1. Supplementary

1.1. Diblock (DB) Synthesis – Polymer A

Polystyrene-macroRAFT was synthesized using thermal initiation in refluxing toluene to a monomer conversion of 50% (15 hrs - 120 °C). The resultant macro-RAFT agent was then precipitated out in Methanol (MeOH) and dried under vacuum (12 hrs - 50 °C). Chain extension was carried out using 2-bromoethylacrylate, to a monomer conversion of 40%, in toluene using Vazo 88 as a radical initiator (6 hrs). The resulting block copolymer was precipitated and washed with MeOH and dried under vacuum (12 hrs - 50 °C). Quaternization is carried out between 1-butylimidazole (3 mol equivalents) and the polybromoethylacrylate block in DMF (24 hrs - 80°C) before anion substitution of the bromide ion through addition of LiTFSI (3 mol equivalents) forming the final product and LiBr (24 hrs - 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ (ppm): 9.18–8.97 (s, 1H, N=C**H**-N), 7.76–7.51 (d, 2H, N–C**H**–C**H**–N), 7.28–6.24 (m, 5H, $C_6\mathbf{H_5}$), 4.50–4.06 (s, 6H, O-C$\mathbf{H_2}$-C$\mathbf{H_2}$-N=CH-N-C$\mathbf{H_2}$), 2.26–2.00 (m, 2H, N-CH_2-C$\mathbf{H_2}$-CH_2-CH_3) 1.93–1.64 (m, 1H, CH_2-C**H**), 1.61–1.17 (m, 2H, C$\mathbf{H_2}$-CH), 0.95–0.81 (m, 5H, N-CH_2-CH_2-C$\mathbf{H_2}$-C$\mathbf{H_3}$)

1.2. Optimised Quasi-block (QB) Synthesis – Polymer B

Initial Polystyrene-macroRAFT synthesis was carried using thermal initiation in refluxing toluene to a monomer conversion of 90% (48 hrs – 120 °C). The reagents were left in-situ before chain extension with 2-bromoethylacrylate in toluene using 427 nm light to initiate polymerization (Kessil LED lamps – 9 h – 70 °C). Final conversion of each monomer for styrene and 2-bromoethylacrylate was 100% and 75% respectively. The resulting block copolymer was precipitated and washed with MeOH and dried under vacuum (12 hrs – 50 °C). Quaternization is carried out between 1-butylimidazole (3 equivalents) and the polybromoethylacrylate block in DMF (24 h – 80 °C) before anion substitution of the bromide ion through addition of LiTFSI (3 mol equivalents) forming the final product and LiBr (24 hrs – 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ (ppm): 9.15–8.89 (s, 1H, N=CH-N), 7.73–7.56 (d, 2H, N-C**H**-C**H**-N), 7.28–6.23 (m, 5H, $C_6\mathbf{H_5}$), 4.45–3.98 (s, 6H, O-C$\mathbf{H_2}$-C$\mathbf{H_2}$-N=CH-N-C$\mathbf{H_2}$), 2.07–1.96 (m, 2H, N–CH_2–C$\mathbf{H_2}$–CH_2–CH_3) 1.86–1.63 (m, 1H, CH_2-C**H**), 1.61–1.15 (m, 2H, C$\mathbf{H_2}$-CH), 0.94–0.80 (m, 5H, N–CH_2–CH_2–C$\mathbf{H_2}$–C$\mathbf{H_3}$).

1.3. Optimised Reverse-order Quasi-block 1 (RQB1) Synthesis – Polymer C

Initial Polybromoethylacrylate-macroRAFT synthesis was carried in toluene using 427 nm light initiation to a monomer conversion of 90% (3 hrs – 70 °C). The reagents were left in-situ before chain extension with styrene in toluene using thermal initiation (72 hrs – 120 °C). Final conversion of each monomer for styrene and 2-bromoethylacrylate was 85% and 100% respectively. The resulting block copolymer was precipitated and washed with MeOH and dried under vacuum (12 hrs – 50 °C). Quaternization is carried out between 1-butylimidazole

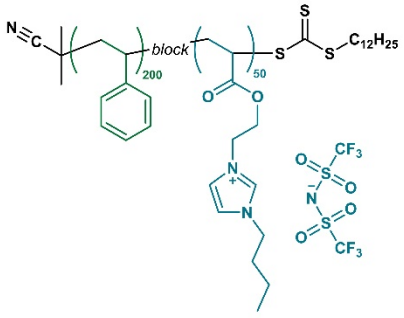
(3 mol equivalents) and the polybromoethylacrylate block in DMF (24 hrs – 80 °C) before anion substitution of the bromide ion through addition of LiTFSI (3 equivalents) forming the final product and LiBr (24 hrs – 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ (ppm): 8.97–8.82 (s, 1H, N=C**H**-N), 7.59–7.40 (d, 2H, N–C**H**–C**H**–N), 7.17–6.16 (m, 5H, C_6**H$_5$**), 4.49–4.01 (s, 6H, O–C**H$_2$**–C**H$_2$**–N=CH–N–C**H$_2$**), 2.07–1.96 (m, 2H, N–CH_2–C**H$_2$**–CH_2–CH_3) 1.92–1.61 (m, 1H, CH_2–C**H**), 1.61–1.10 (m, 2H, C**H$_2$**–CH), 0.92–0.76 (m, 5H, N–CH_2–CH_2–C**H$_2$**–C**H$_3$**).

1.4. Optimised Reverse-order Quasi-block 2 (RQB2) Synthesis – Polymer D

Polybromoethylacrylate-macroRAFT synthesis was carried as in section 3.5.1.3 but to a monomer conversion of 99% (4 hrs – 70 °C). The reagents were left in-situ before chain extension with styrene in toluene using thermal initiation (57 hrs – 120 °C). Final conversion of each monomer for styrene and 2-bromoethylacrylate was 75% and 100% respectively. The resulting block copolymer was precipitated and washed with MeOH and dried under vacuum (12 hrs – 50 °C). Quaternization is carried out between 1-butylimidazole (3 mol equivalents) and the polybromoethylacrylate block in DMF (24 h – 80 °C) before anion substitution of the bromide ion through addition of LiTFSI (3 mol equivalents) forming the final product and LiBr (24 hrs – 80 °C). ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ (ppm): ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ (ppm): 9.19–8.95 (s, 1H, N=C**H**-N), 7.74–7.49 (d, 2H, N–C**H**–C**H**–N), 7.22–6.20 (m, 5H, C_6**H$_5$**), 4.48–4.06 (s, 6H, O-C**H$_2$**-CH2-N=CH-N-C**H$_2$**), 2.08–1.99 (m, 2H, N–CH_2–C**H$_2$**–CH_2–CH_3) 1.87–1.64 (m, 1H, CH_2–C**H**), 1.64–1.14 (m, 2H, C**H$_2$**–CH), 0.94–0.78 (m, 5H, N–CH_2–CH_2–C**H$_2$**–C**H$_3$**).

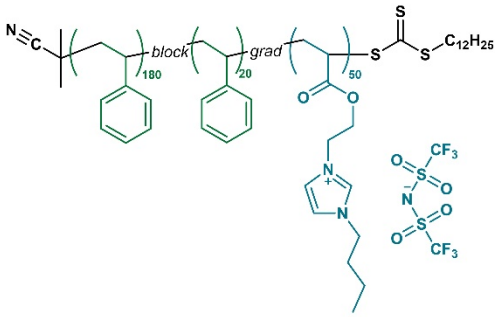
PS(200)-b-PEA(BuIm)TFSI(50)

DB 200:50 (A)



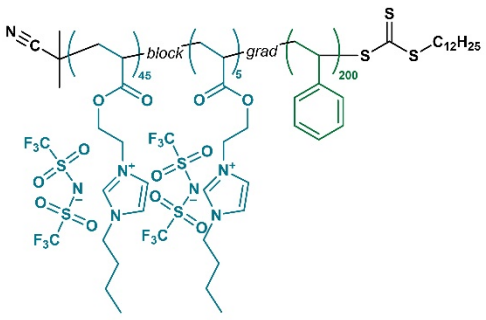
PS(180)-qb-PS/PEA(BuIm)TFSI(20/50)

QB 200:50 (B)



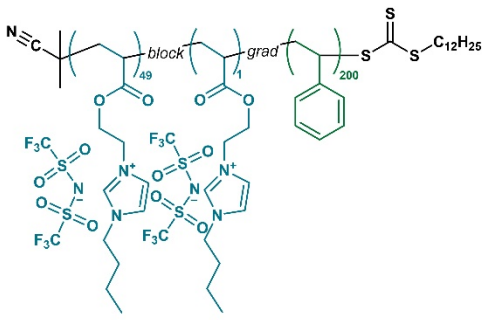
PEA(BuIm)TFSI(45)-qb-PEA(BuIm)TFSI/PS(5/200)

RQB1 50:200 1.0 (C)



PEaBImTFSI(49)-qb-PEA(BuIm)TFSI/PS(1/200)

RQB2 50:200 2.0 (D)



SI Figure 1 *Chemical structure of each of the block (A) and quasi-block (B-D) copolymers used to produce electrolyte materials. Initial degree of polymerization of each block highlighted first followed by a gradient notation to demonstrate the quasi-block nature of the secondary block.*