Electronic Supplementary Information

LCST-type liquid-liquid phase separation behaviour of poly(ethylene oxide) derivatives in an ionic liquid

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Experimental details

Synthesis of PEGE. All reagents were used as received unless otherwise noted. Butoxyethanol and ethyl glycidyl ether were dried over CaH_2 and distilled before use. Potassium naphthalene solution was prepared by a reaction of naphthalene and potassium metal in dry dimethoxyethane under N_2 atmosphere. All the PEGE polymers were synthesized by ring-opening anionic polymerization. Butoxyethanol (5 mmol) and potassium naphthalene (5 mmol) were reacted in dry tetrahydrofuran (100 mL) under N_2 atmosphere and stirred for 15 min. Ethyl glycidyl ether (395 mmol) was added and the mixture was heated at 60 °C overnight. The reaction was quenched by adding 2 M HCl aqueous solution followed by filtration of the precipitated salt. The filtrate was concentrated *in vacuo* and the residue was dissolved in methanol and stirred with ion-exchange resins (Amberlite BM-3) for 24 h. After removing the resins by filtration, the filtrate was evaporated and the residue was mixed with *n*-

hexane (50 v/v%). The solution was cooled in a freezer (ca. –20 °C) to yield a liquid-liquid biphasic solution. The upper phase (*n*-hexane rich phase) was removed and replaced by fresh hexane. This operation was repeated at least three times. The lower phase was concentrated and dried *in vacuo* at 80 °C for 48 h to afford PEGE as a colorless liquid. Yield ~50%.

Synthesis of 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ([C_2mim][NTf_2]). Distilled 1-methylimidazole (79.5 mL, 1.0 mol) was added dropwise to the solution of ethyl bromide (89.6 mL, 1.2 mol) in cyclohexane (100 mL), followed by stirring overnight at room temperature. The resulting precipitates were filtered and recrystallized three times from 2-propanol/ethyl acetate to give 1-ethyl-3-methylimidazolium bromide (146 g, 77%) as a white crystal.

To the aqueous solution of 1-ethyl-3-methylimidazolium bromide (124 g, 0.654 mol), lithium bis(trifluoromethane sulfonyl)amide (208 g, 0.72mol) was added and stirred at room temperature to give a phase-separated solution. The lower phase was separated, diluted with CH_2Cl_2 and thoroughly washed with water until white precipitate was not observed when aqueous phase was mixed with $AgNO_3$ solution. The organic phase was dried over anhydrous $MgSO_4$ and dried under vacuum at 80°C to provide 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide (218 g, 85%) as a colorless liquid.

^{1}H NMR（DMSO-d_6, δ/ppm relative to TMS）: 9.10 (s, 1H), 7.77 (t, 1H, J = 1.4 Hz), 7.68 (t, 1H, J = 1.4 Hz), 4.19 (q, 2H, J = 8.1 Hz), 3.84 (s, 3H), 1.42 (t, 3H, J = 5.4 Hz)

Synthesis of 1-propyl-2,3-dimethylimidazolium bis(trifluoromethane sulfonyl)amide ([C_3dmim][NTf_2]).

1-propyl-2,3-dimethylimidazolium bis(trifluoromethane sulfonyl)amide was prepared in a similar manner to [C_2mim][NTf_2] using 1,2-dimethylimidazole and 1-bromopropane as starting materials.

^{1}H NMR（$CDCl_3$, δ/ppm relative to TMS）: 7.19 (dd, 2H, J = 6.8 and 2.0 Hz), 3.98 (t, 2H, J = 7.3 Hz), 3.73 (s, 3H), 2.54 (s, 3H), 1.91-1.72 (m, 2H), 0.92 (t, 3H, J = 7.4 Hz)