Supporting Information: Poly(diallyldimethylammonium) based poly(ionic liquid) di and triblock Copolymers by PISA as matrices for ionogel membranes

Experimental Part

Materials

Sodium hydroxide pellets(Fisher), bromoacetic acid (Acros, 99%), ammonium chloride (Acros), potassium hydrogen carbonate (Fisher), ethanol (EtOH, Scharlab, 96%), acetone (Scharlab, tech. grade), CH_2Cl_2 (DCM, tech. grade, Scharlab), chloroform ($CHCl_3$, tech. grade, Scharlab), dimethylformamide (DMF, tech. grade, Acros), HCl (tech. grade, Fisher), Lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$, Solvionic, 99.9%) were all used as received. Diallyldimethylammonium chloride solution (DADMAC sol., 65 wt. % in H_2O), 2,2-azobis(2-methylpropionamidine) dihydrochloride (AIBA, 97%), potassium ethyl xanthogenate (96%), 2-bromopropionyl bromide (97%), styrene (St, >99%) magnesium sulfate ($MgSO_4$, >99.5%), triethylene glycol (EG_3, 99%), pyridine (99.5%), acrylamide (>98%) and all deuterated solvents (D_2O, $CDCl_3$) were all purchased from Sigma Aldrich and used as received. Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide (C_3mpyrFSI, Solvionic 99.9%), sodium bis(fluorosulfonyl)imide (NaFSI, Solvionic 99.7%) were used as received.

Characterization

Nuclear Magnetic Spectroscopy (NMR) analysis

The different RAFT agents were analyzed by ^{1}H NMR with a Bruker Advance 300 MHz in $CDCl_3$.

The conversion of MADIX/RAFT polymerization of DADMAC was monitored by ^{1}H NMR with a Bruker Advance 300 MHz in D_2O. The estimation of the conversion of DADMAC was calculated via this formula using the integration of monomer and polymers:

$$conv._{DADMAC}(\%) = \frac{\int_{0.95\,ppm}^{1.85\,ppm} CH_2(PDADMAC)}{\left(\int_{5.50\,ppm}^{5.80\,ppm} CH_2\,(DADMAC) + \int_{0.95\,ppm}^{1.85\,ppm} CH_2(PDADMAC)\right.} \times 100 \qquad (1)$$

Gravimetric analysis

The conversion of St in PISA polymerization was evaluated gravimetrically following this formula:

$$conv._{St}(\%) = \frac{m_{dry} - (m_{liq} \times \frac{m_{macroCTA}}{m_{TOT}} \times 100)}{m_{liq}} \times \frac{m_{TOT}}{m_{St}} \times 100 \qquad (2)$$

where m_{dry} is the mass of solid after drying in oven overnight; mL_{iq} is the mass of the liquid sample; $m_{macroCTA}$, m_{AIBA} and m_{St} correspond respectively to the initial masses of the macroCTA, radical initiator AIBA and styrene; m_{TOT} is the sum of $m_{macroCTA}$, m_{AIBA}, m_{St} and m_{H2O}.

Aqueous Size Exclusion Chromatography (SEC)

The molar mass of the polymers was analyzed by SEC/MALS/RI. The equipment was composed by a LC20 pump (Shimadzu) coupled to a miniDawn Treos multiangle (3 angles) light scattering laser and an OptilabT- Rex differential refractometer (all from Wyatt Technology Corp., USA). Separation was carried out using three columns in series (Ultrahydrogel 120, 250, and 2000 with pore sizes of 120, 250, and 2000 A, respectively, Waters, Barcelona, Spain). The analyses were carried out at 35°C and a 0.3M CH_3COOH/ 0.2M CH_3COONa water solution as mobile phase at a flow rate of 0.6 mL/min. The refractive index increment was dn/dc= 0.1887 mL/g and reported from the literature.[1]

DMF LiTFSI Size Exclusion Chromatography (SEC)

A 1200 Infinity gel permeation chromatograph (GPC, Agilent Technologies) was used to determine M_n, M_w and Đ of the copolymers. The chromatograph was equipped with an integrated IR detector, a PLgel 5 mm MIXED-D column and a PLgel guard column (Agilent Technologies). The eluent was a 0.1 M Li(CF3SO2)2N solution in DMF and the flow rate was of 1.0 mL min-1 at 50ºC. PMMA standards (Agilent Technologies, Mp = 0.55 - 1568 x10^3) were used to perform calibration.

Matrix-Assisted Laser-Desorption Ionization Time of Flight (MADLI-ToF)

MALDI-TOF MS measurements were performed on a Bruker Autoflex Speed system (Bruker, Germany) equipped with a Smartbeam-II laser (Nd:YAG, 355nm, 2 kHz). The spectrum was acquired in linear mode with an average of 5000 shots. The laser power was adjusted during the experiments. Polymer sample was dissolved in MeOH at a concentration of 10 mg/mL. 2,5-DHB was used as a matrix, which was dissolved in MeOH at a concentration of 20 mg/mL. NaTFA was used as cation donor (10 mg/mL dissolved in MeOH). The polymer samples were mixed with the matrix and salt at a 10:5:1 (matrix/polymer/salt) ratio. Approximately 0.5 µL of the obtained mixture were hand spotted on the ground steel target plate.

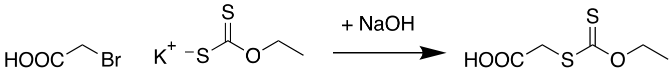
Transmission Electron Microscopy (TEM)

TEM analysis was done on a TECNAI G2 20 TWIN operated at 200 kV and equipped with LaB6 filament. Samples used for TEM analysis were prepared via dispersion into water. A drop of suspension was spread onto a TEM cooper grid (300 Mesh) covered by a pure carbon film and dried at ambient temperature. The grid was glow discharge before put the drop of suspension.

Synthetic part

Synthesis of Monofunctional Chain Transfer Agent (CTA): S-Ethoxythiocarbonyl Mercaptoacetic Acid (XAA)

The synthetic procedure has been modified from the litterature.[2,3] NaOH (2.5g, 62.4 mmol) was first dissolved in chilled MilliQ water (100 mL), followed by addition of bromoacetic acid (1 eq, 8.67 g, 62.4 mmol) until reaching a clear solution. Potassium ethyl xanthogenate (1 eq, 10 g, 62.4 mmol) was then added portion wise to the mixture with a spatula. The solution was stirred at room temperature for 24h, followed by acidification with 4 M HCl_{aq} to pH ~ 1. The resulting mixture was then extracted with chloroform (3 × 150 mL). The combined organic extract was dried over anhydrous $MgSO_4$, filtered twice, and concentrated under vacuum. The solid was dried in oven at rt under vacuum to give the final brown product (8.67 g, 77% yield). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.43 (t, 3H, CH_3), 3.97 (s, 2H, CH_2), 4.65 (q, 2H, CH_2).



Scheme S1. Synthesis of monofunctional CTA: XAA.

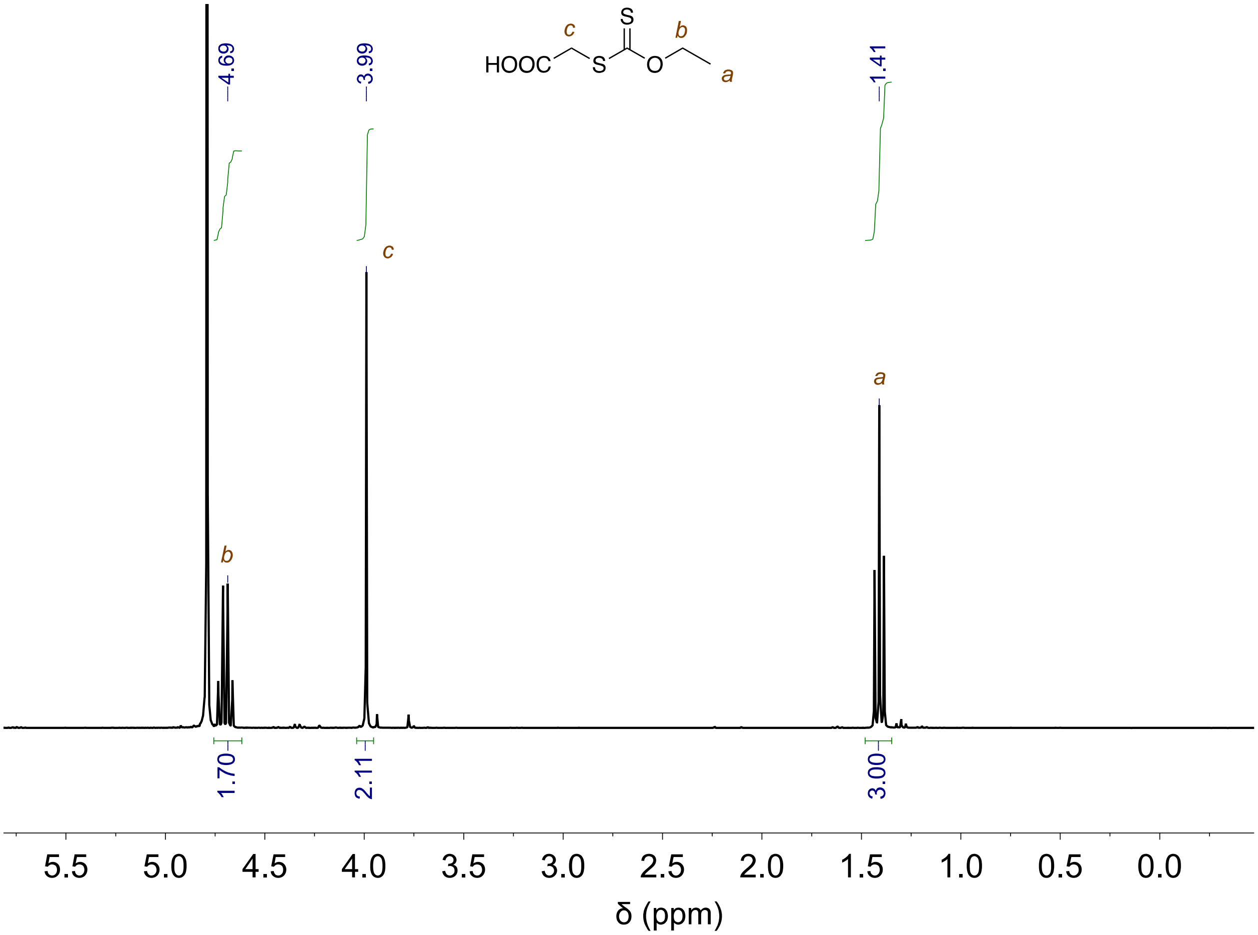


Figure S1. ^{1} H NMR (300 MHz, D_2O) of monofunctional CTA: XAA.

Synthesis of Difunctional CTA: X-PAm-DiEst-PAm-X (X-AdA-X)

A. Synthesis of X-DiEst-X.

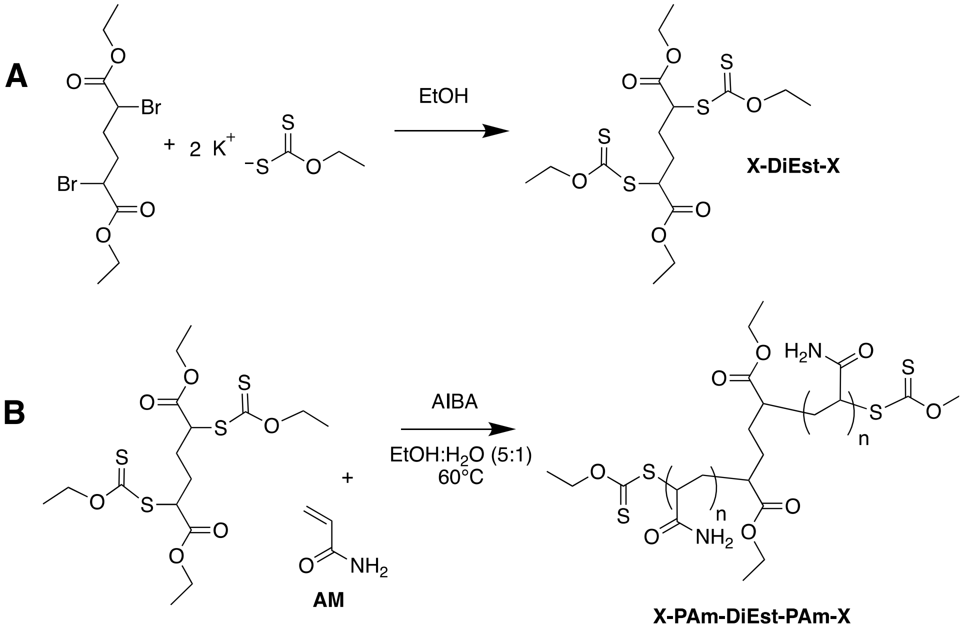
The following procedure was inspired from a patent developed in Rhodia Industries.[4] In a round bottom flask of 500 mL, diethyl meso-2,5-dibromoadipate (10 g ; 27.7 mmol) is dissolved in EtOH (96%) (250 mL) at room temperature. After dissolution, potassium ethyl xanthogenate (11.11 g ; 69.3 mmol) is added in the medium with a spatula during 90 min. The reaction takes place at room temperature during 4h. When the reaction is finished, potassium bromide salt is filtred and EtOH evaporated under vacuum. The product is solubilized in DCM and washed three times in distillated H_2O to remove the excess of potassium ethyl xanthogenate. After evaporation of DCM, the product is dried under vacuum during 24h. A yellow liquid is obtained with a yield of 90 % (11.02 g).

^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 4,65-4,61 (q, 4H, $-S=C-O-C\mathbf{H_2}-CH_3$); 4,42-4,38 (m, 2H, $-CH_2-C\mathbf{H}-CO-O-$); 4,25-4,17 (q, 4H, $-O=C-$ $O-C\mathbf{H_2}-CH_3$); 2,17-1,97 (m, 4H, $-CH-C\mathbf{H_2}-$); 1,46-1,43 (t, 6H, $-S=C-O-CH_2-C\mathbf{H_3}$); 1,33-1,25 (t, 6H, $-$ $O=C-O-CH_2-C\mathbf{H_3}$).

B. Synthesis of X-PAm-DiEst-PAm-X (X-AdA-X).

X-DiEst-X (1 eq, 2.496 g, 5.64 mmol), acrylamide (20 eq, 8.01g, 112.8 mmol) and radical initiator AIBA (0.04 eq, 0.069 g, 0.25 mmol) were placed in a 50 mL Schlenck and dissolved in 5 mL of water and 22 mL of EtOH. The polymerization was followed by ^1H NMR in D_2O and stopped after 1h with the formation of a white precipitate at the bottom of the Schlenck and reaching a conversion close to 50%. The polymer was first dissolved in water (20 mL) and precipitated twice in acetone and dried under vacuum to obtain a clear yellow powder. The polymer was then anaylyzed by ^1H NMR, SEC and MALDI-TOF. The related molecular weight of the X-PAm-DiEst-PAm-X MacroCTA with the corresponding method is $M_{n\ NMR} = 2850$, $DP_{NMR} = 34$; $M_{n\ MALDI} = 1850$, $Đ_{MALDI} = 1.02$, DP = 26.

^1H NMR (300 MHz, D_2O) δ (ppm): 4.67-4.55 (q, 4H, $-S=C-O-C\mathbf{H_2}-CH_3$), 4.26-4.16 4,42-4,38 (m, 2H, $-CH_2-C\mathbf{H}-COO-$), 4.16-4 (t, 2H of the last unit of PAm, $-S-C\mathbf{H}(CONH_2)-CH_2-$), 4.16-4.02 (m, 4H, $O=C-O-C\mathbf{H_2}-CH_3$), 2.66-2.23 (m, 4H, $-CH-C\mathbf{H_2}-$), 2.23-1.38 (m, 3H of PAm units, $-C\mathbf{H}(CONH_2)-C\mathbf{H_2}-$), 1.38-1.28 (t, 6H, $S=C-O-CH_2-C\mathbf{H_3}$, 1.28-1.14 (t, 6H, (m, 4H, $O=C-O-CH_2-C\mathbf{H_3}$).



Scheme S2. Synthesis of Difunctional CTA: X-PAm-DiEst-PAm-X (X-PAm-X)

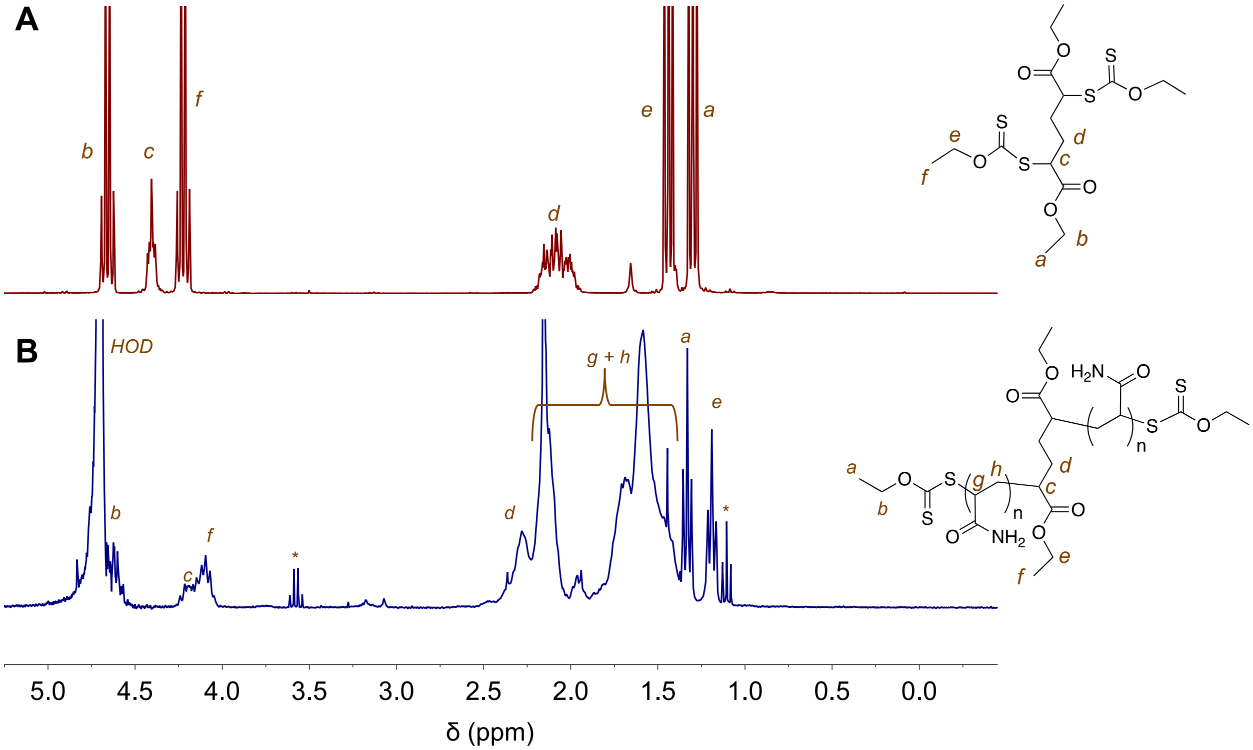


Figure S2. ^{1}H NMR (300 MHz) of difunctional CTA: (A) X-DiEst-X in $CDCl_3$ and (B) X-PAm-DiEst-PAm-X in D_2O (* indicates the remaining ethanol from the purification).

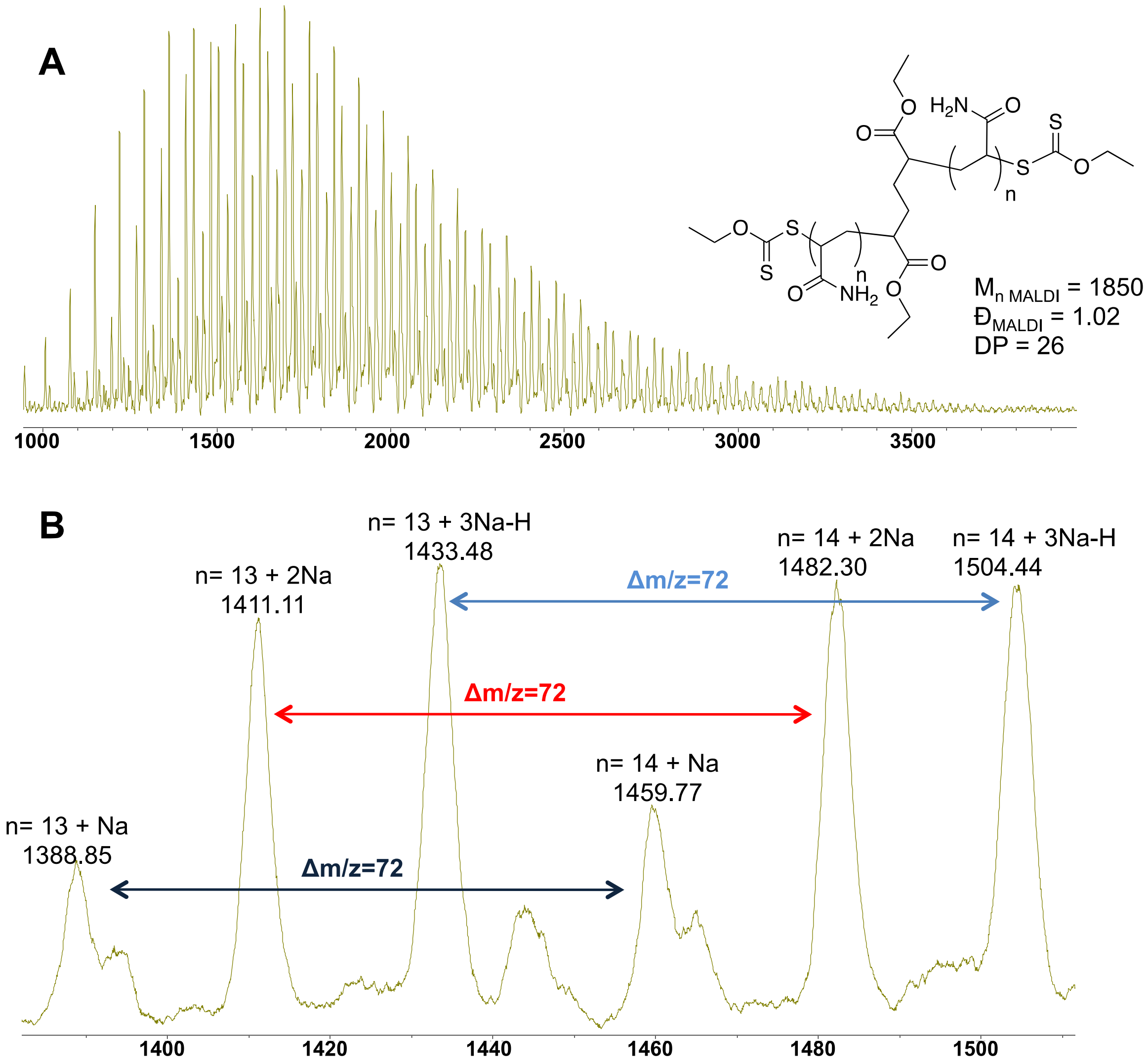


Figure S3. MALDI-ToF analysis of X-PAm-DiEst-PAm-X (X-AdA-X):

MADIX/RAFT Polymerization of DADMAC in water

In a typical experiment, RAFT CTA (XAA) (1 eq, 0.041 g, 0.23 mmol) and radical initiator AIBA (0.3 eq, 0.019 g, 0.07 mmol) were placed in a 50 mL Schlenck tube and solubilized with 8 mL of water. A commercial solution of 65% wt. of DADMAC (175 eq, 10 mL, 6.5 g, 40.37 mmol) is then added in the Schlenck and the mixture is stirred and degassed under N_2 during 30 min. pH of the mixture is close to 5 and the concentration ratio was [DADMAC]/[CTA]/[AIBA] = 175/1/0.3. The polymerization started by immersing the Schlenck in the oil bath pre-heated to 60°C. Aliquots were taken every hour for conversion values calculated by ^1H NMR (See Equation 1) and for molecular weights by GPC, until reaching a maximum conversion of 75%. The final polymer was precipitated in a 1:1 mixture of EtOH:Acetone, the solid was filtrated and placed under vacuum at 40°C to remove the solvents. The precipitated polymer was then analyzed by ^1H NMR in D_2O.

The same procedure was applied varying the concentration ratio and the type of the CTA, *i.e.* X-PAm-X.

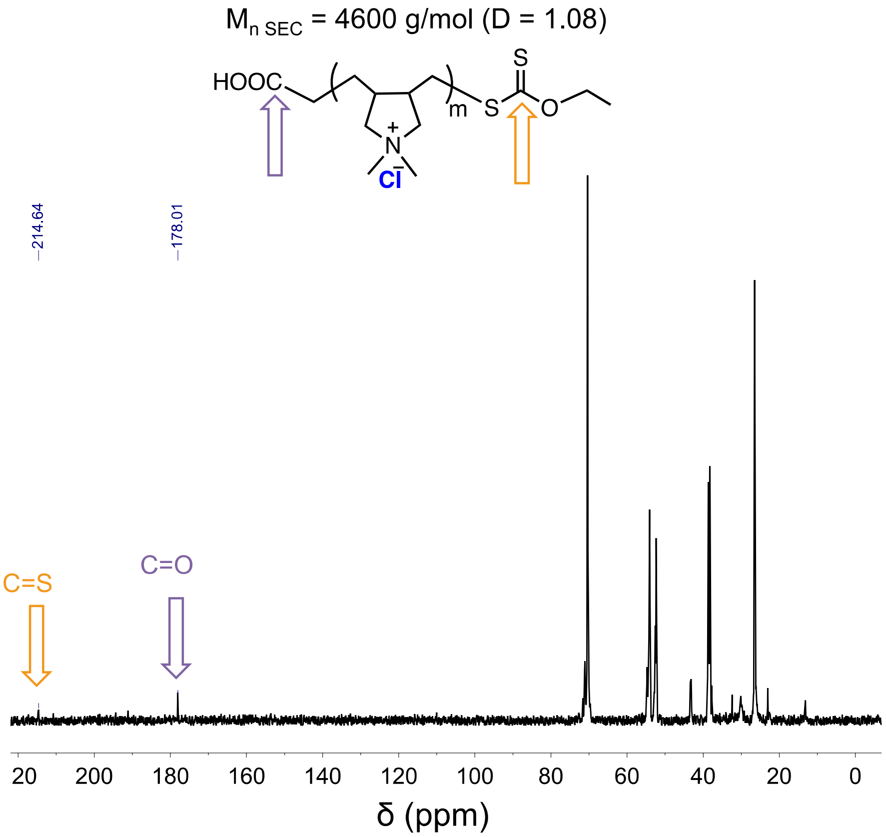


Figure S4. ^{13}C NMR (300 MHz) of small molecular weight PDADMAC.

Synthesis of Poly(Styrene) block copolymer latexes by Polymerization-Induced Self-Assembly (PISA) using PDADMAC macroCTA

All emulsions were carried out in a 50 mL round-bottom flask equipped with a three-way stopcock to avoid the entry of oxygen and allow the sampling. Two main parameters were studied in this section: the type of macroCTA (mono- or difunctional) and the chain length of Poly(Styrene) (PS) by changing the ratio of styrene compared to the macroCTA.

In a typical PISA experiment, monofunctional macroCTA (17 800 g/mol, 0.944 g, 0.053 mmol), AIBA (0.003 g, 0.01 mmol) and 25 mL of MilliQ water were transferred in the round-bottom flask and degassed with N_2 during 30 min. In another flask, distillated styrene was slowly bubbled with N_2 during 30 min. Styrene (2.5 mL, 21.78 mmol) was then transferred in the round-bottom flask, giving a global mixture with a concentration ratio of [St]/[macroCTA]/[AIBA] = 410/1/0.3 and a 88% wt of St solution. The polymerization started by immersing the flask in the oil bath pre-heated to 60°C. Samples were withdrawn to calculate the conversion of St by gravimetric analysis (See Equation 2). After 24h (100% conversion St), the white emulsion is maintained as crude solution in water at + 6°C. Samples from the crude solution were analyzed by TEM and DLS analysis for the determination of the particles size and morphology. Anion exchange is then performed on the final polymer latexes by adding a water solution (5 mL) composed of an excess of $LiNTf_2$ salts (1.1 eq compared to initial amount of macroCTA). This solution was stirred overnight to allow the complete anion exchange and the precipitated polymer is filtrated and washed on filter with water. The molecular weight of the latex (M_n = 30.1 g/mol; M_w/M_n = 1.72) was calculated by SEC in 0.01 M $LiNTf_2$ DMF solution after anion exchange of the copolymer (Cl^-/Tf_2N^-) and using PMMA standards.

Similar procedure was used for difunctional macroCTAs (formation of triblocks) and all data of SEC are mentioned in Table S1 and S2.

Table S1. Aqueous emulsion polymerization of Styrene (12 wt. %) using PDADMAC macroCTA.[a]

Entries	**PDADMAC CTA ($M_{n\ SEC}$)[b]**	**$M_{n\ target\ PS}$ (kg/mol)[c]**	**$DP_{target\ PS}$[c]**	**DLS**		**TEM**
				D_h (nm)	PdI	D_n (nm)
Latex 1	$PDADMAC_{18k}$	43	820	429 ± 6	0.04	230 ± 40
Latex 2	$PDADMAC_{31k}$	74	684	618 ± 14	0.15	320 ± 30
Latex 3	$PDADMAC_{13k}$	20	188	242 ± 1	0.04	156 ± 19
Latex 4	$PDADMAC_{13k}$	6	66	268 ± 6	0.03	143 ± 24
Latex 5	$PDADMAC_{13k}$	60	582	224 ± 5	0.01	150 ± 21

[a] *Conditions: solid content = 12 % wt., Time = 24h.*

[b] *Determined by SEC in H_2O (CH_3COOH/CH_3COONa 0.2/0.3M)*

[c] *Calculation based on the $M_{n\ SEC}$ of macroCTA.*

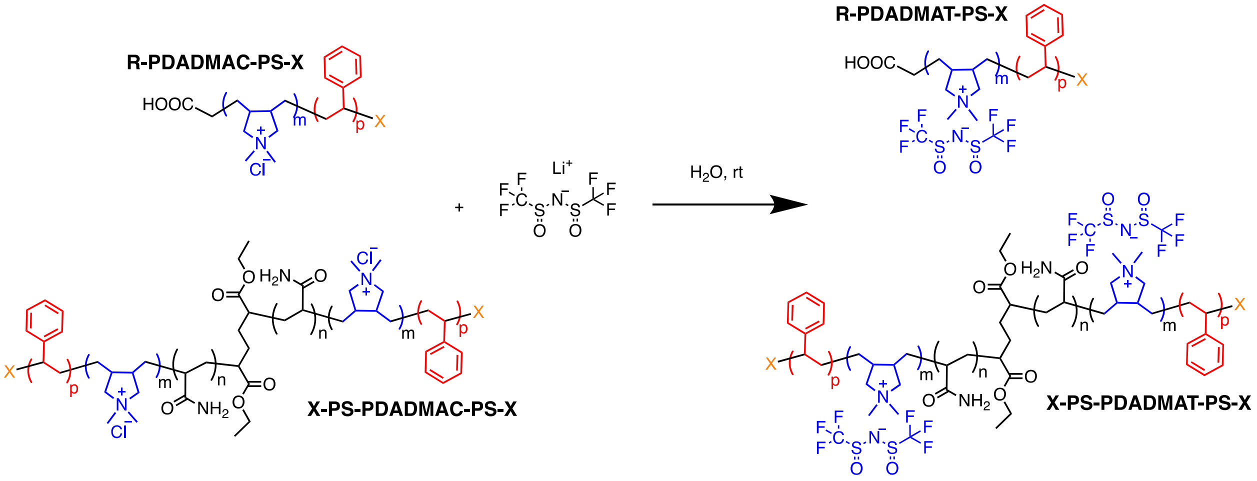
Table S2. Anion exchange data of the block copolymers.[a]

Entries	**PISA**	**Anion exchanged Block copolymers with TFSI anions**		
	PDADMAC CTA ($M_{n\ SEC}$)[b]	**Block copolymers (Target M_n)**	**$M_{n\ PDADMAT\ SEC}$ (kg/mol) [M_w/M_n][c]**	**$M_{n\ block\ copo\ SEC}$ (kg/mol) [M_w/M_n][c]**
1	$PDADMAC_{18k}$	$PDADMAT_{41k}$-PS_{43k}	30.1 [1.72]	96.3 [6.83]
2	$PDADMAC_{31k}$	PS_{37k}-$PDADMAT_{69k}$-PS_{37k}	68.2 [1.64]	90.8 [7.23]
3	$PDADMAC_{13k}$	PS_{10k}-$PDADMAT_{27k}$-PS_{10k}	18 [1.46]	31.1 [7.59]
4	$PDADMAC_{13k}$	PS_{3k}-$PDADMAT_{27k}$-PS_{3k}	18 [1.46]	18.3 [3.48]
5	$PDADMAC_{13k}$	PS_{30k}-$PDADMAT_{27k}$-PS_{30k}	18 [1.46]	66.6 [6.93]

[a] *Conditions: solid content = 12 % wt., Time = 24h.*

[b] *Determined by SEC in H_2O (CH_3COOH/CH_3COONa 0.2/0.3M)*

[c] *Determined by SEC in DMF (0.1M LiTFSI)*



Scheme S3. Anion exchange of PDADMAC with LiNTf$_2$ salt.

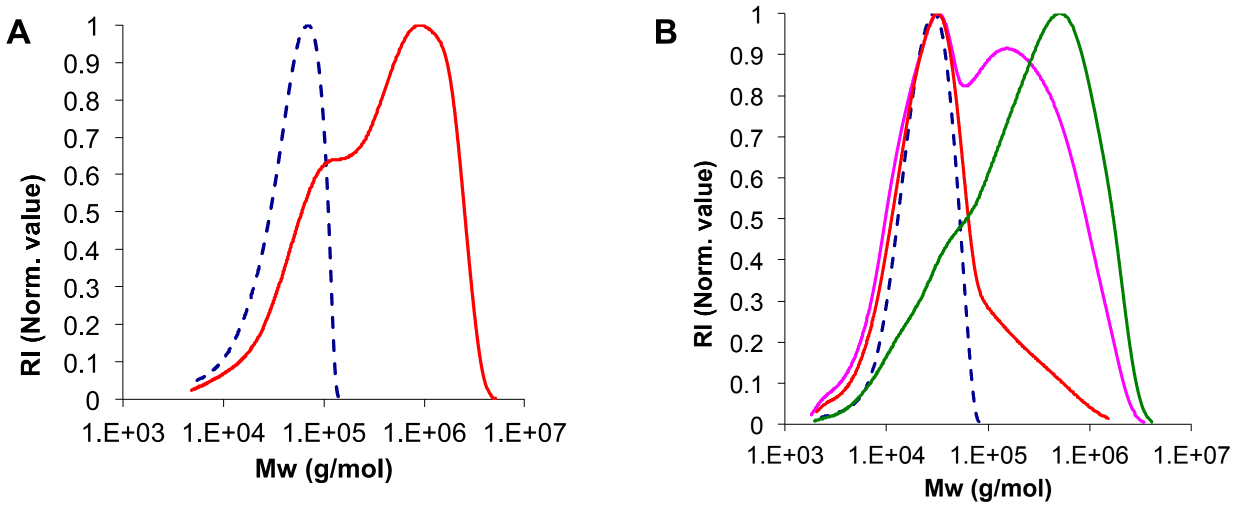


Figure S5. SEC traces of BCPs before centrifugation: (A) formation diblock PDADMAT$_{41k}$ PS$_{43k}$ and (B) formation triblocks PS$_{10k}$-PDADMAT$_{27k}$-PS$_{10k}$ (pink), PS$_{3k}$-PDADMAT$_{27k}$-PS$_{3k}$ (red), PS$_{30k}$-PDADMAT$_{27k}$-PS$_{30k}$ (green).

Ionogel membranes preparation

NaFSI was dissolved in C$_3$mpyrFSI ionic liquid to make the initial ionic liquid electrolyte (ILE) solution. After, ionogel membranes were synthesized by mixing the PS$_{10k}$-PDADMAT$_{27k}$-PS$_{10k}$ with the ILE solution in different ratio. Both ILE and PS$_{10k}$-PDADMAT$_{27k}$-PS$_{10k}$ were mixed in 0.5mL of toluene and stirred for 10 hours. Once the mixture was homogeneous the solubilised ionogel was casted on a Teflon surface and dried under the fume hood for 4 hours. Finally, the ionogel membranes were fully dried at 70°C under vacuum for 10 hours before using them. White self-standing flexible membranes were obtained as it is shown in Figure S6. As a first observation, increasing the ionic liquid concentration in the membrane, results in more flexible and softer membranes. The PS$_{10k}$-PDADMAT$_{27k}$-PS$_{10k}$ can withstand a maximum amount of 70-80 wt.% of ILE solution in a self-standing membrane. Beyond this point the ionogel became soft and not easy to handle it.

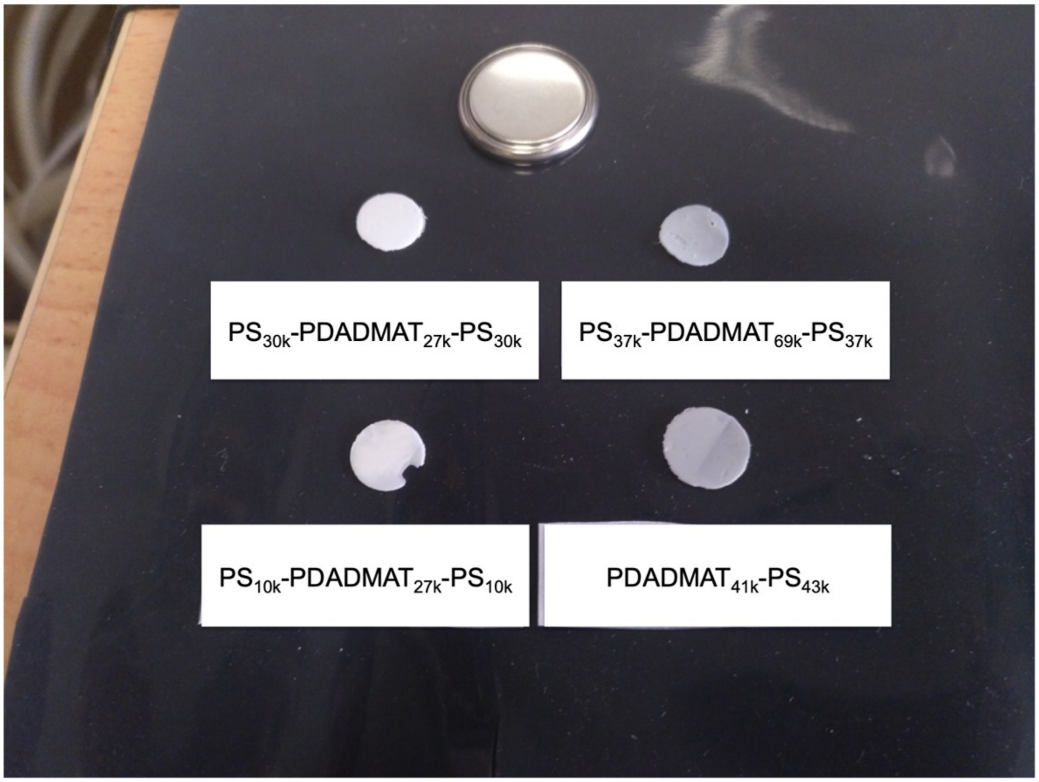


Figure S6. Photograph of PDADMAT-*b*-PS block copolymers.

Ionic conductivity

The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) using a Autolab 302N Potentiostat Galvanostat coupled to a Microcell HC station to control the temperature during the measurements. Circular ionogel membranes were cut and used for the measurements (diameter = 11 mm) with a thickness of 150 µm. The membranes were sandwiched between two stainless steel electrodes and sealed in Teflon Microcell under argon atmosphere in a glove box. The measurements were carried out from 20°C to 80°C with a step of 10°C holding the temperature for 20 minutes before each temperature to allow temperature equilibration. The frequency range was set from 0.1 MHz to 0.1 Hz and the amplitude was 10 mV. Finally, the conductivity was calculated following this equation:

$$\sigma=\frac{l\ 1}{AR_b}$$

Where l the thickness of the sample is, A is the surface of the membrane in contact with the electrode and R_b is the bulk resistance of the sample extracted from the Nyquist plot.

References

(1) Liu, X.; Haddou, M.; Grillo, I.; Mana, Z.; Chapel, J.-P.; Schatz, C. Early Stage Kinetics of Polyelectrolyte Complex Coacervation Monitored through Stopped-Flow Light Scattering. *Soft Matter* **2016**, *12*, 9030–9038.

(2) Kricheldorf, H. R.; Schwarz, G. Poly(thioester)s. *J. Macromol. Sci. Part A Pure Appl. Chem.* **2007**, *44*, 625–649.

(3) Cao, J.; Siefker, D.; Chan, B. A.; Yu, T.; Lu, L.; Saputra, M. A.; Fronczek, F. R.; Xie, W.; Zhang, D. Interfacial Ring-Opening Polymerization of Amino-Acid-Derived N-Thiocarboxyanhydrides Toward Well-Defined Polypeptides. *ACS Macro Lett.* **2017**, *6*, 836–840.

(4) Destarac, M.; Bzducha, W. Controlled Mini-Emulsion Free Radical Polymerization. *PCT Int. Appl.* **2003**, No. WO2003002614A2.