Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplemental Information

Impact of building block structure on ion transport in cyclopropenium-based polymerized ionic liquids

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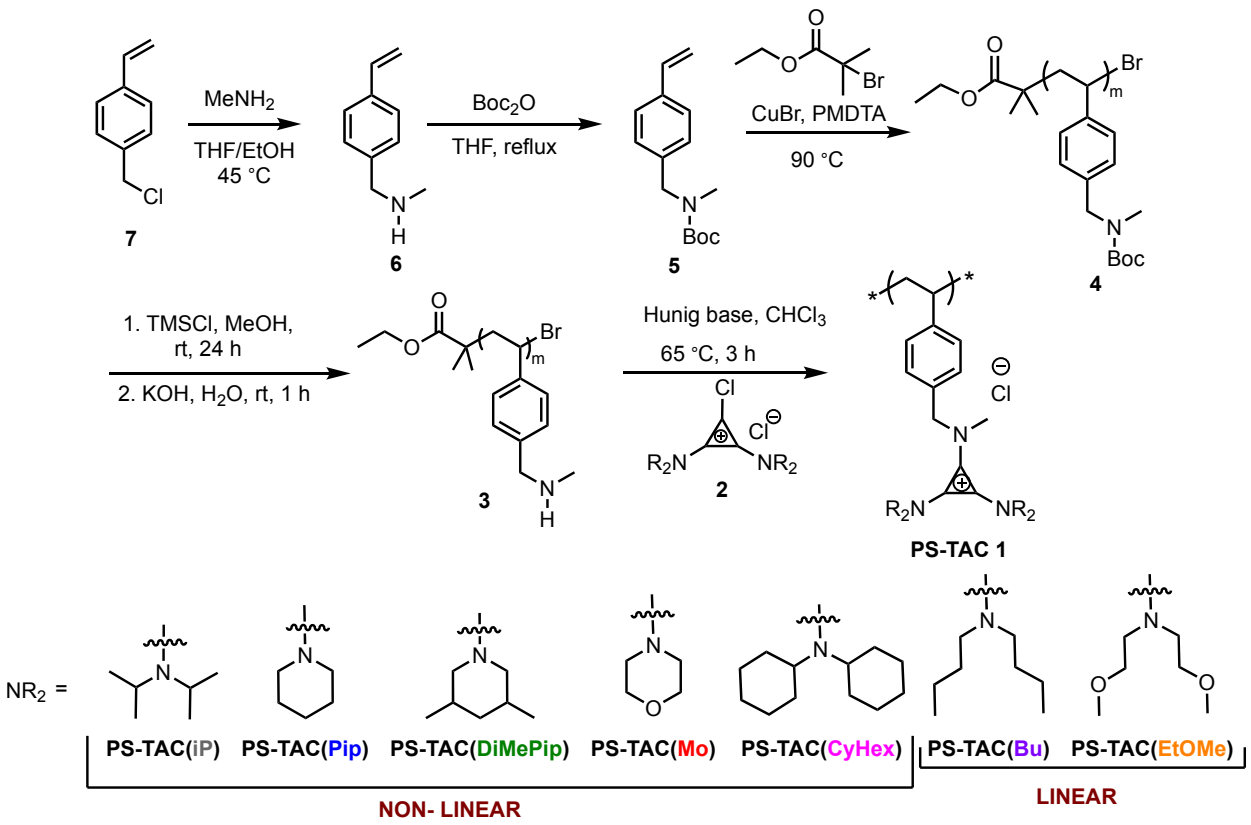


Figure S1. Schematic of the synthesis of the PS-TAC PILs.

The synthesis of **PS-TAC 1** family were prepared by post polymerization functionalization method, reported in the literature[1-3] starting from commercially available vinyl benzyl chloride **7**. Vinyl benzyl chloride on reacting with methyl amine at 45 ºC result in vinyl benzyl methyl amine (**6**) followed by BOC anhydride protection yields **5**. BOC protected monomer (**5**) undergoes ATRP polymerization resulting in **4**. Followed by deprotection and reaction with functionalized cyclopropenium derivative (**2**)[3] results in library of **PS-TAC 1**.

^{1}H spectra were recorded in $CDCl_3$ (except where noted in Experimental Methods) on a Bruker AMX-300, AMX-400, or AMX-500 spectrometer. Data for ^{1}H NMR are reported with chemical shift in reference to residual $CHCl_3$ at 7.26 ppm (δ ppm). The NMR spectra of the resulting polymer are listed in Figures S2-S8 below. The polymers were characterized to quantify their molecular mass (M_n) and dispersity (Đ) on a Waters Alliance 2695 separation module equipped with a PL-aqua gel-OH 8-micron Mixed-M column (300 x 7.5 mm), a Waters 2998 Photodiode Array Detector, and a Waters 2414 Refractometer Detector. Tetrahydrofuran stabilized with dibutylhyrdroxytoluene was used as the eluent at a flow rate of 1ml min^{-1}. PS standards were used for the calibration. The samples were dissolved in tetrahydrofuran stabilized with BHT at 5mg/mL. The instrument was calibrated to polystyrene standards having THF as the mobile phase.

The molecular weights of the systems vary from ~30g/mol-60g/mol (degree of polymerization ~70-137), and PDI between 1.05-1.7. The features we are studying are nanometer-scale correlations in ion transport and morphology, so we do next expect this variation in PDI and molecular weight to have a significant impact on our results.

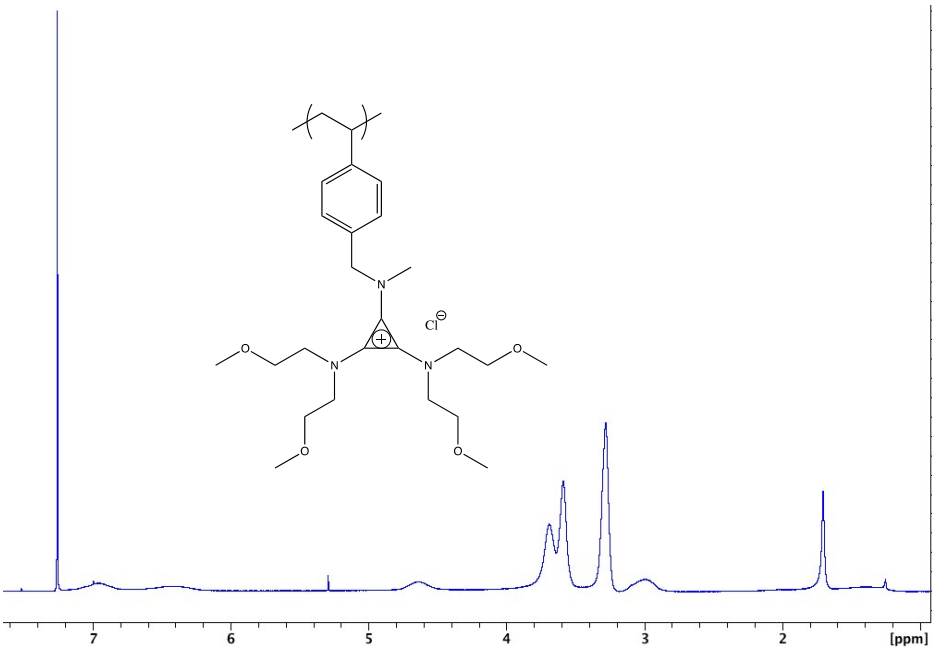


Figure S2. ^{1}H NMR spectrum of PS-TAC(EtOMe).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.21 (b, 62H, Ar**H**), 4.8- 4.40 (b, 34H, ArC**H$_2$**N), 3.85-3.48 (b, 242H, $C_3(N(CH_2C\mathbf{H_2}OCH_3)_2)_2$, $C_3(N(CH_2CH_2OC\mathbf{H_3})_2)_2$), 3.40-2.84 (b, 204H, NC**H$_3$,** $C_3(N(\mathbf{C}H_2CH_2OCH_3)_2)_2$), 1.65-0.71 (b, 82H, ArC**H**C**H$_2$**) Yield-66%

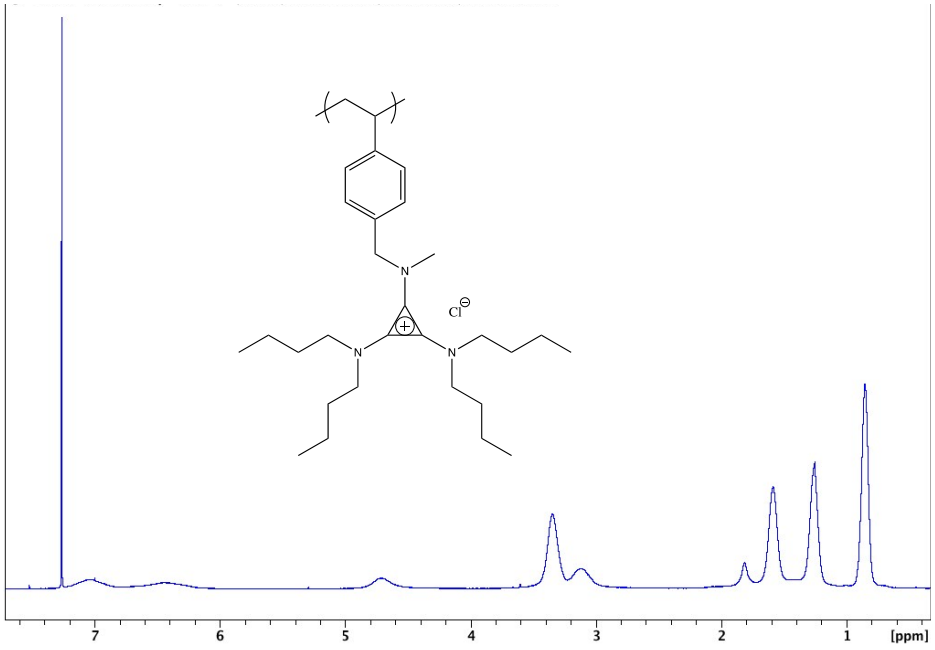


Figure S3. ^{1}H NMR spectrum of PS-TAC(Bu).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.12 (b, 1169H, Ar**H**), 4.9- 4.47 (b, 518H, ArC**H$_2$**N), 3.62-2.91 (b, 3008H, $C_3(N(C\mathbf{H_2}CH_2CH_2CH_3)_2)_2$, NC**H$_3$**) 1.94-0.63 (b, 9265H, ArC**H**C**H$_2$**, $C_3(N(CH_2\mathbf{C}H_2CH_2CH_3)_2)_2$), $C_3(N(CH_2CH_2C\mathbf{H_2}CH_3)_2)_2$), $C_3(N(CH_2CH_2CH_2C\mathbf{H_3})_2)_2$) Yield-42%[2]

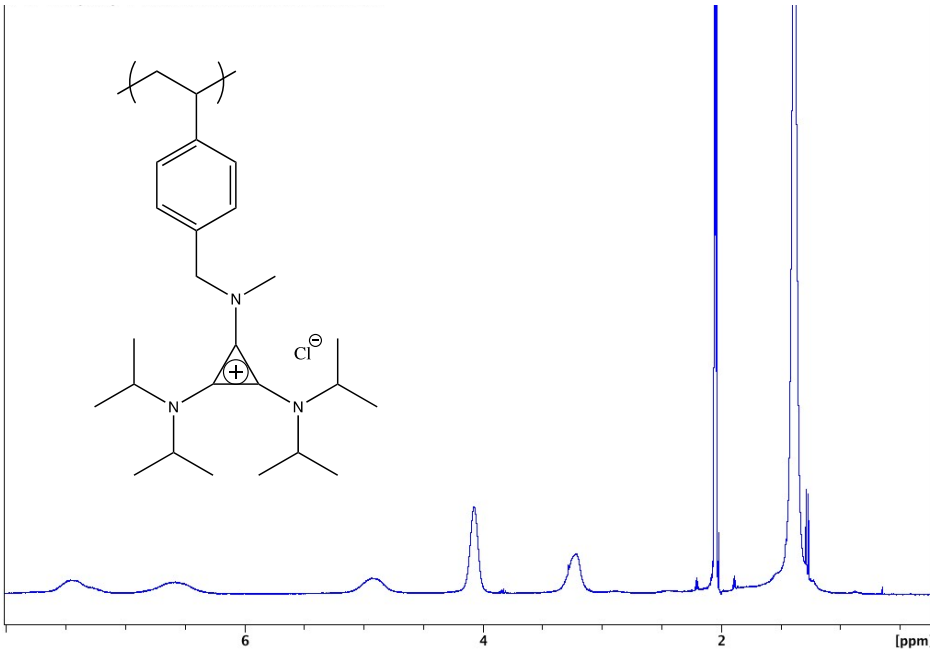


Figure S4. ^{1}H NMR spectrum of PS-TAC(iP).
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.60-6.35 (b, 500H, Ar**H**), 5.22-4.62 (b, 248H, ArC**H**$_2$N), 4.22-3.94 (b, 460H, $C_3(N(C\mathbf{H}(CH_3)_2)_2)$), 3.39-3.07 (b, 333H, NC**H**$_3$), 1.68-0.77 (b, 3052H, ArC**H**C**H**$_2$, $C_3(N(CH(C\mathbf{H}_3)_2)_2)$) Yield 65%

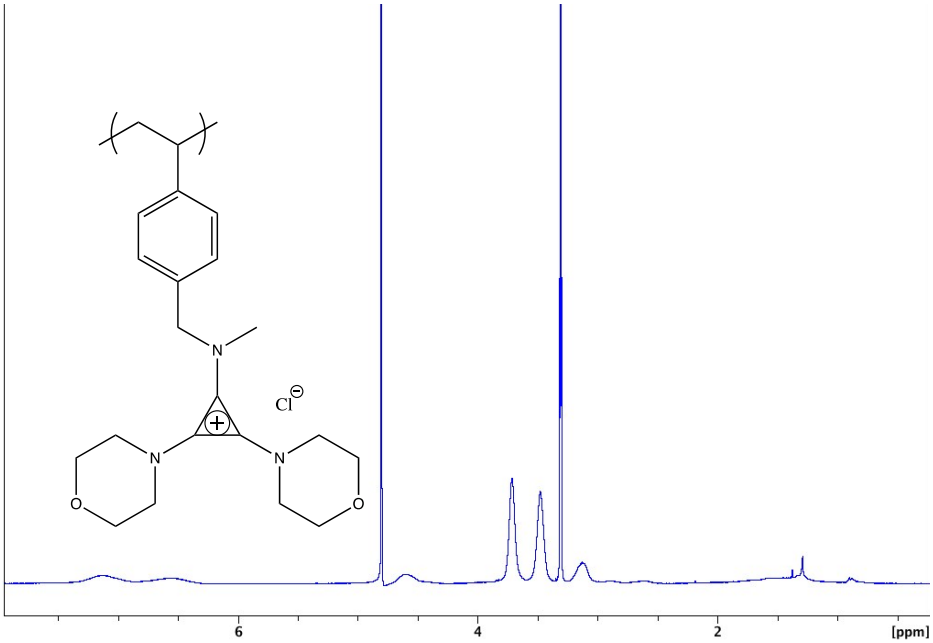


Figure S5. ^{1}H NMR spectrum of PS-TAC(Mo).
^{1}H NMR (400 MHz, CD_3OD) δ 7.51-6.20 (b, 440H, Ar**H**), 4.72- 4.29 (b, 162H, ArC**H**$_2$N), 3.79-3.63 (b, 516H, $C_3(N(CH_2)_2(C\mathbf{H}_2)_2O)_2)$, 3.57-3.38 (b, 505H, $C_3(N(C\mathbf{H}_2)_2(CH_2)_2O)_2)$, 3.24-3.03 (b, 198H, NC**H**$_3$), 1.71-0.82 (b, 370H, ArC**H**C**H**$_2$) Yield 91%

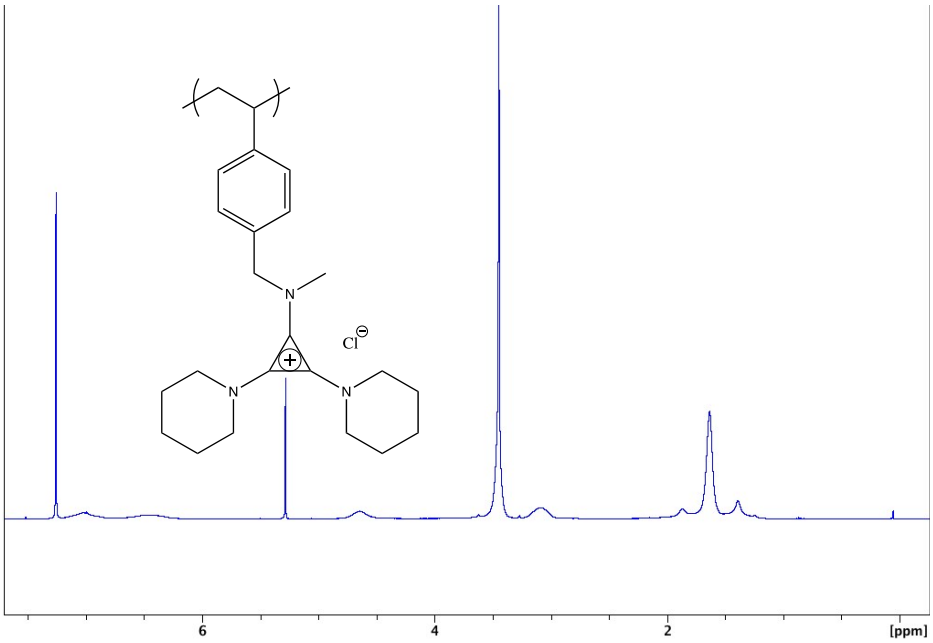


Figure S6. ^{1}H NMR spectrum of PS-TAC(Pip).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-6.20 (b, 1391H, Ar**H**), 4.72- 4.29 (b, 642H, ArC**H$_2$**N), 3.64-3.26 (b, 5409H*, C_3(N(C**H$_2$**)$_2$(CH_2)$_2$ CH_2)$_2$), 3.24-2.92 (b, 960H, NC**H$_3$**), 1.98-1.18 (b, 5904H, C_3(N(CH_2)$_2$**(CH_2)$_2$CH_2**)$_2$, ArC**H**C**H$_2$**) *water overlap @ δ 3.49 Yield 86%

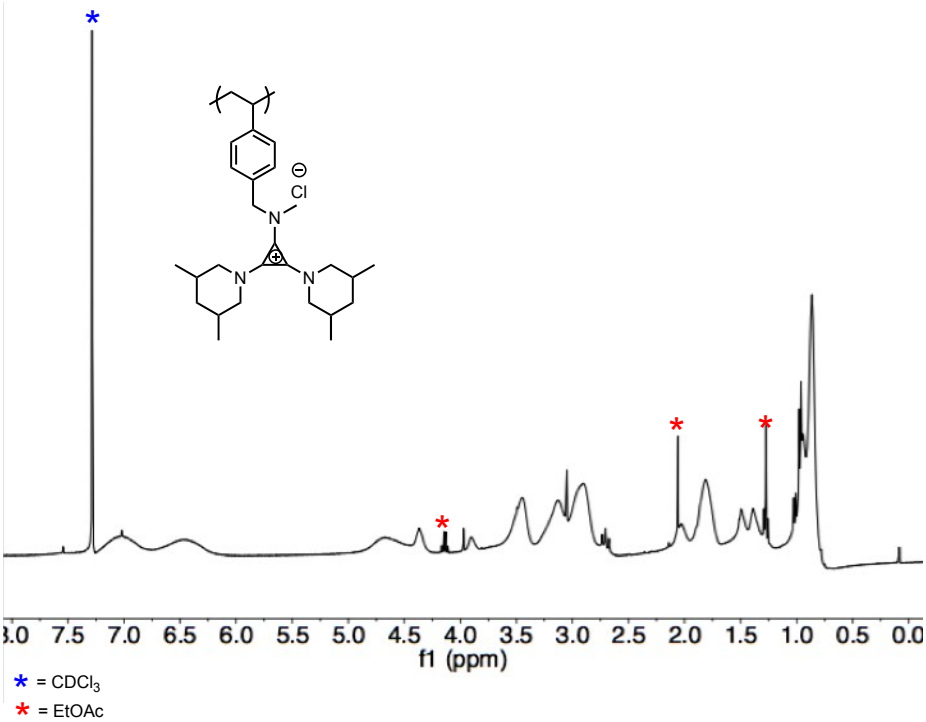
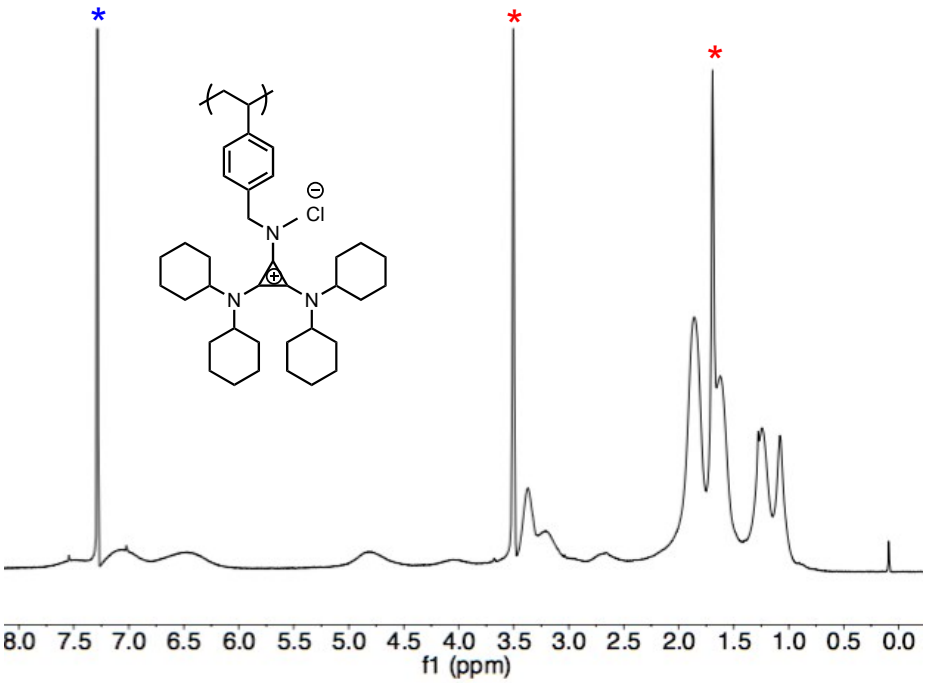


Figure S7. ^{1}H NMR spectrum of PS-TAC(DiMePip).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-6.21 (b, 84H, Ar**H**), 4.9- 4.40 (b, 61H, ArC**H2**N), 3.75-2.79 (b, 221H, C3(N(C**H**2)2(CH2)2CH2) 2, NC**H3**), 1.97-1.32 (b, 131H,) C3(N(CH2)2(C**H**)2C**H**2) 2), 1.65-0.71 (b, 181H,) ArC**H**C**H2**), C3(N(CH2)2(CH-**CH3**)2C**H**2) 2) Yield 40%



* = $CDCl_3$
* = MeOH, H_2O

Figure S8. ^1H NMR spectrum of PS-TAC(CyHex).
^1H NMR (400 MHz, $CDCl_3$) δ 7.27-6.08 (b, 43H, Ar**H**), 5.13-4.52 (b, 20H, ArC$\mathbf{H_2}$N), 3.49-3.02 (b, 50H, NCy**H**, NC$\mathbf{H_3}$), 2.31-0.0.94 (b, 348H, Cy**H**, ArC**H**C$\mathbf{H_2}$). Yield 75%

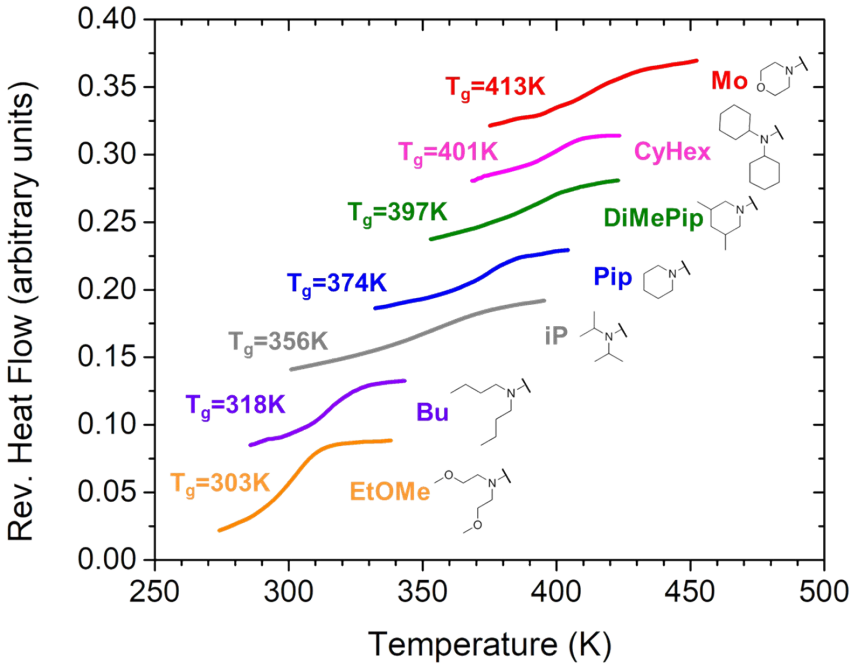


Figure S9: Reversible heat flow from temperature modulated DSC measurements of the PS-TAC polymers. All data shown is from the second cooling (cooling rate 5°C/min) of each system. Data is shifted vertically.

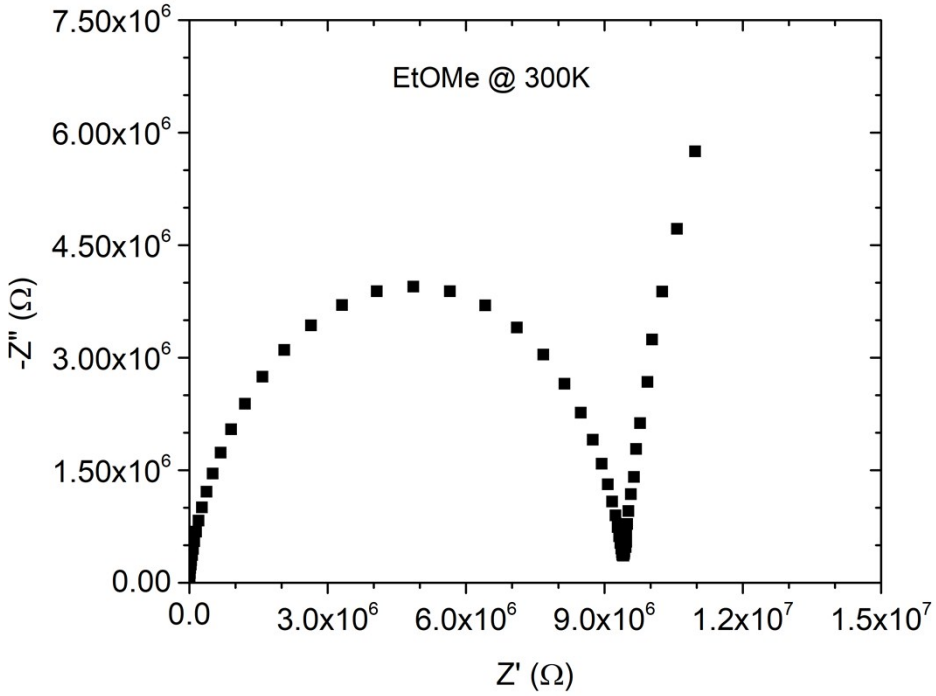


Figure S10: Representative example of impedance data of [PS-TAC][Cl] polymer. The high-frequency resistance is obtained from an equivalent circuit model fit.

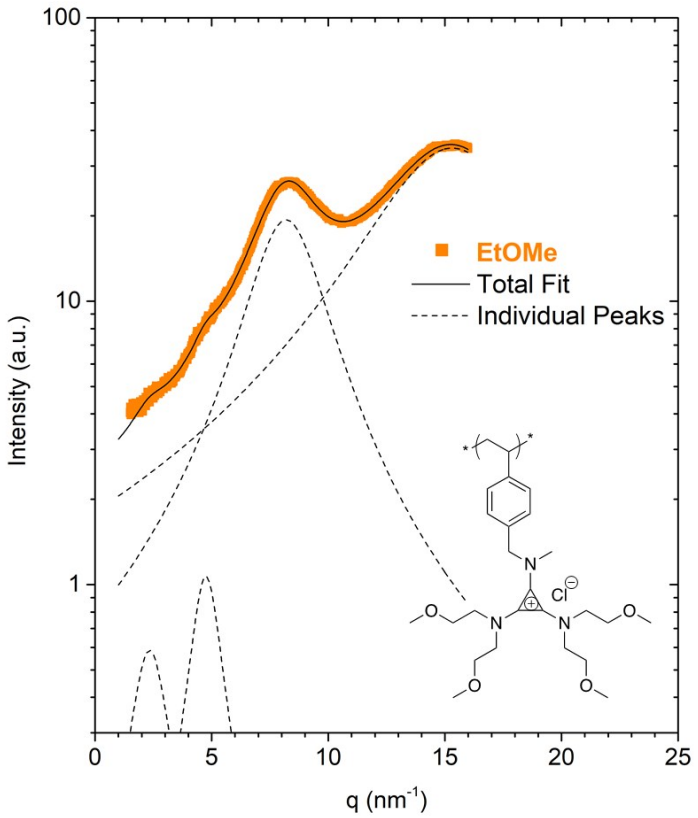


Figure S11: Representative example of fitting X-ray scattering data to Lorentzian peak functions. The total fit is the sum of the Lorentzian fits of the 4 individual peaks.

Table S1: Peak positions, and ratio of the intensity, I_a/I_i, of all of the PS-TAC PILs, determined from the Lorentzian fits.

Functional Group	d_b (nm)	d_o (nm)	d_i (nm)	d_a (nm)	Peak intensity ratio I_a/I_i
iP	2.04	--	0.71	0.50	3.43
Mo	2.05	--	0.72	0.45	8.75
Pip	2.48	1.13	0.75	0.46	4.22
DiMePip	2.22	1.26	0.82	0.49	7.30
CyHex	2.97	--	0.88	0.48	7.64
EtOMe	2.69	1.32	0.77	0.41	3.84
Bu	2.19	1.21	0.83	0.42	3.32

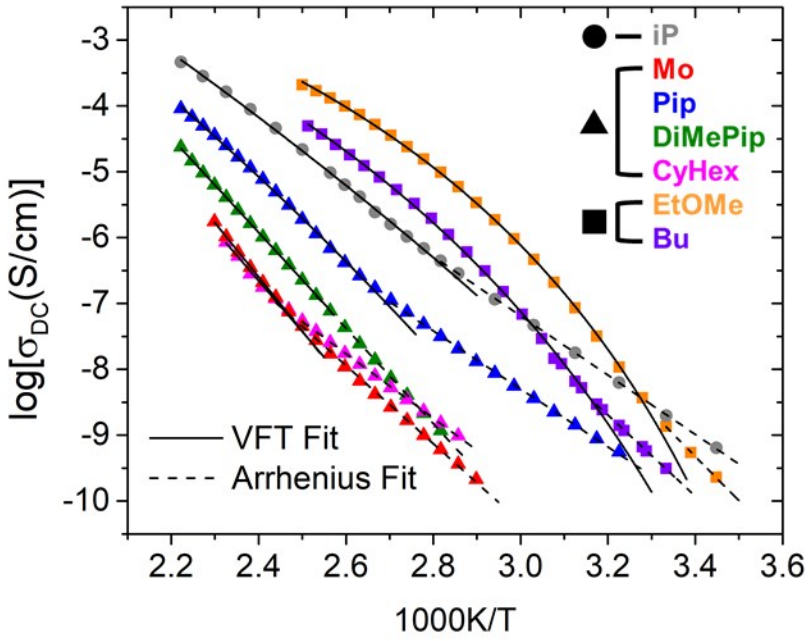


Figure S12: Conductivity vs. inverse temperature of the PS-TAC polymers, including VFT Fits (above Tg) and Arrhenius fits (below Tg). The data above the glass transition temperature of the polymer were fit to a VFT fit, and the data below the glass transition temperature of the polymer were fit to an Arrhenius fit. While the data above Tg were fit to VFT, the fit line is plotted to below Tg, to compare the Arrhenius fit at those temperatures.

Table S2: Activation energies of decoupled ion transport below Tg for the PS-TAC systems.

Functional Group	E_a (kJ/mol)
iP	86.2
Mo	113.6
Pip	84.3
DiMePip	138.5
CyHex	93.5
EtOMe	128.6
Bu	118.8

References:

1. Freyer, J. L.; Brucks, S. D.; Gobieski, G. S.; Russell, S. T.; Yozwiak, C. E.; Sun, M.; Chen, Z.; Jiang, Y.; Bandar, J. S.; Stockwell, B. R.; et al. Clickable Poly(Ionic Liquids): A Materials Platform for Transfection. *Angew. Chemie - Int. Ed.* **2016**, *55* (40), 12382–12386.
2. Brucks, S. D.; Freyer, J. L.; Lambert, T. H.; Campos, L. M. Influence of Substituent Chain Branching on the Transfection Efficacy of Cyclopropenium-Based Polymers. *Polymers (Basel).* **2017**, *9* (3).
3. Jiang, Y.; Freyer, J. L.; Cotanda, P.; Brucks, S. D.; Killops, K. L.; Bandar, J. S.; Torsitano, C.; Balsara, N. P.; Lambert, T. H.; Campos, L. M. The Evolution of Cyclopropenium Ions into Functional Polyelectrolytes. *Nat. Commun.* **2015**, *6*, 1–7.