

Supporting Information

Synthesis of Triblock Copolymers Composed of Poly(vinylidene fluoride-*co*-hexafluoropropylene) and Ionic Liquid Segments

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Experimental

Materials. All reagents were used without further purification. 4-(chloromethyl)benzoyl chloride, lithium peroxide, 2-[2-(2-chloroethoxy)ethoxy]ethanol, sodium iodide, methacryloyl chloride, 1-butylimidazole, 2,6-di-*tert*-butyl-4-methylphenol, sodium tetrafluoroborate, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), 3-mercapto propionic acid, potassium phosphate, carbon disulfide, sodium sulfate, 2,2'-azobis(2-methylpropionitrile), anhydrous acetonitrile, anhydrous dimethyl formamide were purchased from the Aldrich Chemical Co. Vinylidene fluoride (VDF) and hexafluoropropylene (HFP) were purchased from SynQuest Laboratory Inc. and used as received.

Synthesis of 4-chloromethyl benzoyl peroxide (2). To a 20 mL aqueous solution of Li₂O₂ (1.38 g, 30 mmol), 4-(chloromethyl)benzoyl chloride (4.44 g, 23.5 mmol) in Et₂O/hexane (40 mL, 1:1) was added slowly at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. The reaction mixture was diluted by addition of chloroform (100 mL), and filtered and washed with water (2×30 mL). The organic phase was separated, and the aqueous phase was extracted with chloroform (2×20 mL). The combined organic phases were dried over MgSO₄. Removal of solvent yielded a white solid (1.8 g, 45%). ¹H NMR (CDCl₃, ppm): δ 8.12 (d, ArH), 7.56 (d, ArH), 4.67 (s, -CH₂Cl).

Synthesis of the telechelic P(VDF-HFP) with benzyl chloride terminal groups. 4-Chloromethyl benzoyl peroxide (350 mg, 1.6 mmol), and acetonitrile (30 mL) were added into 70 mL Parr reactor with a magnetic stir. The gas-condense transfer of VDF (6 mL, 0.06 mol) and HFP (21 mL, 0.22 mol) were carried out with rigorous exclusion of oxygen and moisture through a dual-manifold Schlenk line with 10^{-6} Torr high vacuum. The reactor was immersed in oil bath at 90 °C for 5 h. After residual gases were discharged, the solvent was evaporated, and the residue was dissolved in acetone and precipitated from chloroform. P(VDF-HFP) was collected and dried *in vacuo* at 60 °C. ^1H MMR (acetone- d_6 , ppm): δ 8.10 (d, ArH), 7.70 (d, ArH), 4.83 (s, $-\text{CH}_2\text{Cl}$), 3.2 ($-\text{CF}_2\text{CH}_2-\text{CF}_2\text{CH}_2-$, head-to-tail structure), 2.5 ($-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$, tail-to-tail structure). ^{19}F NMR (acetone- d_6 , ppm): δ -70.0 to -80.0 ($-\text{CF}_2\text{CF}(\text{CF}_3)$), -88.0 to -95.0 ($-\text{CH}_2\text{CF}_2-\text{CH}_2\text{CF}_2$), -110.0 ($-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CF}(\text{CF}_3)$), -113.0 to -116.0 ($-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2-$), -179 to -185 ($-\text{CF}_2\text{CF}(\text{CF}_3)$). M_n (NMR) 16 kDa.

Synthesis of P(VDF-HFP) macro-CTA. To a suspension of K_3PO_4 (3.89 g, 11.5 mmol) in acetone (15 mL), 3-mercapto propionic acid (0.5 mL, 5.75 mmol) was added and the reaction mixture stirred for 20 min. After adding carbon disulfide (0.66 mL, 10.9 mmol), the mixture was stirred overnight. The telechelic P(VDF-HFP) (2 g) was dissolved in 5 mL acetone, added to the reaction mixture and stirred overnight at 80 °C. After the resulting solids were filtered off and the solvent was evaporated, the residue was dissolved in acetone and precipitated from chloroform. ^1H MMR (acetone- d_6 , ppm): δ 8.10 (d, ArH), 7.70 (d, ArH), 4.83 (s, $-\text{CH}_2\text{Cl}$), 3.2 ($-\text{CF}_2\text{CH}_2-\text{CF}_2\text{CH}_2-$, head-to-tail structure), 2.5 ($-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$, tail-to-tail structure).

Synthesis of 1-[2-methacryloyloxy]-3, 6-dioxa-octyl]-3-butylimidazolium tetrafluoroborate (MDBIm-BF₄). 8-Iodo-3,6-dioxaoctan-1-ol(triethylene-glycol monoiodohydrin). 2-[2-(2-Chloroethoxy)ethoxy]-ethanol (33.6 g, 0.2 mol), and NaI (30 g) were refluxed in 100 mL of dry acetone for 3 days. The precipitate was filtered off and the solvent was evaporated. The residue was dissolved in ether, filtered from insoluble parts, and evaporated. The crude product as brownish oil was used without further

purification. Yield: 43 g (83%). ^1H NMR (CDCl_3 , ppm): δ 2.42 (s, -OH), 3.29 (t, -CH₂-I), 3.5-3.8m (m, -O (CH₂-CH₂-O)₂ -CH₂-).

8-Iodo-3,6-dioxa-octyl methacrylate. 8-Iodo-3,6-dioxaoctan-1-ol (39 g, 0.15 mol) was dissolved in 400 mL of dry ether, and added triethylamine (15.2 g, 0.15 mol). While cooling with ice, methacryloyl chloride (15.7 g, 0.15 mol) in 50 ml ether was added slowly. The mixture was stirred overnight, filtered, and extracted with water, then dried over MgSO_4 , and evaporated to produce the product as yellow oil. Yield: 40.3 g (82%) yellow oil. ^1H -NMR (CDCl_3 , ppm): δ 1.96 (s, =C-CH₃), 3.27 (t, -CH₂-I), 3.5-3.9 (m, CH₂-O-CH₂-CH₂-O-CH₂-), 4.31 (t, -COO-CH₂-), 5.59 (s, CH=C-COO-trans), 6.14 (s, CH=C-COO-cis).

1-[2-methacryloyloxy]-3, 6-dioxa-octyl]-3-butylimidazolium tetrafluoroborate (MDBIm-BF₄). To a mixture of 1-butyl imidazole (4.96 g, 0.040 mol), and 8-iodo-3,6-dioxa-octyl methacrylate (13.12 g, 0.040 mol), 0.1 g of 2,6-di-*tert*-butyl-4-methylphenol was added. The reaction mixture was stirred at 40 °C for 48 h. The mixture was dissolved in 24 mL of anhydrous acetonitrile and was added to a suspension of NaBF₄ (5.27 g, 0.048 mol) in 50 mL of anhydrous acetonitrile. After the mixture was stirred for 48 h at room temperature, the sodium bromide precipitate was removed by filtration, and the filtrate was concentrated. The concentrated filtrate was diluted with methylene chloride (200 mL) and filtered through a silica gel column. The removal of methylene chloride yielded the imidazolium-containing monomer as a yellow viscous liquid. ^1H NMR (DMSO-d_6 , ppm): 9.21 (s, -N=CH-N-), 7.80 (d, -N-CH=CH-N-), 6.01 (s, CH=C-COO-trans), 5.70 (s, CH=C-COO-cis), 4.37 (t, -COO-CH₂-), 4.20 (t, -CH₂-N-), 3.5-3.9 (m, CH₂-O-CH₂-CH₂-O-CH₂-), 1.87 (s, =C-CH₃), 1.78 (m, -CH₂-CH₂-CH₃), 1.25 (m, -CH₂-CH₂-CH₃), 0.89 (t, -CH₃). ^{13}C NMR (DMSO-d_6 , ppm): 14.1, 18.6, 19.6, 32.4, 49.7, 64.6, 69.6, 70.5, 122.8, 123.4, 126.7, 136.6, 137.1, 167.3. MS: $[\text{C}_{17}\text{H}_{29}\text{O}_4\text{N}_2]^+$ calcd. 325, found 325.

Synthesis of the triblock copolymers. Different compositions of the triblock copolymers were prepared in the RAFT polymerization. Typical procedure: A reactor charged with AIBN (6.76 mg, 4×10^{-5} mol), P(VDF-HFP) macro-CTA ($M_n = 23$ kg/mol; 950 mg, 4×10^{-5} mol), MDBIm-BF₄ (0.82 g, 2×10^{-3} mol, 1.64 g, 4×10^{-3} mol, 2.46 g,

6×10^{-3} mol, respectively), and DMF (30 mL) was carried out with rigorous exclusion of oxygen and moisture through a dual-manifold Schlenk line with 10^{-6} Torr high vacuum. After the reactor was immersed in oil bath at 70 °C for 24 h., the reactor was rapidly cooled in cold water. The solvent was evaporated, and the residue was dissolved in acetone and precipitated in chloroform. The polymer was collected and dried *in vacuo* at 60 °C.

Anion-exchange reaction. Anion-reaction reaction of the triblock copolymer was conducted in acetonitrile at room temperature. Polymers **1-3** (0.5 g) and an excess amount of LITFSI were dissolved in acetonitrile (10 mL) and stirred for 48 h. The triblock copolymers was precipitated in deionized water, washed with deionized water several times and then dried *in vacuo* at 60 °C to obtain the triblock copolymers with TFSI counter-anion (Polymers **4-6**).

Characterization

The chemical compositions of the polymers were determined from ^1H and ^{19}F NMR on a Bruker AM-300 spectrometer. The thermal transition data were obtained by a TA Instruments Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10°C/min. The measurement temperature range was -80 to 200 °C. The glass transition temperature T_g was determined by the midpoint of total heat flow curve in the thermal transition region. The thermo-gravimetric analysis (TGA) measurement was performed on a TA Instrument model Q50 at a heating rate of 10 °C/min under N_2 from room temperature up to a maximum of 800 °C. T_d is onset decomposition temperature.

Broadband Dielectric Relaxation Spectroscopy (DRS). DRS measurements were performed on a Concept 40 system from Novocontrol GmbH, and measured over the frequency range 10 mHz to 10 MHz. Temperature was controlled by a Quatro temperature control system with a precision of greater than ± 0.1 °C. All copolymers were measured over the temperature range from -140 °C to 150 °C, well above the calorimetric T_g . Samples were prepared for DRS measurements by solution casting thin films, typically 60-70 μm thick, from a good solvent directly onto brass electrodes, 15 mm in diameter. A smaller, 5 mm diameter upper electrode was pressed onto each film.

Samples were dried under vacuum (2-3 μ bar) at room temperature ($T > T_g$) prior to measurement, and were transferred from the oven to the spectrometer as quickly as possible to avoid moisture absorption. The effects of water on glassy state dynamics are well known, so great care was taken to minimize the sample exposure to moisture.

Small-angle X-ray scattering (SAXS) was performed on a Molecular Metrology SAXS at room temperature, using Cu K_α radiation (wavelength = 1.5418 Å). The SAXS is equipped with a 2-D detector, and the scattering vector (q) range was calibrated with silver behenate.

Wide angle X-ray scattering (WAXS) was performed on a Rigaku DMAX-Rapid Microdiffractometer equipped with a 2-D detector at room temperature, also using Cu K_α radiation. For both SAXS and WAXS, software routines were used to evaluate the scattering intensity as a function of the diffraction angle of, 2θ , or q , defined as $q = 4\pi \sin(\theta)/\lambda$. Depending on the scattering intensity, samples were exposed from twenty minutes to two hours.

The same samples used for DRS measurements were used for scattering experiments. After DRS measurements were complete, samples were carefully removed from the brass electrodes and mounted in the SAXS or WAXS sample holder.

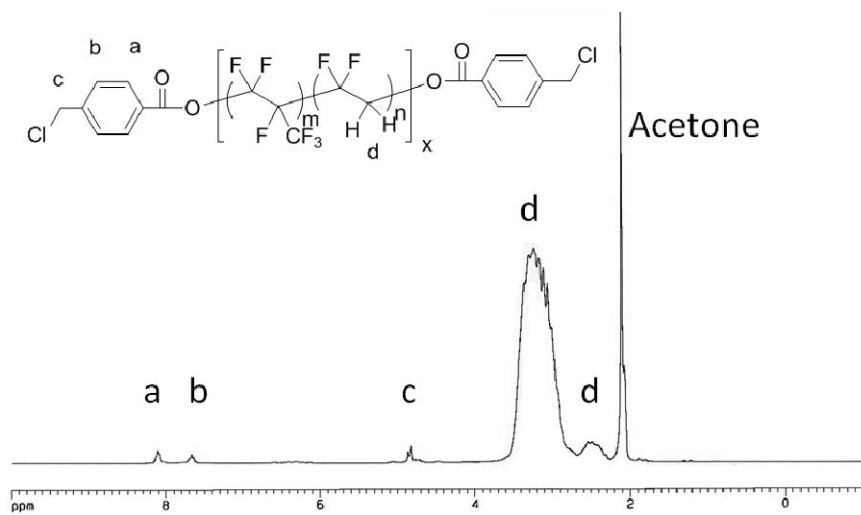


Figure S1. ¹H NMR spectrum of the telechelic P(VDF-HFP) terminated with benzyl chlorine groups.

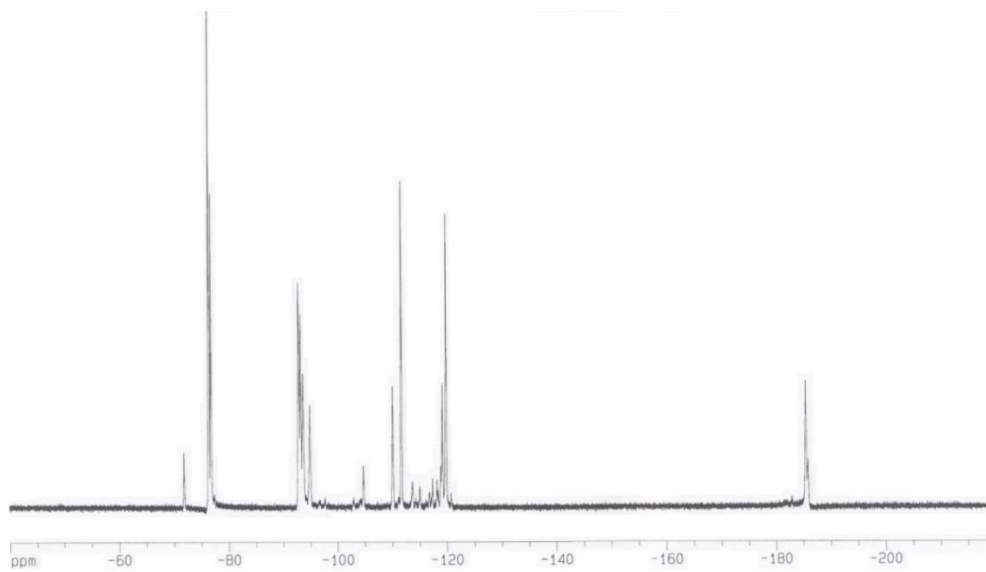


Figure S2. ¹⁹F NMR spectrum of the telechelic P(VDF-HFP) terminated with benzyl chlorine groups.

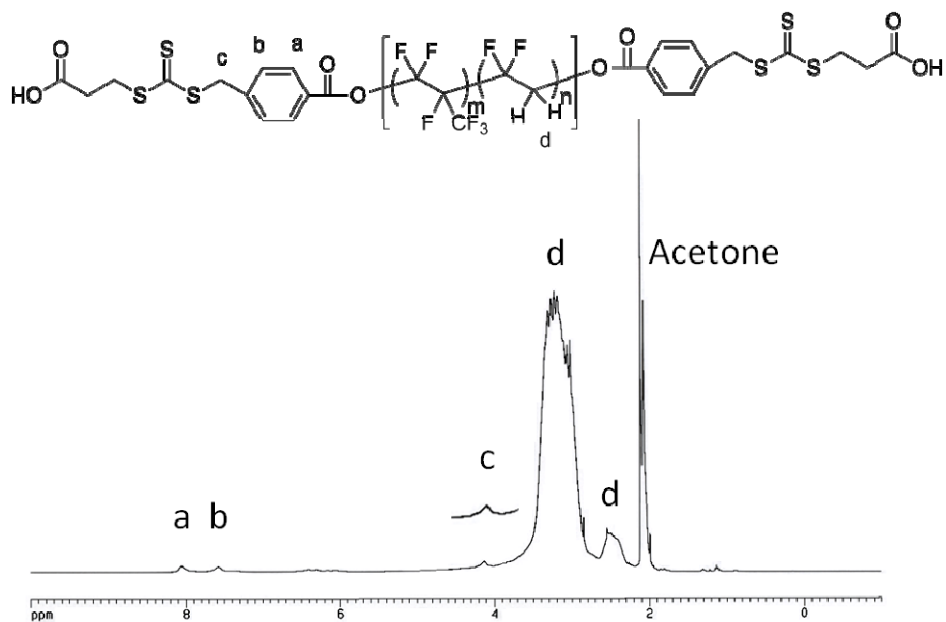


Figure S3. ¹H NMR spectrum of the P(VDF-HFP) macro-CTA.

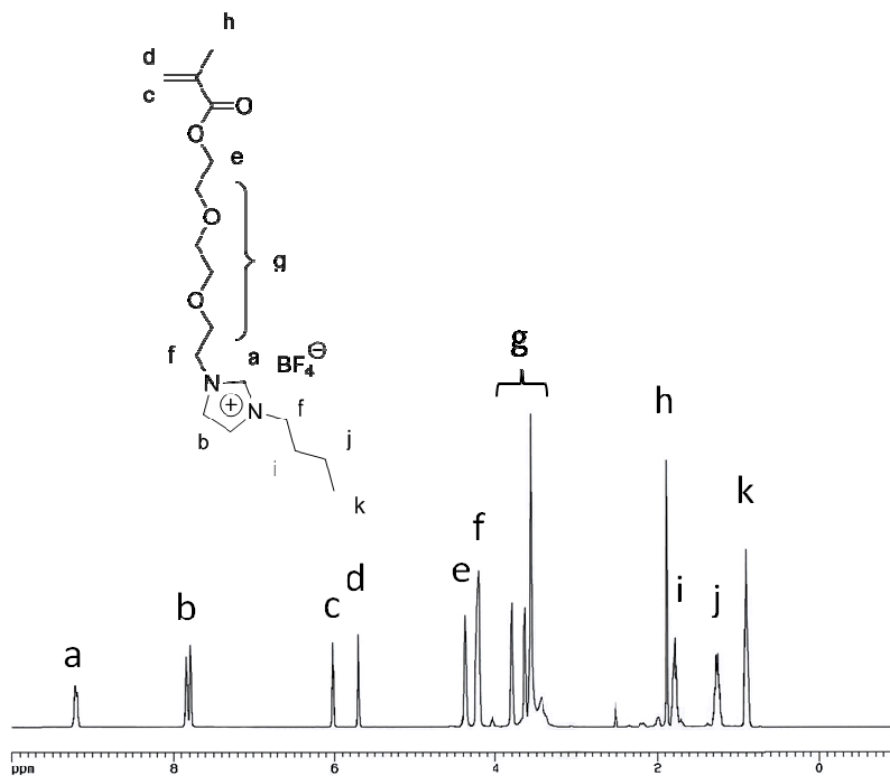


Figure S4. ¹H NMR spectrum of the monomer MDBIm-BF₄.

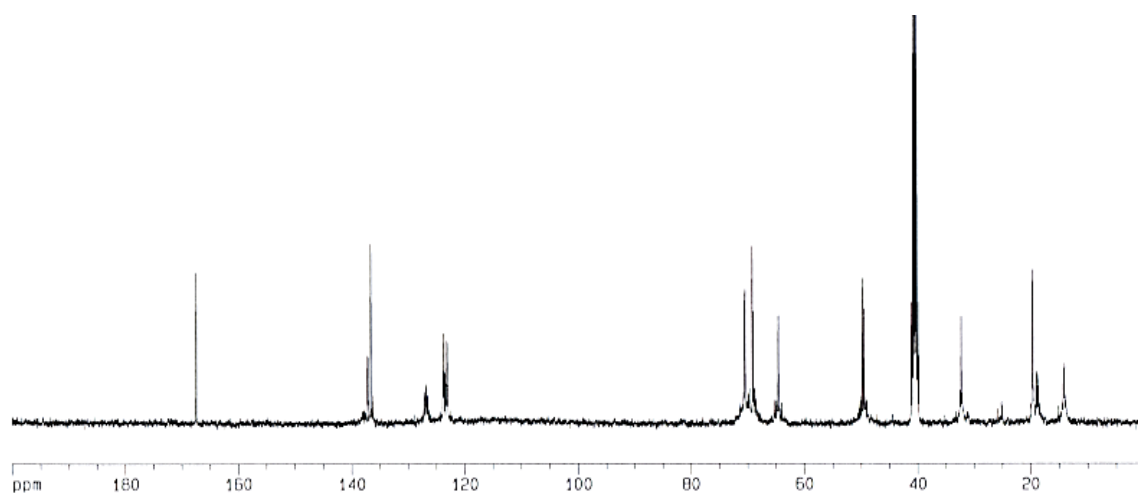


Figure S5. ^{13}C NMR spectrum of the monomer MDBIm-BF₄.

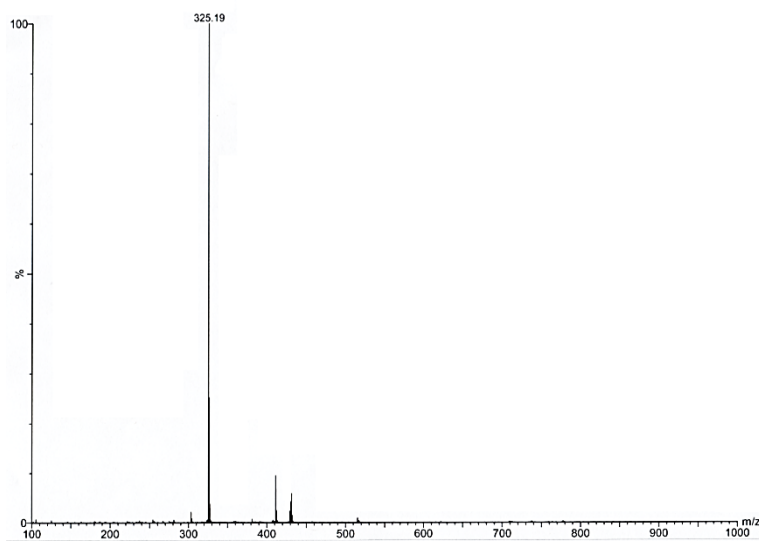


Figure S6. Mass spectrum of the monomer MDBIm-BF₄.

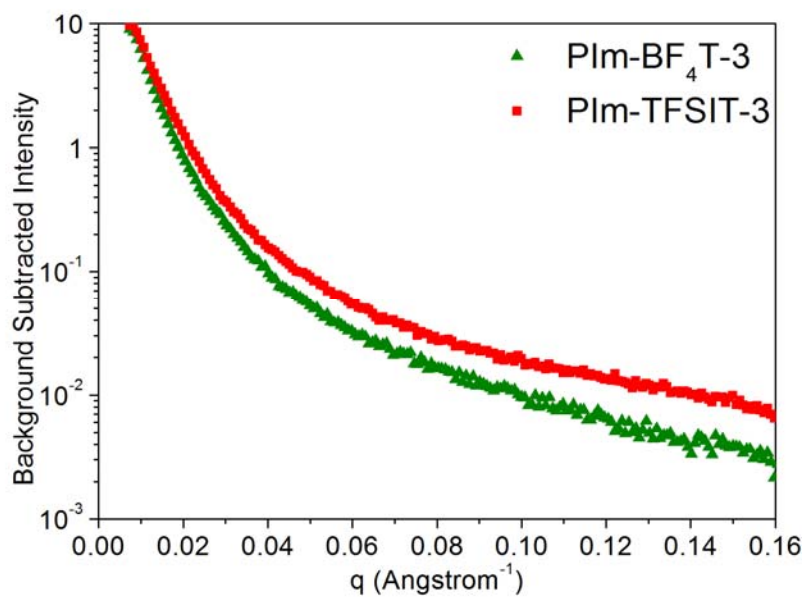


Figure S7: Background-subtracted SAXS intensity as a function of scattering vector for PIm-BF₄T-3 (Polymer 3) and PIm-TFSIT-3 (Polymer 6).

The chemical composition of P(VDF-HFP) was calculated according to the following

$$\text{equation: VDF mol\%} = \left[\frac{I_2+I_3+I_4}{2} \right] / \left[\frac{I_2+I_3+I_4}{2} + \frac{I_1}{2} \right] \times 100\%$$

Table S1: Assignments of the ^{19}F NMR signals of the telechelic P(VDF-HFP).

Chemical Shift (ppm)	Structure	Integrals
-70 to -80	$-\text{CF}_2\text{CF}(\text{CF}_3)-$	I_1
-88 to -95	$-\text{CH}_2\text{CF}_2-\text{CH}_2\text{CF}_2-$	I_2
-110	$-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CF}(\text{CF}_3)-$	I_3
-113, -116	$-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2-$	I_4
-119	$-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CF}(\text{CF}_3)-$	
-179, -185	$-\text{CF}(\text{CF}_3)\text{CF}_2$	

Table S2: Conductivity VFT fitting parameters.

Sample	σ_0 (S/cm)	B (± 10 K)	T_0 (± 3 °C)
Polymer 4	$10^{0.1}$	2950	-99
Polymer 5	$10^{-0.9}$	1980	-72
Polymer 6	$10^{-0.5}$	1850	-69
Polymer 1	$10^{-0.8}$	2990	-103
Polymer 2	$10^{-0.9}$	2530	-93
Polymer 3	$10^{-1.4}$	2030	-79

The changes in the Vogel temperature likely reflect changes in the fragility of each system. The Vogel temperatures follow the glass transition temperature trend within each series.