Supporting Information for Polycation Radius of Gyration in a Polymeric Ionic Liquid (PIL): The PIL Melt is not a Theta Solvent

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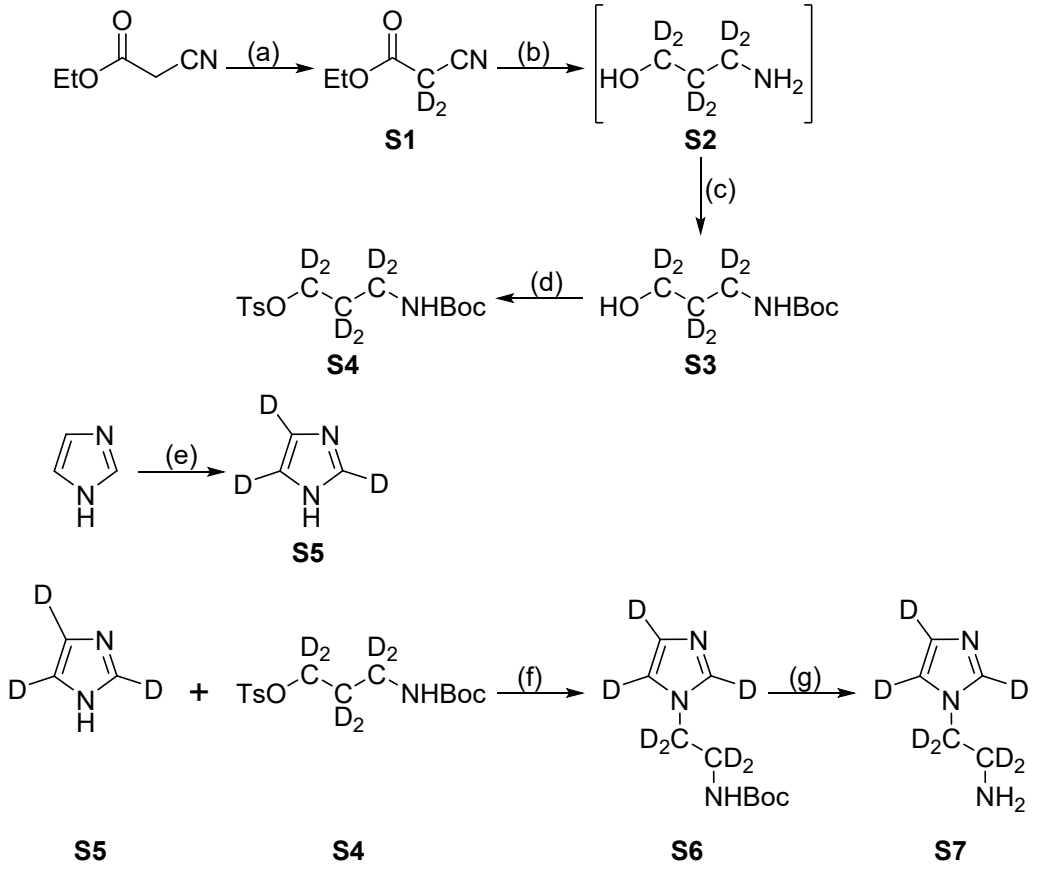
Synthesis of 1-(3-aminopropyl)imidazole-d_9



Scheme S1. Synthesis of 1-(3-aminopropyl)imidazole-d_9. Reagents and Conditions: (a) D_2O, EtOD, reflux, 1 h, quant.; (b) $LiAlD_4$, diethyl ether, 0 °C-rt, 2 h; (c) $(Boc)_2O$, Et_3N, MeOH, rt, 16 h, 51% over 2 steps; (d) TsCl, Et_3N, DMAP, CH_2Cl_2, rt, 16 h, 55%; (e) D_2O, 250 °C, 3 days, 72%; (f) NaH, DMF, 0 °C-rt, 16 h, 90%; (g) TFA, CH_2Cl_2, 0 °C-rt, 4h, quant.

Ethyl cyanoacetate-d_2 (**S1**)

Ethyl cyanoacetate (20 g, 0.18 mol) was suspended in D_2O (200 mL) and EtOD (10 mL) was added until dissolution was achieved. The clear solution was heated at 100 °C for 1 hour. After cooling to room temperature, the ethanol was removed under reduced pressure. The aqueous mixture was transferred to a separating funnel and extracted with ethyl acetate (3 x 150 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was dried in vacuo to obtain ethyl cyanoacetate-d_2 (20 g, 98%) as a colourless liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.25 (2H, q, *J* = 7.18 Hz), 3.45-3.42 (residual), 1.30 (3H, t, *J* = 7.17 Hz) ppm; ^{2}H NMR (61.4 MHz, $CDCl_3$) δ 3.43 (2D, bs) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 113.2, 63.1, 14.0 ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, $CDCl_3$) δ 163.0, 113.2, 63.1, 24.5, 14.0 ppm.

3-Amino-1-propanol-d_6 (**S2**)

$LiAlD_4$ (9.5 g, 226 mmol) was added portion wise to a solution of ethyl cyanoacetate-d_2 (13 g, 113 mmol) in anhydrous diethyl ether (400 mL) at 0 °C. The reaction mixture was stirred at this temperature for 30 minutes and then for a further 2 hours at room temperature. The mixture was cooled again to 0 °C and carefully quenched with water (9.5 mL), followed by aqueous sodium hydroxide (15%, 9.5 mL) and then more water (28.5 mL). The mixture was stirred until a free-flowing white solid had formed in a bright yellow solution (15 minutes). Anhydrous magnesium sulfate was added to remove excess water and the solids removed by filtration through a pad of Celite©. The solids were washed with diethyl ether (100 mL) and the filtrate analysed by TLC and mass spectrometry. It was found that the product was not in the filtrate and hence the bright yellow/orange solids were transferred back into the reaction flask and stirred with 200 mL of ethanol at reflux for 30 minutes. The hot yellow suspension was filtered through a pad of Celite© and the filtrate concentrated under reduced pressure to obtain 3-amino-1-propanol-d_6 as a yellow oil, R_f = 0.1 (1:9 methanol, dichloromethane. Potassium permanganate); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.27 (3H, bs) ppm; ^{2}H NMR (61.4 MHz, DMSO-d_6) δ 3.40 (2D, bs), 1.43 (2D, bs) ppm (note one signal obscured by DMSO peak); ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, DMSO-d_6) δ 58.0, 39.8, 37.8 ppm; MS (ESI+) $[M + H]^+$: 82.1.

tert-Butyl (3-hydroxypropyl)carbamate-d_6 (**S3**)

To a solution of 3-amino-1-propanol-d_6 (7.5 g, 92 mmol) in methanol (200 mL) at 0 °C was added triethylamine (25.8 mL, 185 mmol) followed by a solution of Boc anhydride (20.2 g, 92 mmol) in methanol (15 mL), slowly. The reaction mixture was warmed to room temperature and stirred for 16 hours. The volatiles were removed under reduced pressure and the residue taken up in dichloromethane (250 mL) and washed with citric acid (10%, 2 x 150 mL) and brine (100 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was dried *in vacuo* to obtain *tert-b*utyl (3-hydroxypropyl)carbamate-d_6 (10.5 g, 51% over 2 steps) as an orange oil, R_f = 0.5 (1:1 ethyl acetate, hexane. Potassium permanganate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (1H, bs), 2.76 (1H, bs), 1.43 (9H, s) ppm; ^{2}H NMR (61.4 MHz, $CDCl_3$) δ 3.62 (2D, bs), 3.24 (2D, bs), 1.61 (2D, bs) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.3, 79.7, 28.5 ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, $CDCl_3$) δ 157.3, 79.7, 58.5, 36.3, 31.8, 28.5 ppm; MS (ESI+) $[M + Na]^+$: 204.2.

Carbamic acid, N-[3-[[(4-methylphenyl)sulfonyl]oxy]propyl]-, 1,1-dimethylethyl ester-d_6 (**S4**)

To a solution of the alcohol (10.3 g, 56.8 mmol) in anhydrous dichloromethane (120 mL) was added triethylamine (9.5 mL, 68.2 mmol), 4-(dimethylamino)pyridine (690 mg, 5.7 mmol) and tosyl chloride (13 g, 68.2 mmol) as a solution in dichloromethane (20 mL) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 16 hours. The solvent was removed under reduced pressure and the residue purified by flash column chromatography using ethyl acetate, hexane (1:9 to 3:7) as an eluent to obtain the tosylate (10.5 g, 55%) as a yellow oil, R_f = 0.4 (3:7 ethyl acetate, hexane. Potassium permanganate, or vanillin (white)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (2H, d, *J* = 8.26 Hz), 7.34 (2H, d, *J* = 8.06 Hz), 2.44 (3H, s), 1.41 (9H, s) ppm; ^{2}H NMR (61.4 MHz, $CDCl_3$) δ 4.06 (2H, bs), 3.13 (2H, bs), 1.80 (2H, bs) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.0, 145.0, 133.0, 130.0, 128.0, 79.5, 28.5, 21.8 ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, $CDCl_3$) δ 156.0, 145.0, 133.0, 130.0, 128.0, 79.5, 67.4, 36.2, 28.5, 21.8 ppm; MS (ESI+) $[M + Na]^+$: 358.2.

Imidazole-d_6 (**S5**)

Imidazole (10 g, 147 mmol) was dissolved in D_2O (100 mL) and heated in a Parr reactor (450 mL) at 250 °C (900-1050 Psi) for 3 days. The very dark reaction mixture was filtered through a pad of Celite©, washed with water (3 x 50 mL) and concentrated under reduced pressure. Residual water was removed by azeotropic distillation with toluene and *in vacuo* to obtain imidazole-d_3 (7.5 g, 72%) as a light brown crystalline solid, ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.13 (1H, bs), 7.73 (residual), 7.07 (residual) ppm; ^{2}H NMR (61.4 MHz, DMSO-d_6) δ 7.68 (1D, bs), 7.06 (2H, bs) ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, DMSO-d_6) δ 135.1, 121.5 ppm; MS (ESI+) $[M + H]^+$: 72.1.

tert-Butyl [3-(1H-imidazol-1-yl)propyl]carbamate-d_9 (**S6**)

To a solution of imidazole-d_3 (1.66 g, 23.3 mmol) in anhydrous dimethylformamide (80 mL) at 0 °C was added sodium hydride (60% in mineral oil, 0.93 g, 23.3 mmol), portion wise. The mixture was stirred for 30 minutes before a solution of tosylate **S4** (9.4 g, 28.0 mmol) in dimethylformamide (15 mL) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 16 hours. After cooling to 0 °C a saturated aqueous solution of sodium hydrogen carbonate was added (10 mL) to quench the reaction. The mixture was diluted with brine (80 mL) and the aqueous phase extracted with a mixture of isopropanol and chloroform (1:9, 3 x 100 mL). The combined extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by flash column chromatography using methanol, dichloromethane (1:39 to 1:19) as an eluent to obtain *tert*-butyl [3-(1H-imidazol-1-yl)propyl]carbamate-d_9 (4.9 g, 90%) as a yellow-orange oil, R_f = 0.35 (1:19 methanol, dichloromethane. Potassium permanganate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.81 (1H, bs), 1.42 (9H, s) ppm; ^{2}H NMR (61.4 MHz, CD_2Cl_2) 7.48 (1D, bs), 6.99 (2D, bs), 3.93 (2D, bs), 3.04 (2D, bs), 1.87 (2D, bs) ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, $CDCl_3$) δ 156.2, 136.8, 129.1, 118.5, 79.7, 43.7, 37.0, 30.6, 28.5 ppm; MS (ESI+) $[M + H]^+$: 235.2.

1-(3-Aminopropyl)imidazole d_9 (**S7**)

The Boc protected amine **S6** (4.9 g, 20.9 mmol) was dissolved in anhydrous dichloromethane (25 mL), cooled to 0 °C and treated with trifluoroacetic acid (12 mL, 157 mmol). The mixture was warmed to room temperature and stirred for 4 hours. The volatiles were removed under a stream of nitrogen and then *in vacuo*. The residue (TFA salt) was dissolved in 1 M NaOH (20 mL, pH = 12) and saturated with solid NaCl. The aqueous mixture was extracted with a mixture of isopropanol and chloroform (1:4), dried over anhydrous magnesium sulfate and concentrated under reduced pressure to obtain 1-(3-aminopropyl)imidazole-d_9 (2.8 g, 100%) as a yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (residual), 7.14 (residual), 6.87 (residual), 3.97 (residual), 3.09 (2H, bs), 2.47 (residual), 1.73 (residual) ppm; ^{2}H NMR (61.4 MHz, MeOD) 7.69 (1D, bs), 7.18 (1D, bs), 7.01 (1D, bs), 4.06 (2D, bs), 2.62 (2D, bs), 1.92 (2D, bs) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 137.2 (due to some back exchange at C2 position of the imidazole) ppm; ^{13}C{^{1}H, ^{2}H} NMR (101 MHz, $CDCl_3$) δ 136.9, 127.9, 118.9, 42.7, 37.1, 32.3 ppm; MS (ESI+) $[M + H]^+$: 57.1% d_9, 29.9% d_8, 6.3% d_7, 0.8% d_6.

Table S1. Scatterer information. *Molecular volumes (v_m) and SLDs (ρ) of system components.*

Scatterer	v_m (Å^3)	ρ (10^{-6} Å^{-2})
H-PIL$^+$	280	1.51
d-PIL$^+$	294	4.77
BMIm$^+$	161	0.98
TFSI$^-$	323	2.65

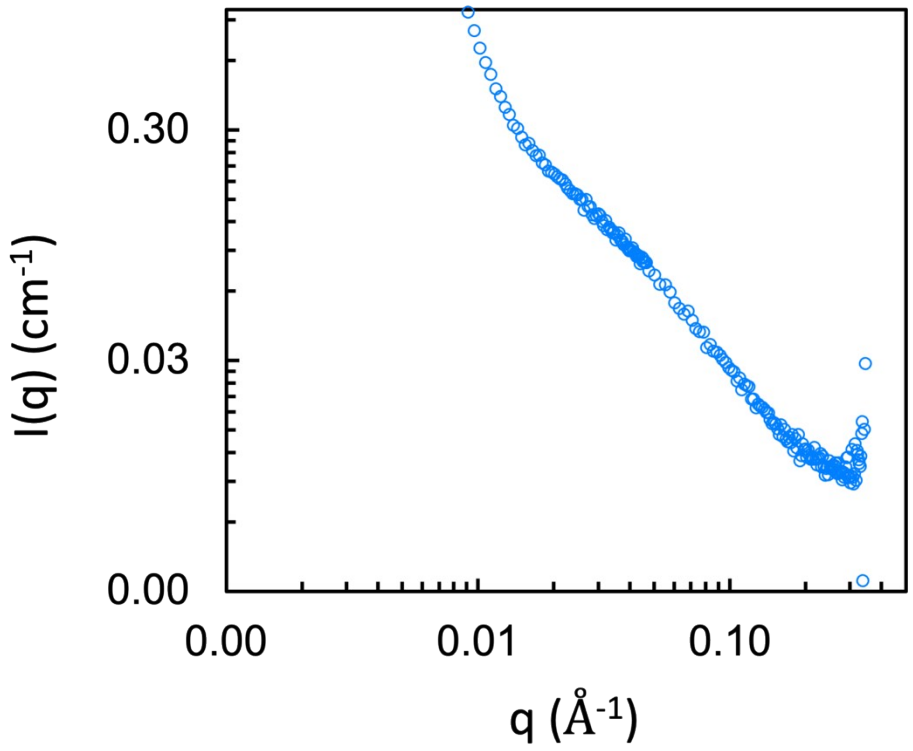


Figure S1. SANS of d-PIL:H-PIL at 95%v/v H-PIL. The SANS of a d-PIL:H-PIL blend at a composition of 49:3:48 (d-PIL$^+$:H-PIL$^+$:TFSI). The Guinier regime of the polycation is dominated by low q scattering from the microvoids and the plateau is almost completely hidden making the quality of the fit poor.

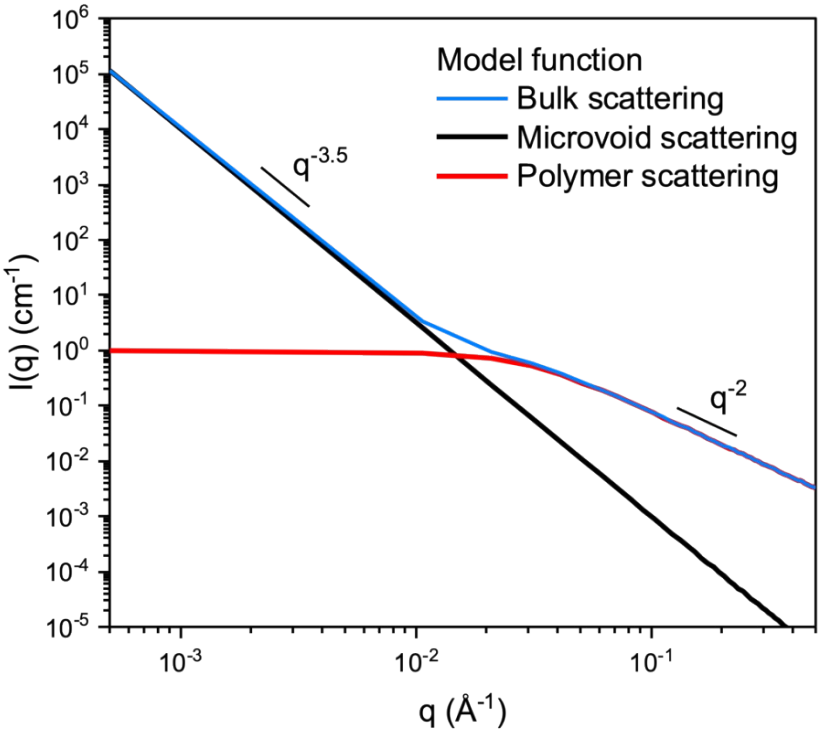


Figure S2. Combined scattering model of a pure PIL. To fit the data, the Guinier-Porod is used to model the low q upturn due to microvoids and is added to the Gaussian coil function model used to model the poly(cation) scattering in the PIL.

Table S2. Parameters of model fit to d-PIL:H-PIL blends. *Incoherent background (B), radius of gyration of microvoids ($R_{g,v}$), dimension variable (s), Porod exponent (m), intensity at q = 0 (I_0), and apparent radius of gyration of polycation in PIL blends ($R_{g,p}$).*

T (°C)	%v/v d-PIL$^+$	d-PIL$^+$:H-PIL$^+$:TFSI$^-$	B (cm^{-1})	$R_{g,v}$[a] (μm)	s[a]	m[a]	I_0[b] (cm^{-1})	Apparent $R_{g,p}$[b] (Å)
25	8	8:44:48	0.37	1.3	0	3.5	0.67	42± 0.5
	13	13:39:48	0.36	1.5	0	3.5	1.65	52± 0.5
	26	26:26:48	0.31	2.1	0	3.5	2.30	52± 0.5
80	8	8:44:48	0.37				0.73	45 ± 0.5
	13	13:39:48	0.36				1.66	53 ± 0.5
	26	26:26:48	0.31				2.42	54 ± 0.5

[a] Parameter fit in low q void model. [b] Parameter fit by high q coil model.

Table S3: Parameters of model fit to d-PIL:H-IL solutions. *Volume fraction of undissolved polymer aggregates (ϕ_{agr}), nominal radius of undissolved polymer aggregates (R), and apparent radius of gyration of polycation in mixtures (R_g).*

T (°C)	%v/v d-PIL$^+$	d-PIL$^+$: H-BMim$^+$: TFSI$^-$	B (cm^{-1})	ϕ_{agr}[a] (10^{-4})	R[a] (Å)	Apparent R_g[b] (Å)
25	1.5	1.5:26.5:72	0.40	11	200 ±24	59 ± 0.5
	3	3:16.5:80.5	0.43	5.5	257 ± 29	50 ± 0.3
	4.5	4.5:15:80.5	0.44	12	265 ± 18	41 ± 0.2
	8	8:28:64	0.37	6.3	130 ± 31	39 ± 0.3
	10	10:27:63	0.36	52	89 ± 26	35 ± 0.2
	13	13:25:62	0.31	28	106 ± 30	26 ± 0.2
80	1.5	1.5:26.5:72	0.40	4	230 ± 153	60 ± 0.2
	3	3:16.5:80.5	0.43	3.4	254 ± 103	51 ± 0.7
	4.5	4.5:15:80.5	0.44	13	240 ± 14	41 ± 0.5
	8	8:28:64	0.37	11	84 ± 29	40 ± 0.3
	10	10:27:63	0.36	17	100 ± 24	35 ± 0.3
	13	13:25:62	0.31	31	109 ± 23	26 ± 0.2

[a] Parameter given by sphere model. [b] Parameter given by monodispersed Gaussian coil model.

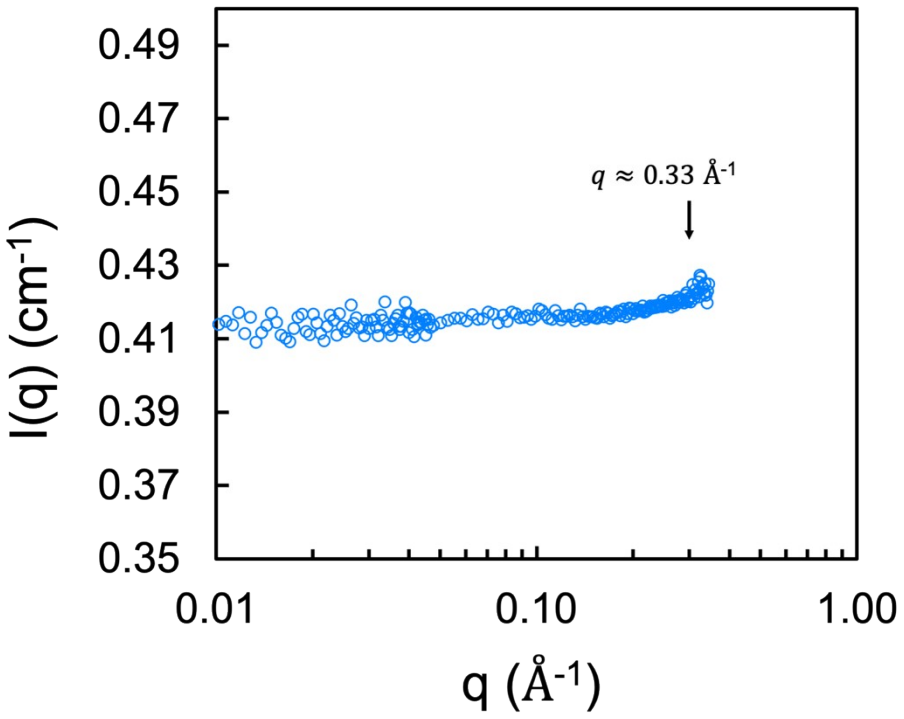


Figure S3. SANS of BMIm TFSI. The SANS of BMIm TFSI shows a high q upturn characteristic of imidazolium based ILs. A high q upturn is the start of a 'prepeak' induced by the local ordering of alkyl chains. This high q feature begins at ~0.33 Å^{-1}.

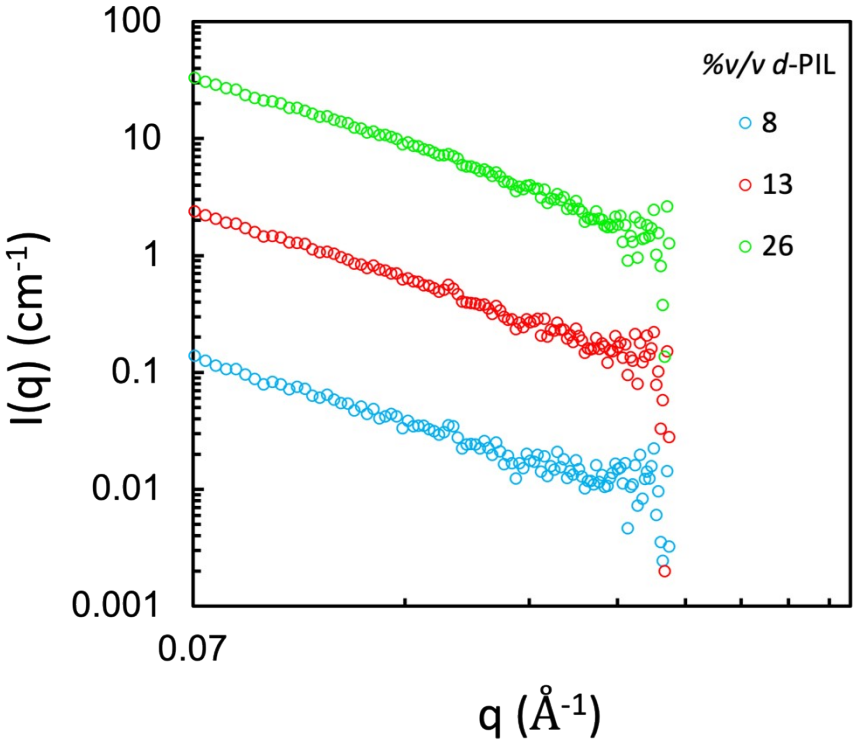


Figure S4. High q upturn in poly(3MAPIm)TFSI. An upturn at high q is observed in the SANS of the pure PIL due to the start of a charge alternation peak.