion gel sample IG14 prepared by route B.

ix) Thermogravimetric analysis results of ion gels produced by route A and B

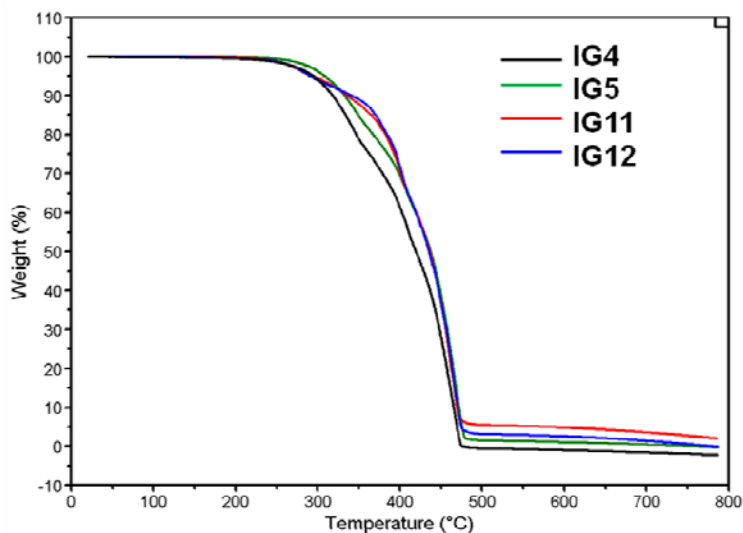


Fig. S2 TGA overlay of different ion gels (IG4 and IG5 were synthesized by route A and IG11 and IG12 were synthesized by route B).

ix) Measurement of ionic conductivity of ion gels by impedance spectroscopy

Ion gel discs were placed in between two mirror finished steel electrodes (12 mm diameter) covered with Teflon casing to measure ionic conductivity. The impedance spectra of all samples were recorded at 23 °C and the resistance for each sample was obtained by extrapolating the linear plot (for highly conductive and low polymer content samples) or by fitting circle to the kinetic control part of the plot (for low conductive and high polymer content samples, for IG1, IG3 and IG7). In general, impedance spectra followed the Nyquist plot for Warburg impedance (for highly conductive and low polymer content samples) or the Nyquist diagram for mixed circuit (for lower conductive and high polymer content samples). The actual resistance of each sample was the real part of the resistance (Z') where the imaginary part of resistance (Z'') is assumed to be zero.

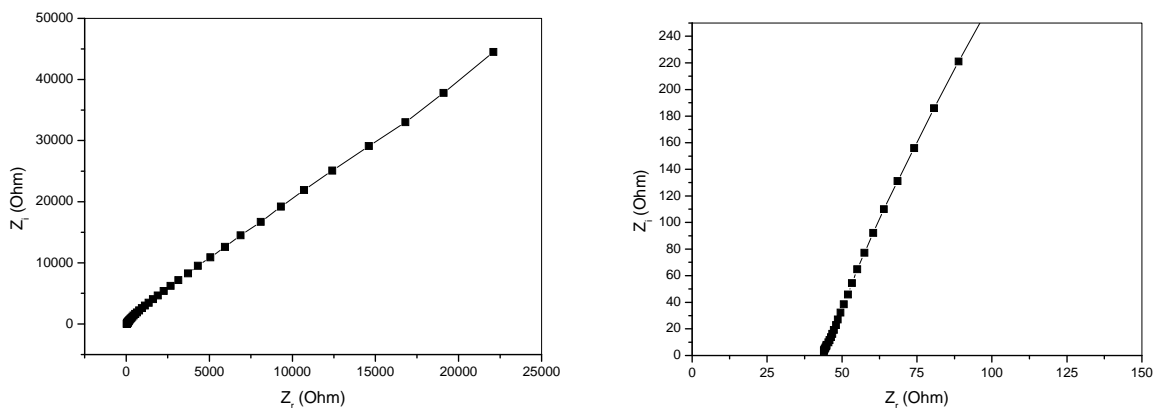


Fig. S3 Impedance spectrum of IG6.

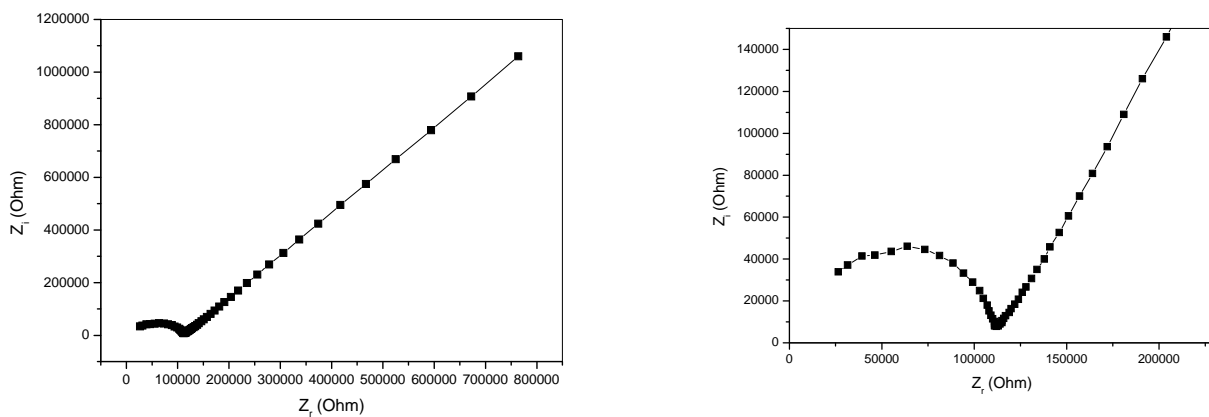


Fig. S4 Impedance spectrum of IG3.

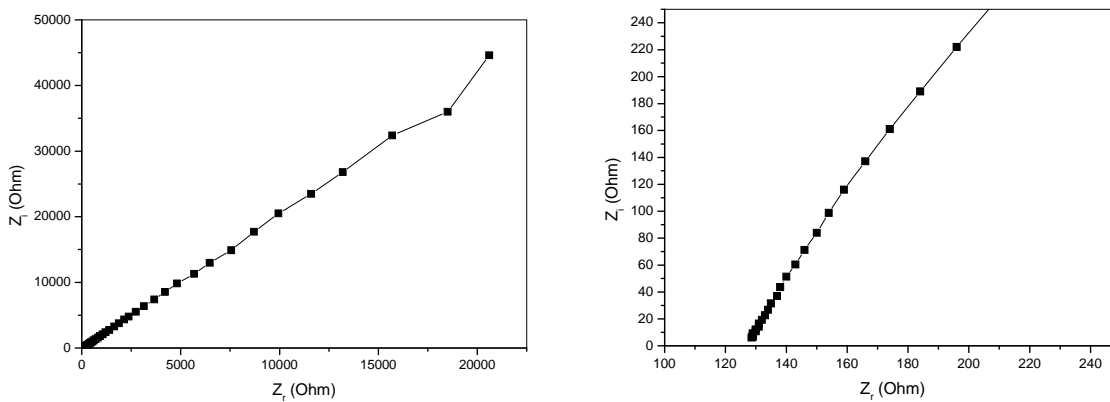


Fig. S5 Impedance spectrum of IG14.

xi) References

- 1) M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, **127**, 4976.
- 2) S. Jana, H. Yu, A. Parthiban and C. L. L. Chai, manuscript submitted to *J. Polym. Sci.: Part A: Polym. Chem.*