

Supporting information

Solvent and catalyst free vitrimeric poly(ionic liquid) electrolyte

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Materials and methods

3-Chloropropan-1-ol 98 %, triethylamine ≥ 99 %, N-methyl pyrrolidine 96 %, sodium hydride 60% in dispersion in mineral oil, tri(ethylene glycol) 99 %, 2,2'-Azobis(2-methylpropionitrile) (AIBN) and 4-vinylbenzyl chloride 90% were purchased for Sigma Aldrich. Acryloyl chloride 96 % was provided by ABCR. Lithium bis(trifluoromethanesulfonyl)imide 99 % was obtained from IOLITEC GmbH. All other chemicals were used without further purification unless otherwise stated. Prior to polymerization (AIBN) was recrystallized in methanol. DCM and THF were dried prior to use for synthesis.

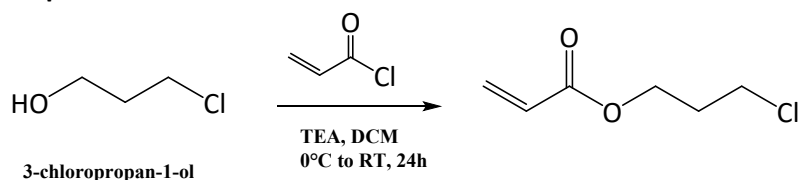
^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using Varian VnmrS 400 MHz NMR spectrometer. Deuterated chloroform and deuterated dimethyl sulfoxide were used as solvents. Chemical shifts (δ) were given in parts per million (ppm) and coupling constants in hertz. MestReNova was used for spectra interpretations.

Size exclusion chromatography (SEC) measurements were performed on a Viscotek GPCmax VE 2001 equipped with CLM3008 and GMHHRN18055 columns. 10 mM LiTFSI in DMF was used as a solvent and poly(styrene) (PS) was used as calibration standard.

The wide-angle X-ray diffraction (WAXD) measurements were performed in transmission mode using a SAXSLAB laboratory setup (Retro-F) equipped with an AXO microfocus X-ray source and an AXO multilayer X-ray optic (ASTIX) as monochromator for Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). A DECTRIS PILATUS3 R 300K detector was used to record the 2D scattering patterns. The 2D WAXD pattern were integrated via SAXSGUI in order to obtain 1D WAXD pattern. The sample to detector distance was about 10 cm. A twin pinhole system was used for the measurements with an aperture size of about 0.9 mm and 0.4 mm. The polymer film was placed on a Linkam stage and fixed with double sided adhesive tape. The measurement was performed under vacuum at a temperature of 21 °C with a measurement time of 5 min.

S1. Synthesis of N-[(2-acryloyloxy)propyl]-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (M1)

Step 1



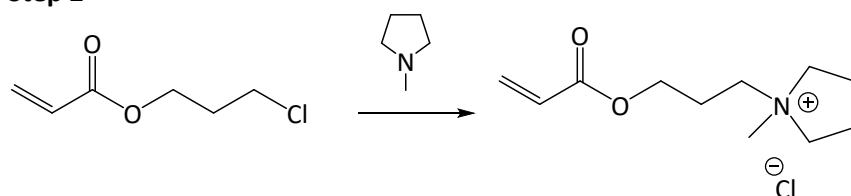
A two-neck flask was equipped with a septum and a magnetic stirring bar. To the solution of 3-chloropropanol (3.1 g, 33 mmol) and triethylamine (5.20 mL, 37 mmol) in DCM (50 mL) acryloyl chloride (3.17 g, 35 mmol) was slowly added while stirring. The reaction mixture was cooled in an ice bath. After addition, the reaction mixture was allowed to warm up to room temperature and kept for

stirring for 16 hours. Reaction mixture was poured into saturated NaHCO_3 solution (25 mL). The organic layer was collected and washed three times with water (3×15 mL) and dried over anhydrous Na_2SO_4 and filtered. Subsequently, the solvent was removed under vacuum. Purification of the product was done by column chromatography (hexane/ethyl acetate ratio 9/1, $R_f = 0.45$). Yield 78%.

^1H NMR (400 MHz, CDCl_3 -*d*) δ 6.40 (dd, $J = 17.3, 1.4$ Hz, 1H), 6.11 (dd, $J = 17.3, 10.4$ Hz, 1H), 5.83 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.30 (t, $J = 6.1$ Hz, 2H), 3.62 (t, $J = 6.4$ Hz, 2H), 2.19 – 2.08 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.95, 130.94, 128.17, 61.20, 41.13, 31.59.

Step 2

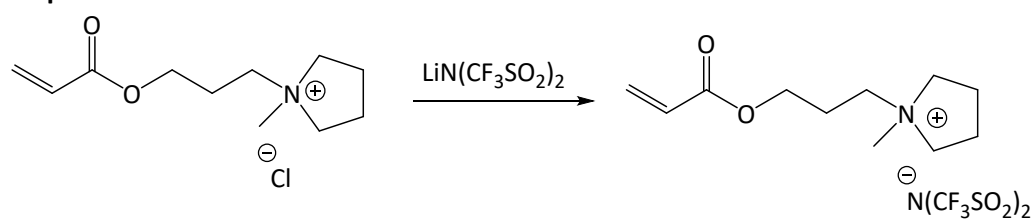


3-chloropropyl acetate (5.2 g, 28 mmol) and N-methyl pyrrolidine (2.42 g, 28 mmol) in MeCN (80 mL) was refluxed overnight at 80 °C in a one neck flask equipped with a reflux condenser and a magnetic stirring bar. The solvent was removed under vacuum at 35 °C. After removing the solvent, the crude product was dissolved in water and washed three times using DCM. After evaporating water, the product was obtained as viscous oil. Yield 85%.

^1H NMR (400 MHz, DMSO-*d*₆) δ 6.36 (dd, $J = 17.3, 1.5$ Hz, 1H), 6.16 (dd, $J = 17.3, 10.4$ Hz, 1H), 5.97 (dd, $J = 10.4, 1.5$ Hz, 1H), 4.16 (t, $J = 6.2$ Hz, 2H), 3.61 – 3.38 (m, 6H), 3.01 (s, 3H), 2.16 – 2.02 (m, 6H).

^{13}C NMR (100 MHz, DMSO-*d*₆): δ 165.78, 132.43, 128.49, 63.99, 61.79, 60.62, 47.98, 23.34, 21.51.

Step 3



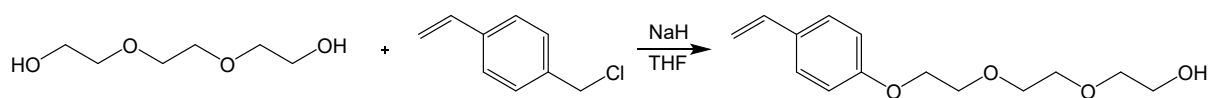
N-[(2-acryloyloxy)propyl]-N-methyl pyrrolidinium chloride (5.0 g, 21 mmol) was dissolved in 50 mL of water and the solution of lithium bis(trifluoromethanesulfonyl)imide (10.3 g, 36 mmol) in 50 mL water was added. The mixture was kept for stirring at room temperature overnight. The product was extracted using DCM (3×50 mL). The organic phase was washed with water and dried over anhydrous Na_2SO_4 . The solvent was removed under the vacuum and colorless (slightly yellowish) viscous oil was obtained as a final product. Yield 78%.

^1H NMR (400 MHz, DMSO-*d*₆): δ 6.36 (dd, $J = 17.3, 1.5$ Hz, 1H), 6.16 (dd, $J = 17.3, 10.4$ Hz, 1H), 5.97 (dd, $J = 10.4, 1.5$ Hz, 1H), 4.17 (t, $J = 6.2$ Hz, 2H), 3.56 – 3.39 (m, 6H), 2.99 (s, 3H), 2.19 – 2.04 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.75, 132.33, 128.48, 125.51 – 114.58 (m), 64.04, 61.73, 60.78, 47.96, 23.30, 21.51.

^{19}F NMR (400 MHz, DMSO-d_6) δ -78.74.

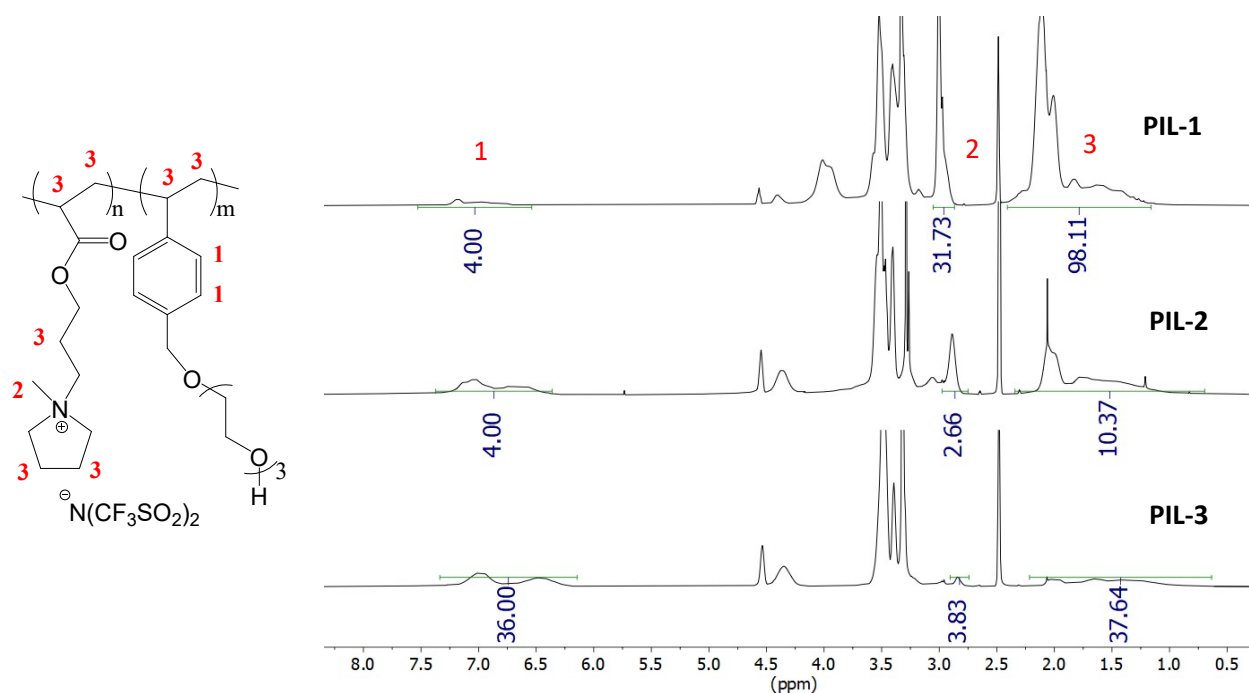
S2. Synthesis of triethyleneglycol-mono-4-vinylbenzylether (M2)



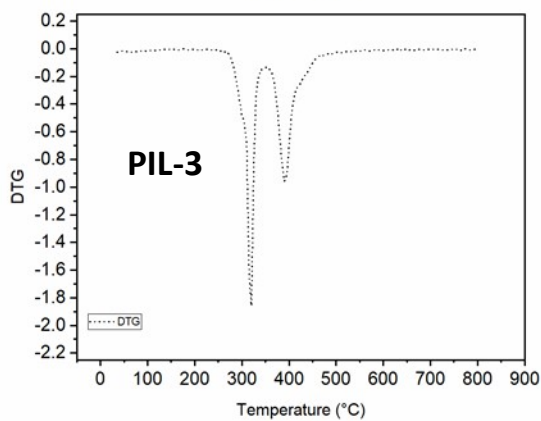
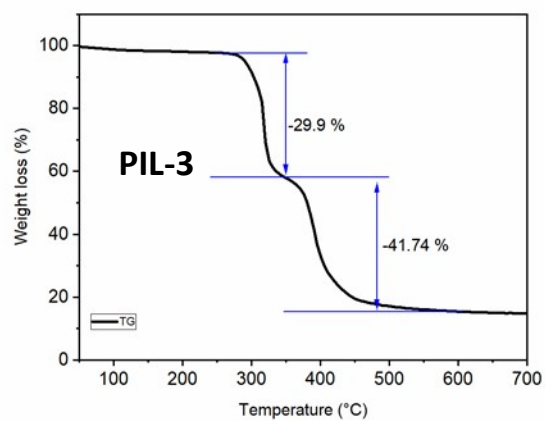
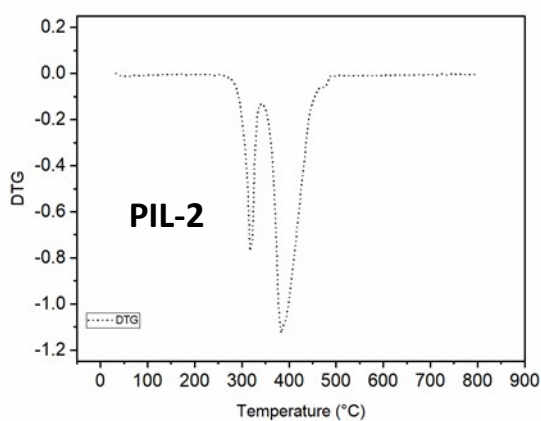
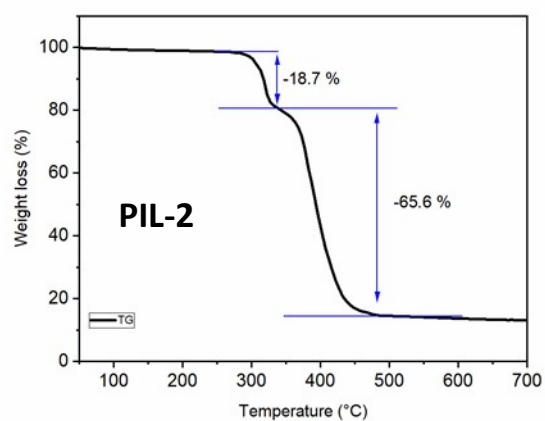
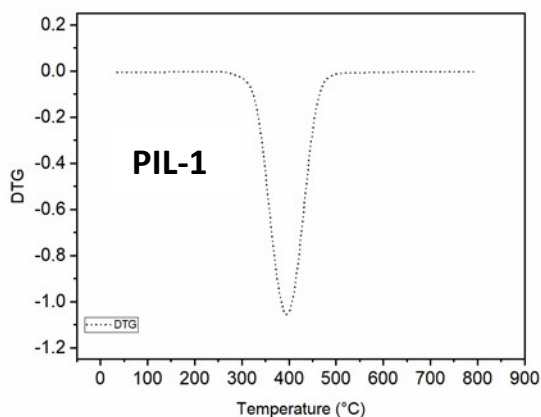
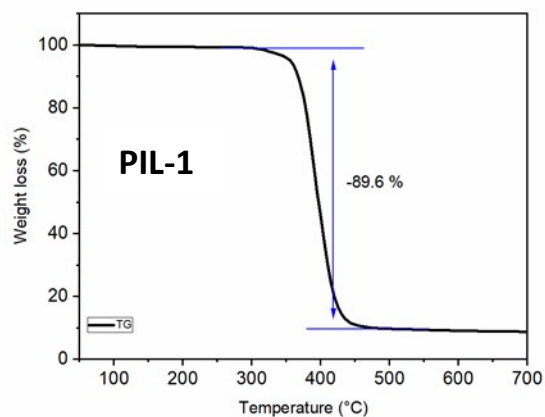
To the mixture of dry THF (30 mL) and NaH (1.67 g, 0.042 mol), tri(ethylene glycol) (15 g, 0.1 mol) was gradually added under cooling with an ice bath. The reaction mixture was stirred for one hour, followed by the dropwise addition of 4-vinylbenzyl chloride (3 g, 0.02 mol). Finally, the mixture was refluxed at 65 °C for 6 hours under N_2 atmosphere. The reaction was quenched with water, followed by the removal of THF by a rotovapor. The crude product was extracted by chloroform. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed by a rotovapor. The product was purified by silica gel column chromatography with ethyl acetate as an eluent ($R_f=0.37$), giving a light-yellow liquid (3.5 g, yield 70%).

^1H NMR (400 MHz, CDCl_3) δ 7.42 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 6.70 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.73 (dd, $J = 17.6, 0.9$ Hz, 1H), 5.23 (dd, $J = 10.9, 0.9$ Hz, 1H), 4.55 (s, 2H), 3.76 – 3.57 (m, 12H), 2.53 (t, $J = 6.1$ Hz, 1H).

S3. Proton NMR of PIL-1, PIL-2 and PIL-3



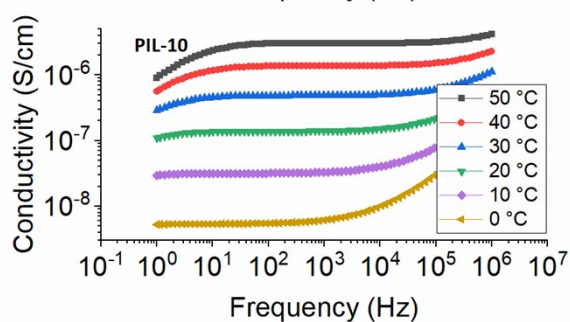
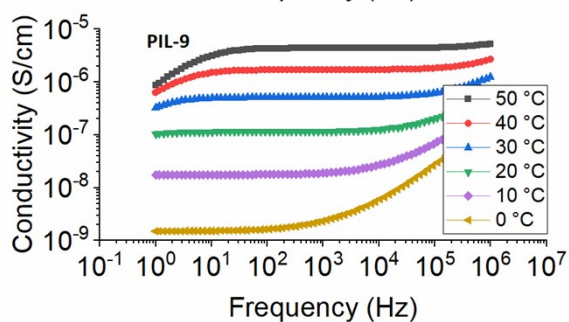
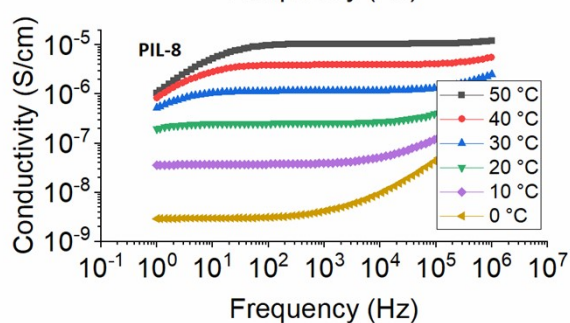
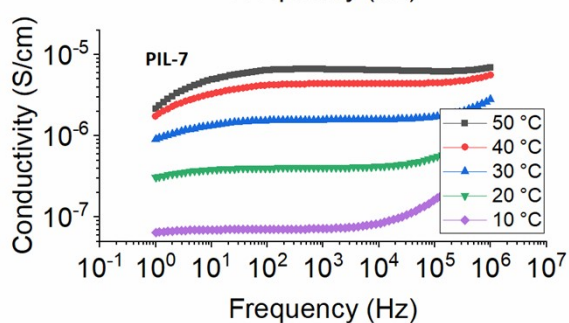
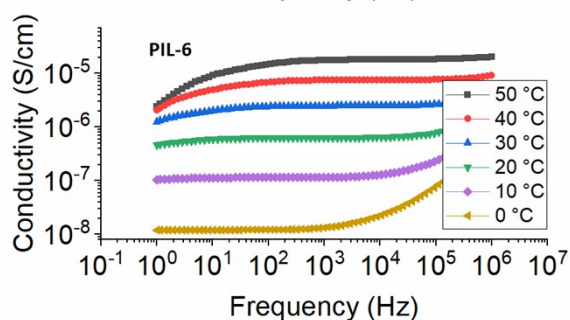
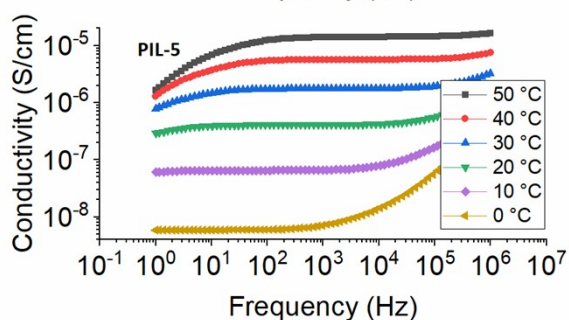
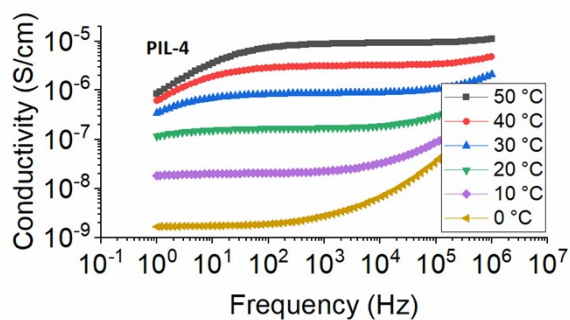
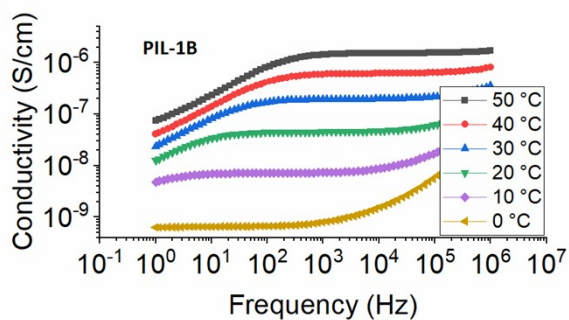
S4. TGA of PIL-1, PIL-2 and PIL-3



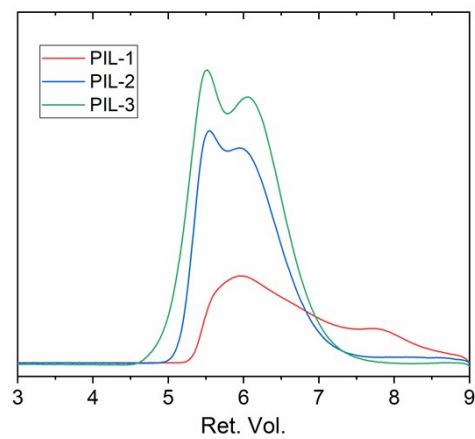
S5. Vitrimeric PIL compositions

Sample	PIL-1B	PIL-4	PIL-5	PIL-6	PIL-7	PIL-8	PIL-9	PIL-10
LiTFSI/EO	0	0.1	0.2	0.3	0.4	0.5	1	2
Boric acid (mmol)	0.11	0.11	0.11	0.11	0.11	0.11	0.11	0.11
Boric acid (mg)	6.78	6.78	6.78	6.78	6.78	6.78	6.78	6.78
LiTFSI (mmol)	0.00	0.10	0.20	0.30	0.39	0.49	0.99	1.97
LiTFSI (mg)	0.00	28	57	85	113	141	283	565

S6. BDS measurements of PILs



S7. SEC curves of PIL-1, PIL-2 and PIL-3



S8. Wide angle X-ray diffraction (WAXD) of PIL-1B, PIL-4 and PIL-9

