Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Poly(ionic liquid)s with controlled architectures and their use in the making of ionogels with high conductivity and tunable rheological properties

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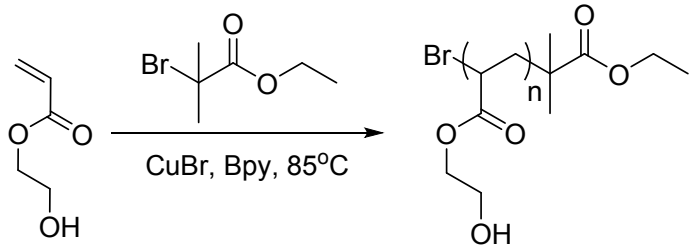
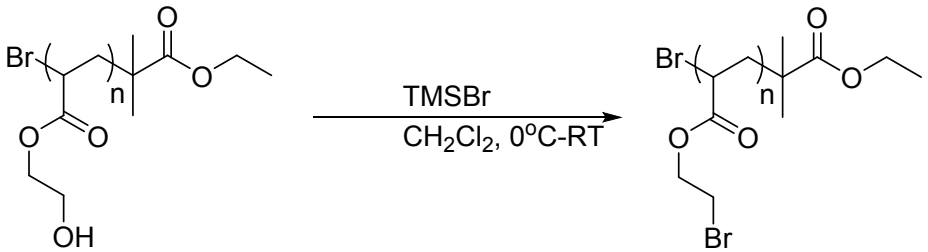
Polymerization of HEA using EBiB intitiator.



HEA **POH**

Polymerization was conducted in the bulk using a reactant ratio of M:I:Cu:Bpy = 240:1:1:2. The reactants, initiator EBiB (I, 0.055 g, 0.26 mmol), HEA (M, 6.4 g, 55.2 mmol), 2,2'-bipyridine ligand (Bpy, 0.060 g, 0.385 mmol), and CuBr catalyst (Cu, 0.030 g, 0.21 mmol), were mixed and degased under argon bubbling at room temperature. Stirring the resulting dark brown solution at 85ºC intiated the polymerization. Polymerization started immediately, leading to an increase in viscosity of the solution. After 4 hours the polymerization was quenched by adding water. The solution was diluted with deionized water and transferred into a dialysis membrane (spectra/por membrane, MWCO=1000) where it was dialyzed against a large volume of deionized water. At 2 hours intervals throughout the dialysis (2 days) the external water was replaced with fresh water. Finally, the dialysis bag's content was filtered and lyophilized to yield 2.1 g (corresponding to *ca* 32% conversion) of the expected polymer (**POH2**), M_n = 8300 (^{1}H NMR), 7944 (SEC, universal calibration); PDI = 1.25 (DOSY), 1.16 (SEC). For other characterizations: see below.

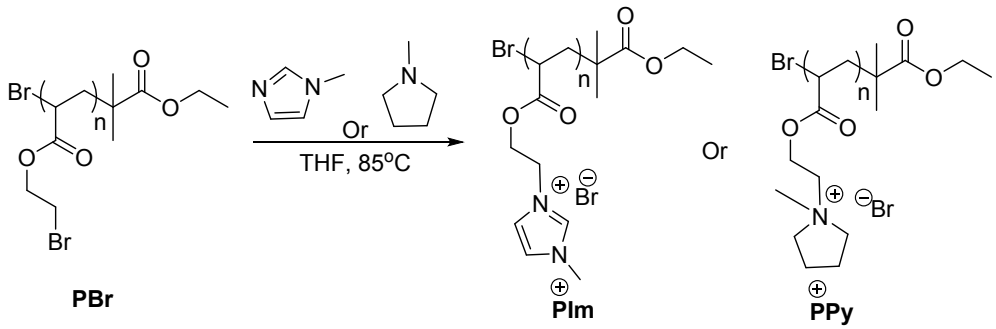
Synthesis of PBEA(PBr2) by bromination of PHEA(POH2).



POH **PBr**

Excess amount of trimethylsilyl bromide (7.2 g, 47.1 mmol) (3 equiv. with respect to –OH group of the **PHEA**) was added drop-wise to a 2.1 g polymer suspension in CH_2Cl_2 (24 mL) at 0ºC .The solution was slowly allowed to warm to room temperature. After 24 hours of stirring the brominated polymer became completely soluble in CH_2Cl_2 and was then precipitated in cold methanol (100 mL). The polymer was extensively washed with methanol (50mL x2) and dried under vacuum at 50°C. Yield = 2.80 g (86.6%), M_w = 12800 (^{1}H NMR), PDI = 1.15 (DOSY) For other characterizations: see below

Synthesis of poly ionic liquids (P3) by quarternization reactions of PBEA (P2).



In a typical reaction, a solution of polymer in THF (50 g/L) and 1-methylimidazole or 1-methylpyrrolidine (5 equiv. for each –Br group in the polymer chain) was refluxed at 85°C for 12h under argon atmosphere. Once the solvents were removed, the polymer was dissolved in methanol and re-precipitated in THF. The process was repeated twice to remove excess reagent, then the resulting polymers were dried under vacuum. Yield = 75%, M_w = 18700 (^{1}H NMR). For other characterizations, see below

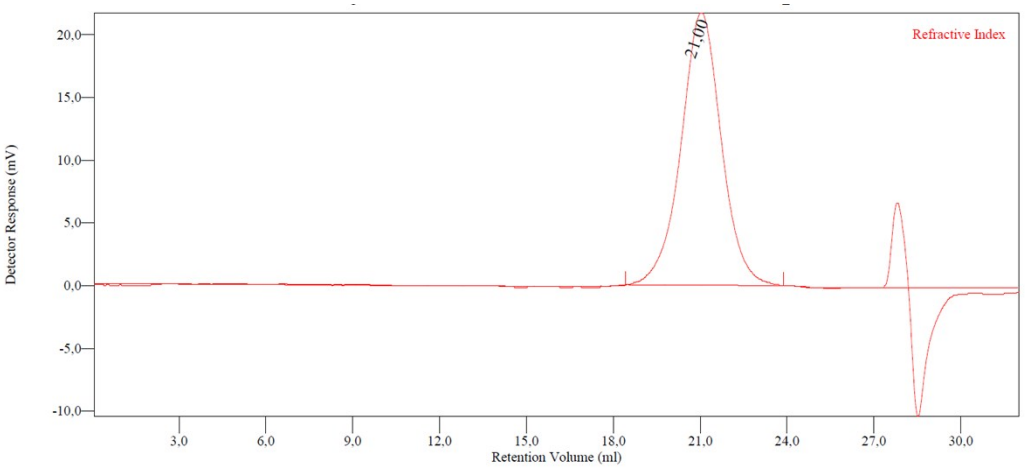


Figure S1. GPC trace of **POH.**

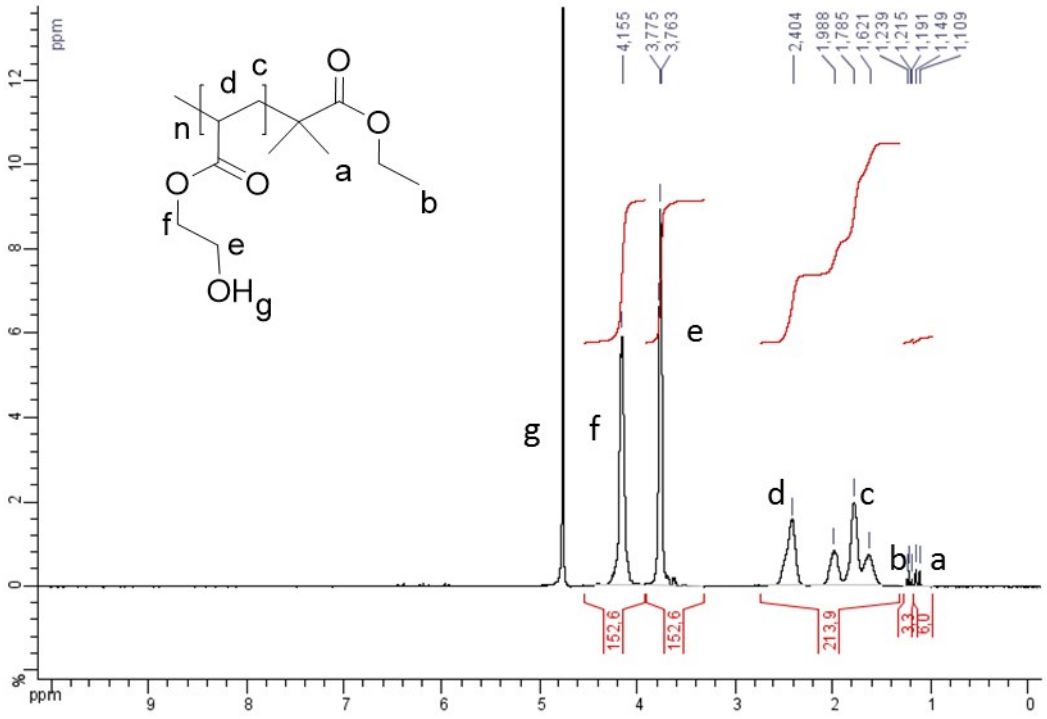


Figure S2. ^{1}H NMR for **POH** in D_2O.

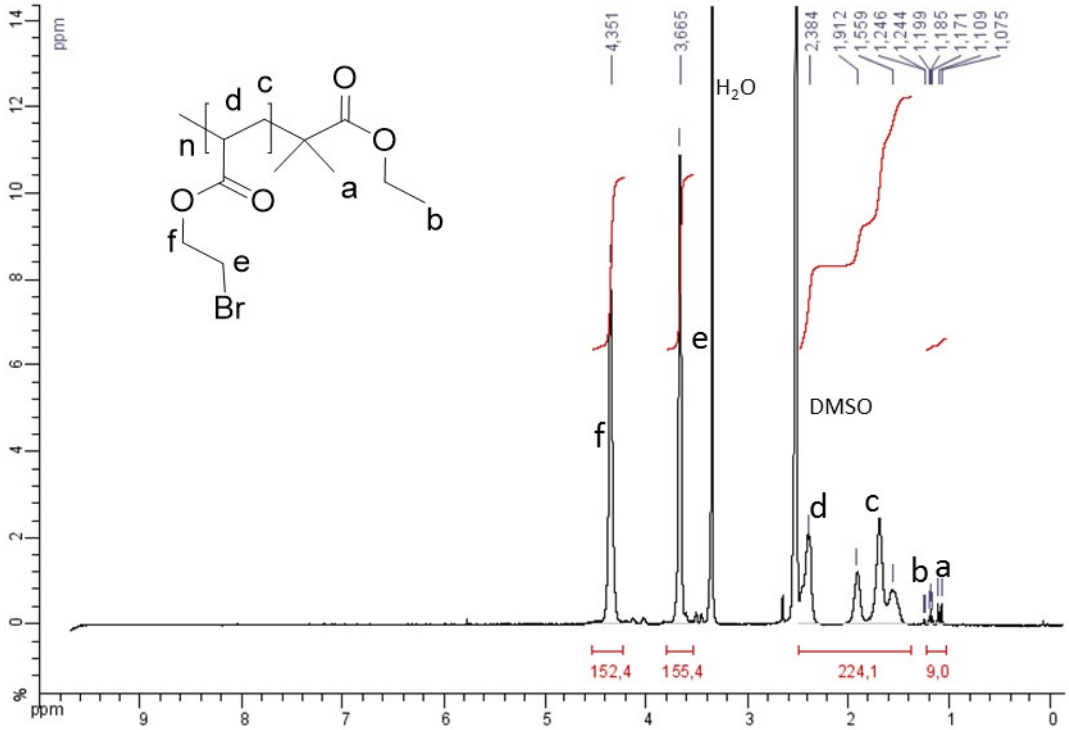
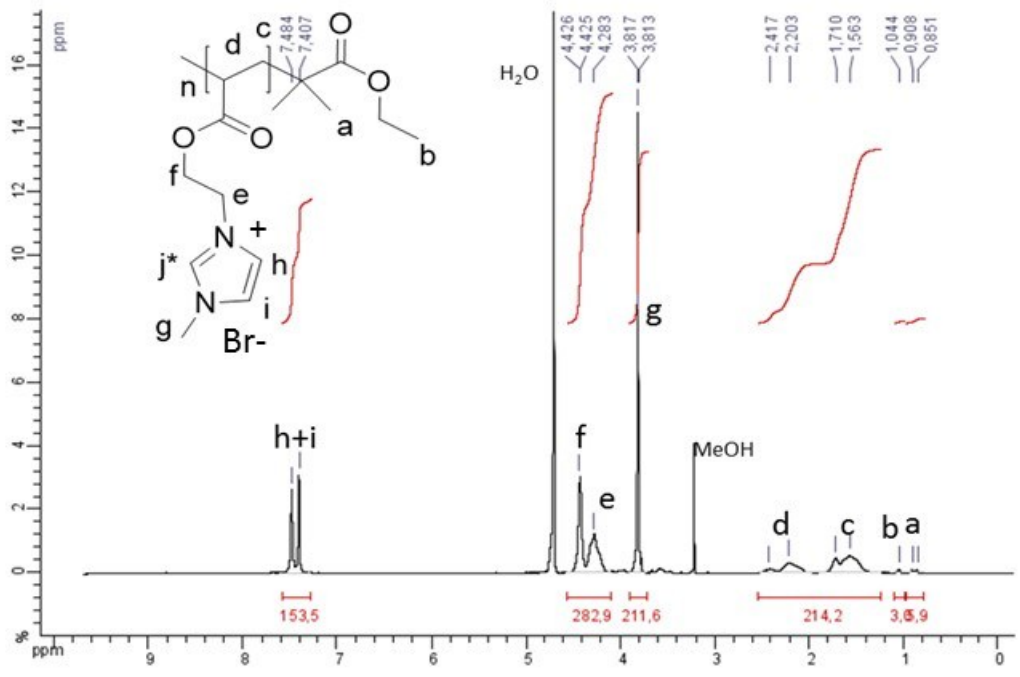


Figure S3. ^{1}H NMR for **PBr** in d6-DMSO.



* exchangeable proton not always seen in protic solvents

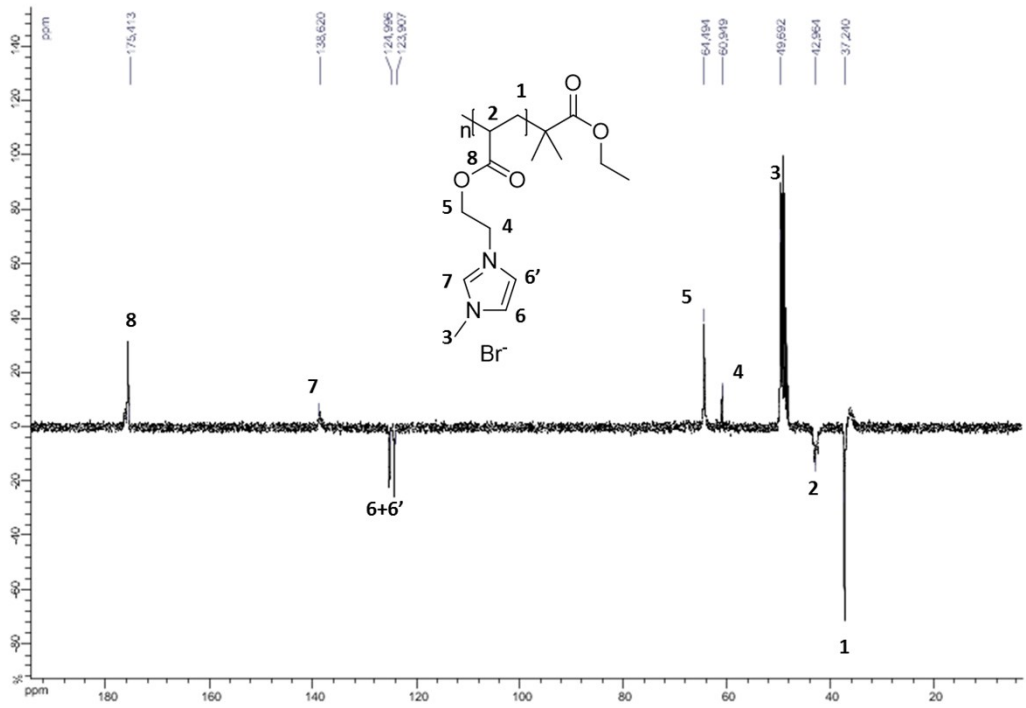


Figure S4. 1H NMR (top) and ^{13}C NMR (J-MOD, bottom) for **PIm^{+}Br^{-}** in CD_3OD. Note that 3 overlaps with the CD_3OD carbon signal.

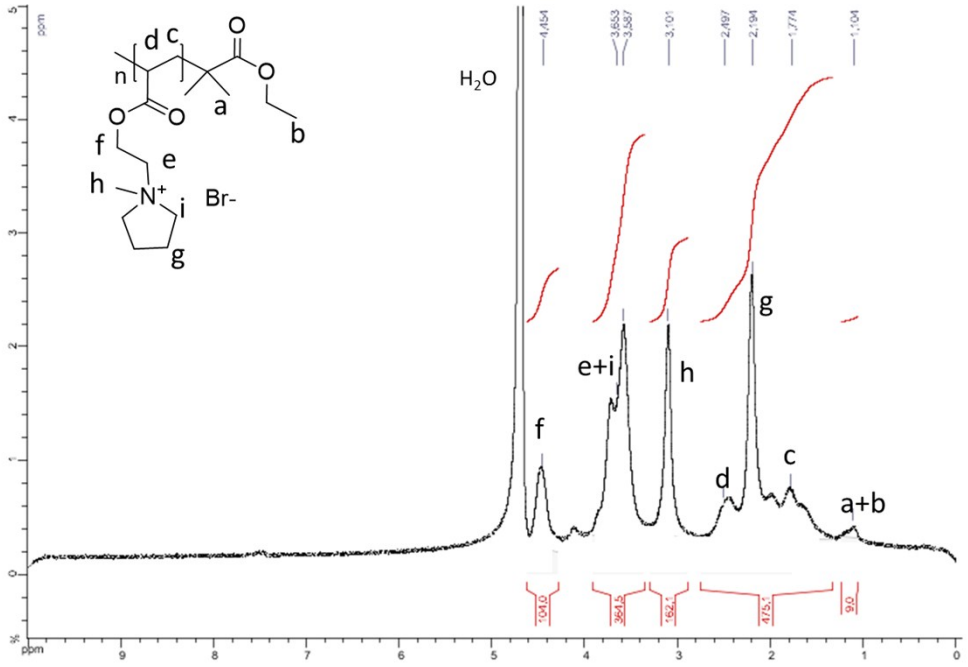


Figure S5. 1H NMR for **PPy$^+$Br$^-$** in D_2O.

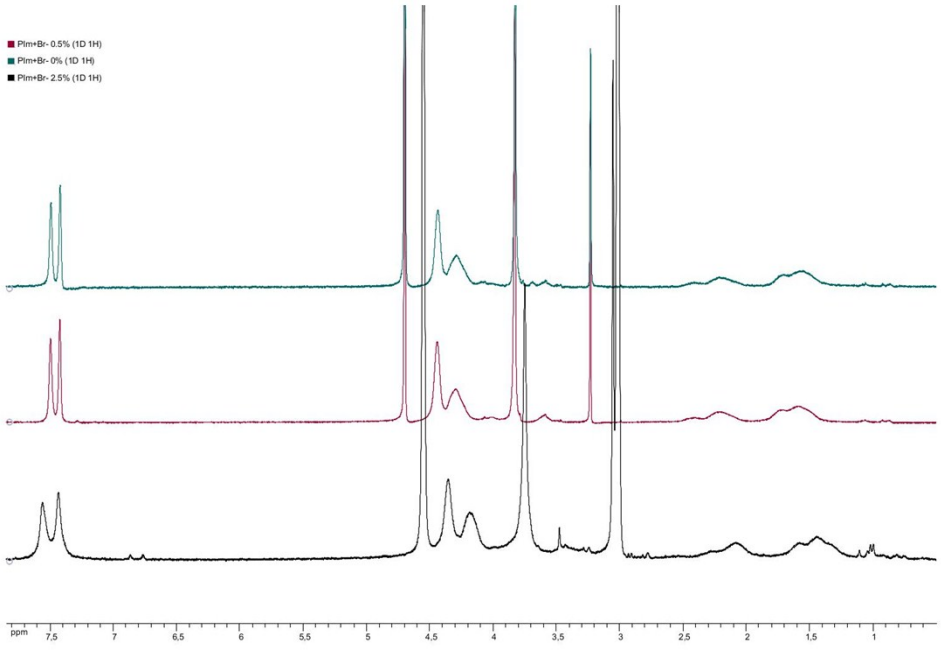


Figure S6. ^{1}H NMR Spectra for **PIm$^+$Br$^-$ 0** (green, NMR solvent D_2O), **PIm$^+$Br$^-$ 0.5** (red, NMR solvent D_2O) and **PIm$^+$Br$^-$ 2.5** (black, NMR solvent MeOD).

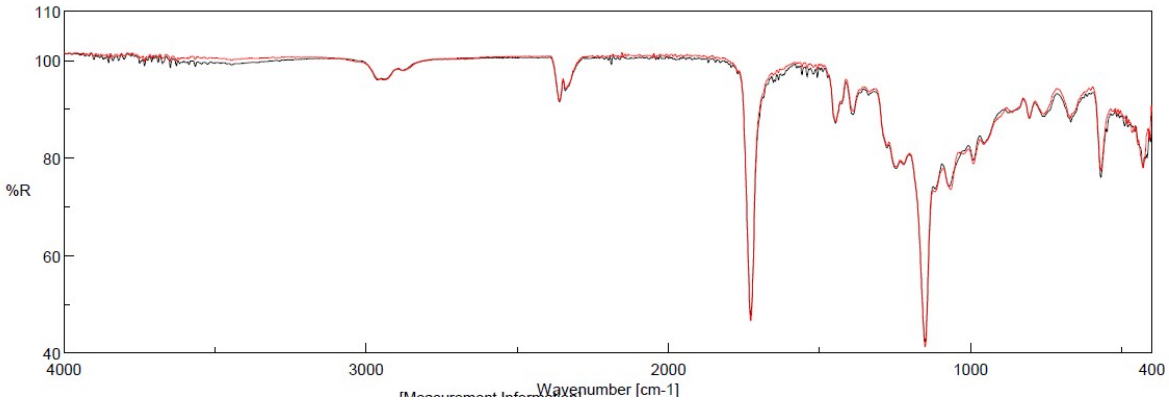


Figure S7. overlay of the IR spectra for **PBr** (black), and **PBr$^-$ 2.5** (red)

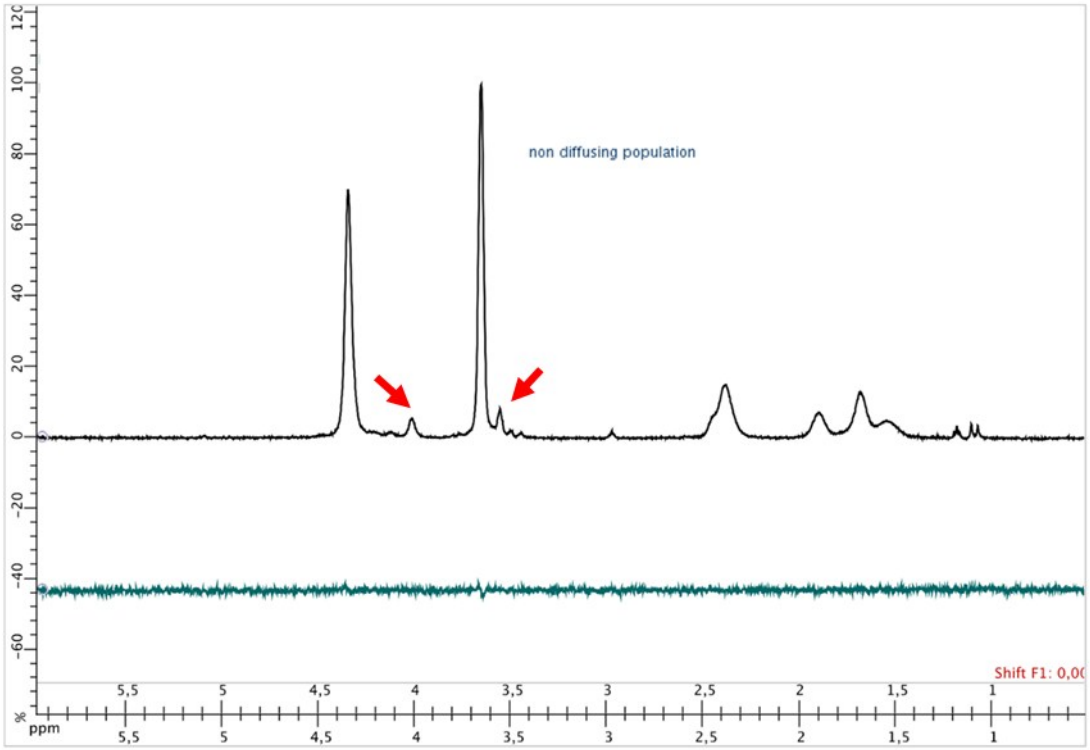


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Figure S8. Comparison of the ^{1}H spectra obtained at high-gradient (47 G.cm^{-1}) for **PBr** (green) and **PBr0.5** (black) evidencing the presence of non diffusing species in the latter which are not seen in the former. The red arrow indicate the peaks which we attribute to the cross-linker (O-CH2: 4.05ppm; N-CH_2: 3.6ppm) that were not visible on the NMR spectra of **PIm$^+$Br$^-$X** and **PPy$^+$Br$^-$X**

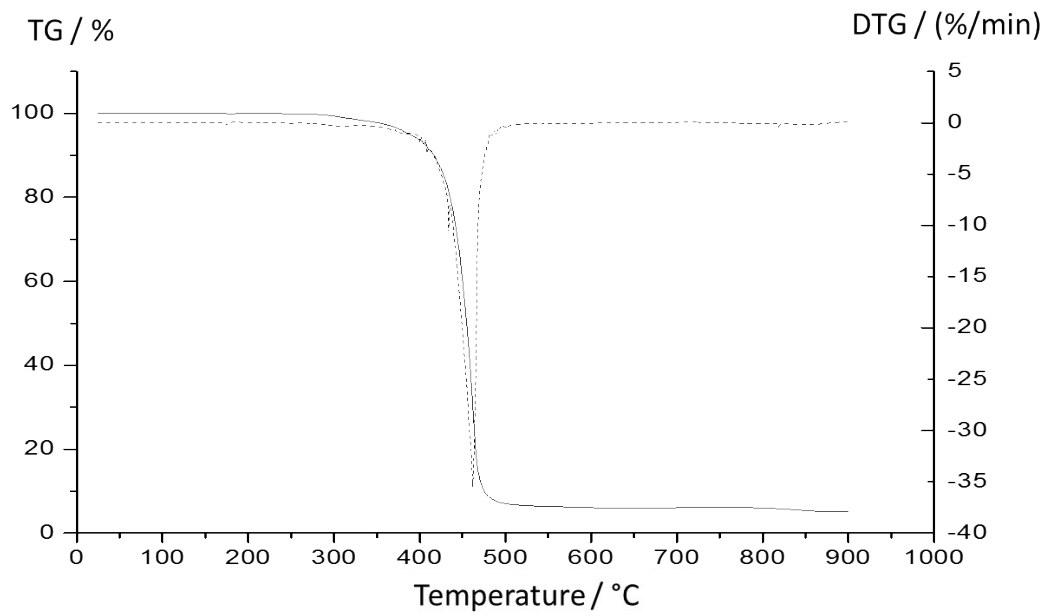


Figure S9. TGA spectrum of 15% wt. gel of $PPy^{+}NTf_2^{-}$0.5 (0.5g/2ml $Py_{14}NTf_2$ solid line), and first derivative of the spectrum (dashed line)

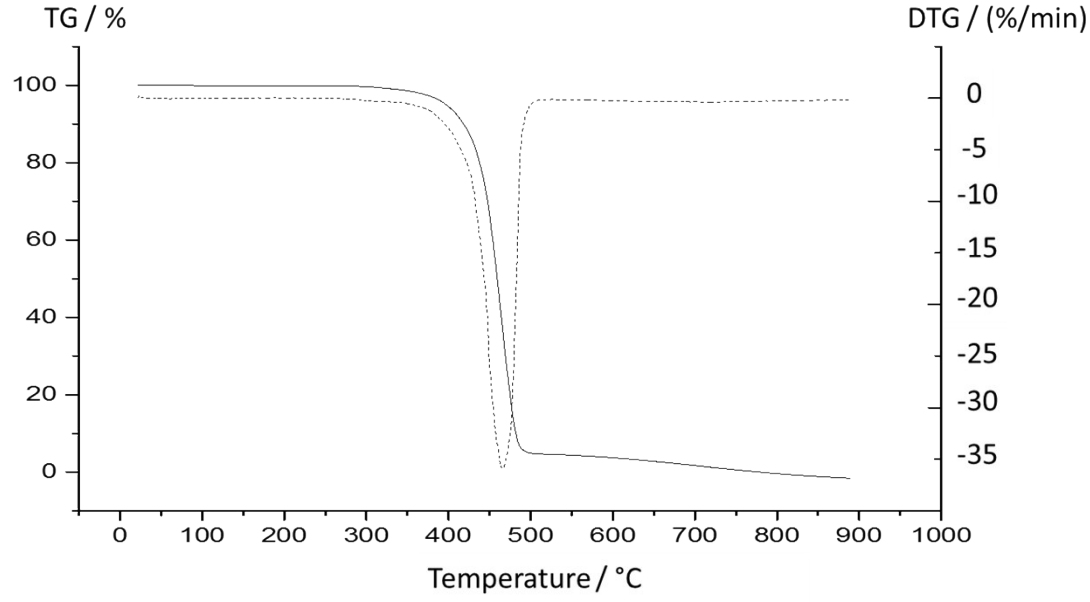
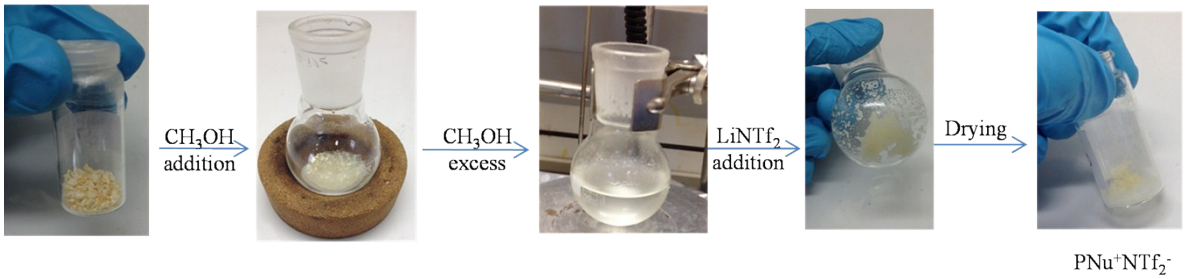


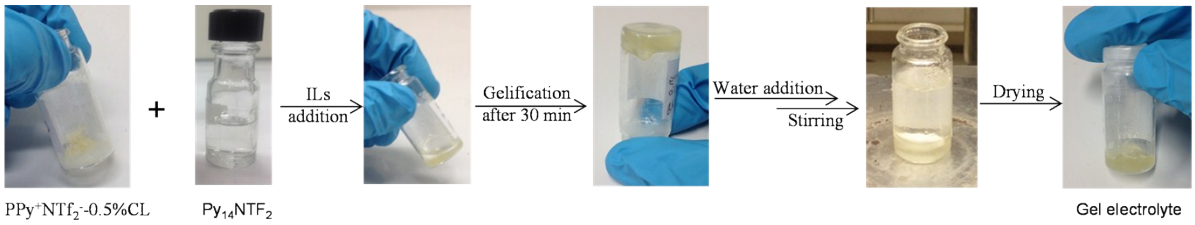
Figure S10. TGA spectrum of 25% wt. gel of $PIm^{+}NTf_2^{-}$2.5(1g/2ml $C_1C_6ImNTf_2$, solid line), and first derivative of the spectrum (dashed line)

Anionic methathesis



Scheme S1: Metathesis reaction of poly(ionic liquids) **PNu$^+$Br$^-$X** into **PNu$^+$NTf$_2^-$X**.

Gel preparations and purification



Scheme S2: Gel formation and purification of **PPy$^+$NTf$_2$0.5** with **PY$_{14}$NTf$_2$**.

Table S1: Ratio of polymer and ionic liquids for ionic gel formation.

Polymer/IL	**$PIm^+NTf_2^-$ 0%**	**$PIm^+NTf_2^-$ 2%**	**$PIm^+NTf_2^-$ 2.5%**	**$PIm^+NTf_2^-$ 2.5%**	**$PPy^+NTf_2^-$ 0%**	**$PPy^+NTf_2^-$ 0.5%**
Weight of polymer	0.5 g	0.5 g	0.5 g	1g	0.5 g	0.5 g
$C_1C_6ImNTf_2$	2ml	2ml	2ml	2ml	-	-
$Py_{14}NTf_2$	-	-	-	-	2mL	2mL
observation	flowing	flowing	flowing slowly	not flowing	flowing	not flowing