Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary material

New aromatic polymer electrolytes for application in lithium metal batteries

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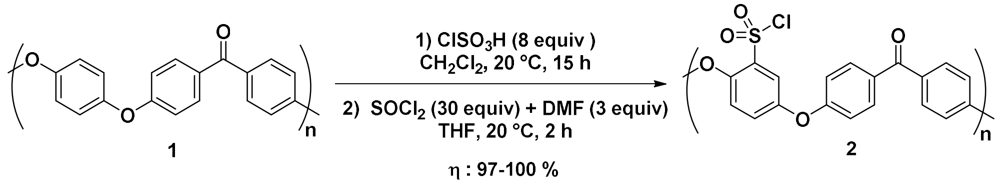
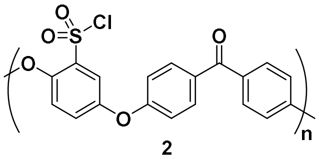
Summary:

Preparation of 2:



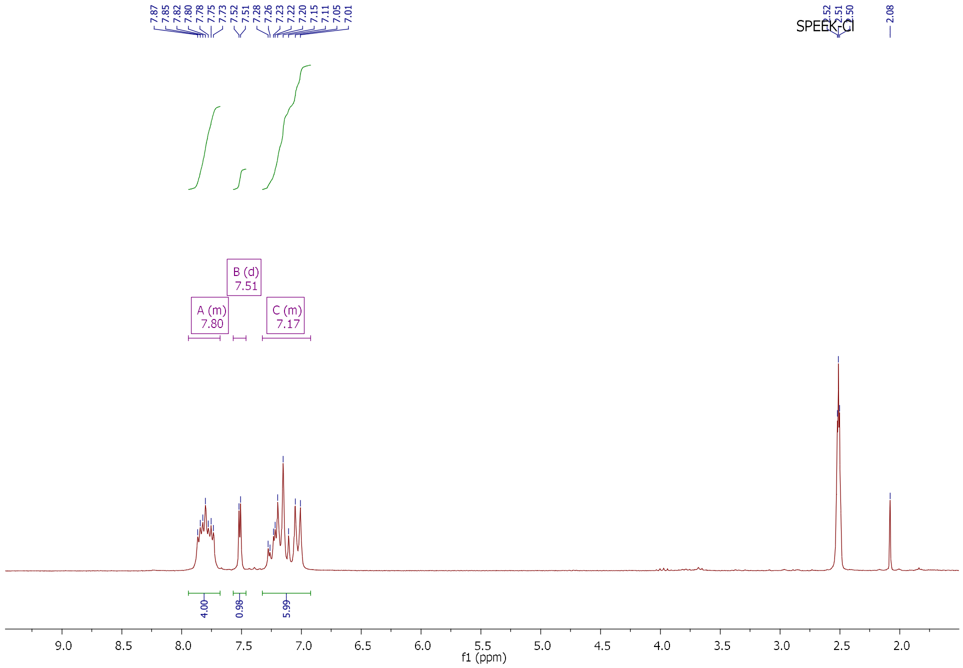
Preparation of 2: To a suspension of PEEK (**1**) (10.0 g, 34.7 mmol) in dry CH_2Cl_2 (350 mL), was added chlorosulfonic acid (18.5 mL, 278 mmol). The resulting suspension was stirred at room temperature for 15 h [Note that below five 15 hours the chlorosulfonation was only partial, but beyond this duration, neither difference nor degradation were observed]. The supernatant was separated and thionyl chloride (76 mL, 1.04 mol) and dry *N,N*-dimethyformamide (11 mL, 174 mmol) were added to the remaining gel. The resulting red slurry was stirred at room temperature for 2 h and was further diluted by the slow addition of dry THF (200 mL) [a homogeneous red solution was obtained]. The upper layer of the resulting two-phase system was separated and added dropwise to a stirred solution of isopropanol (500 mL). A precipitation was observed. The precipitate was filtered off, washed with acetonitrile (2 × 250 mL) [to remove by-products and the excess acid] and dried under vacuum. Polymer **2** was obtained (13.2 g, 34.1 mmol) as a white solid with a 98% yield.

Structural characterization of 2:

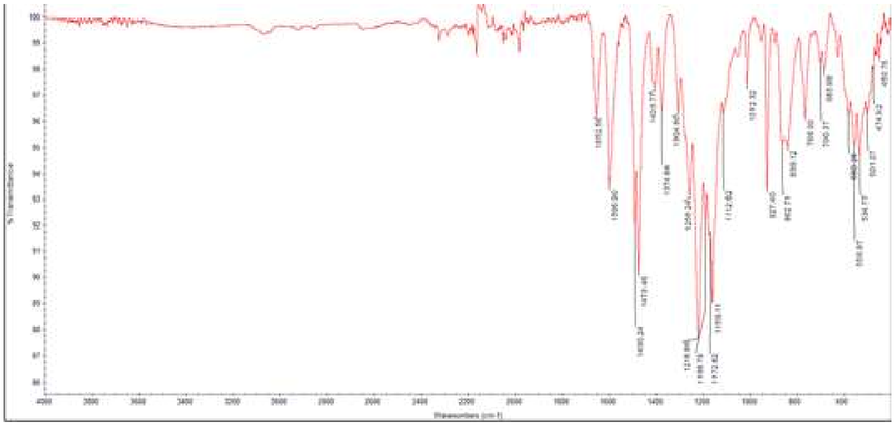


2

^{1}H NMR (200 MHz, DMSO) δ 7.94 – 7.68 (m, 4H), 7.51 (d, J = 2.9 Hz, 1H), 7.33 – 6.92 (m, 6H).

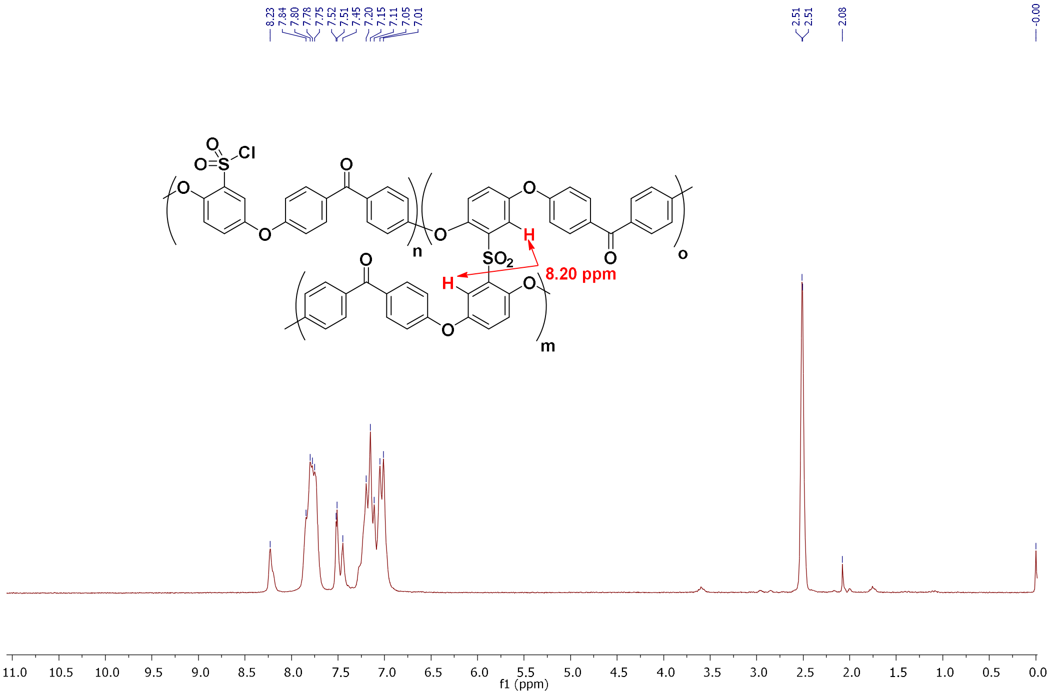


IR ν (cm $^{-1}$) : 1654, 1597, 1473, 1375, 1257, 1217, 1159, 927, 764

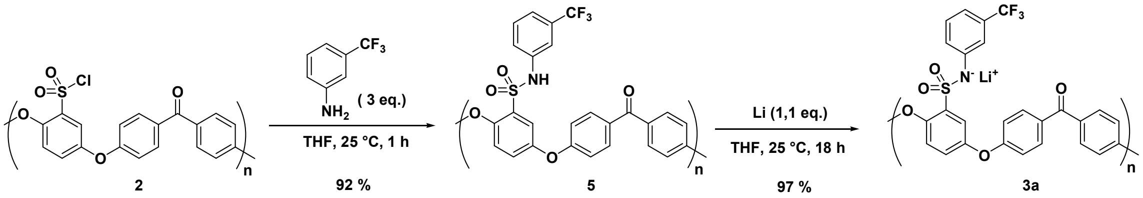


The amount of polymer reticulation could be quantified by ^{1}H RMN, by the integration of the proton appearing at 8.20 ppm, corresponding to the proton of a disulfonated unit. This proton at 8.20 ppm was absent from non-reticulated polymer **2**, indicating the absence of reticulation.

Structural characterization of 2 (26% of cross-linking):

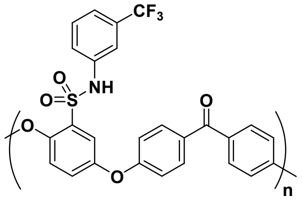


Preparation of polymeric sulfonimide lithium salts (method 1)



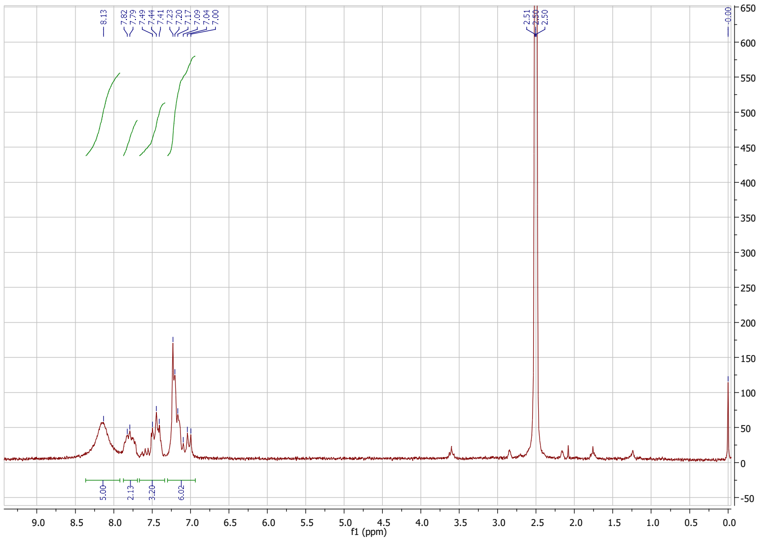
In a 50 mL flask, 3-(trifluoromethyl)aniline (0.625 mg, 3.88 mmol) was added to 20 mL THF under nitrogen. A solution of polymer **2** (500 mg, 1.29 mmol) in 20 mL of THF was prepared and slowly added to the amine solution and stirred at room temperature for 1 h. The resulting homogeneous solution was evaporated and a solid film was obtained. The film was dissolved in 12 mL of THF and precipitated with 75 mL of acetonitrile. The resulting product **5** was washed 3 times with 10 mL of acetonitrile (an excess of amine was used to trap the HCl formed during the process) and dried under vacuum overnight (10^{-2} mbar).

Structural characterization of 5:

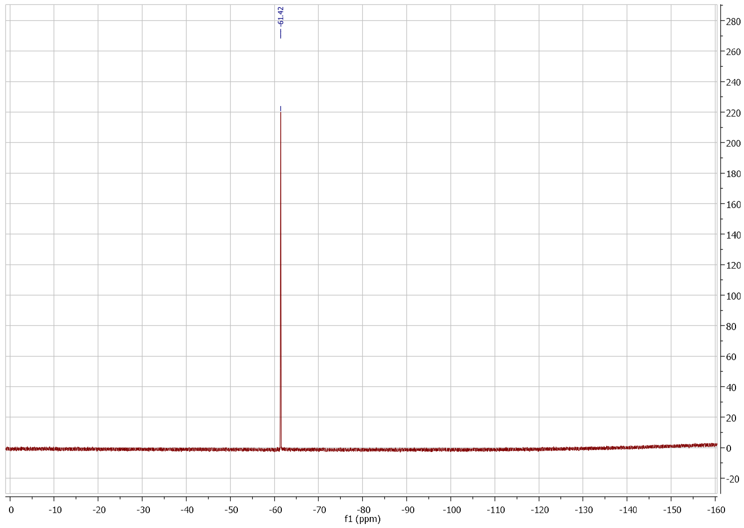


5

^{1}**H NMR** (200 MHz, DMSO) δ 8.36 – 7.92 (m, 5H), 7.87 – 7.69 (m, 2H), 7.66 – 7.33 (m, 3H), 7.30 – 6.94 (m, 6H).



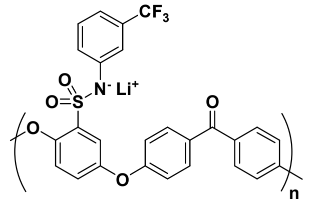
^{19}F NMR (188 MHz, DMSO-d$_6$) δ -61,42 (s, 3F)



IR ν (cm^{-1}) : 1644, 1595, 1493, 1471, 1414, 1326, 1223, 1157, 1118, 109, 927

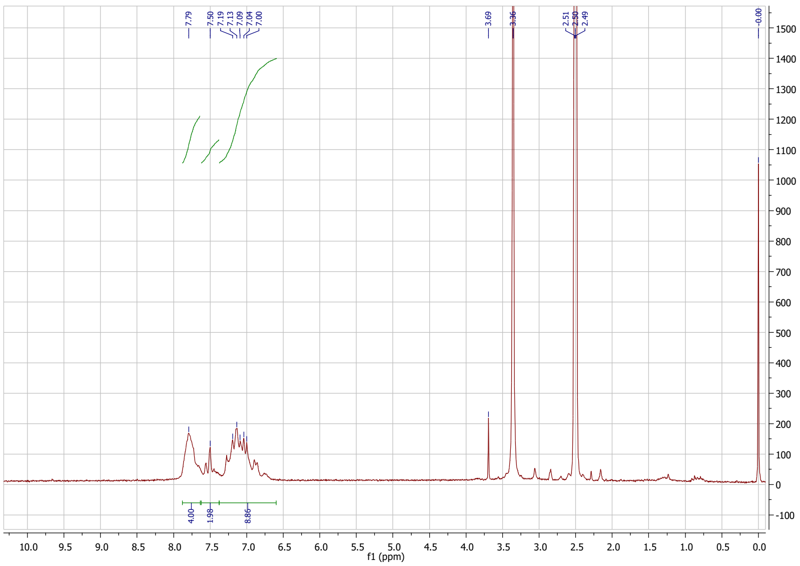
The polymer **5** (200 mg, 0.39 mmol) was added to 5 mL of THF in a 25 mL flask under nitrogen. Lithium metal (3 mg, 0.429 mmol) was slowly added to the solution and the mixture was stirred overnight at room temperature. The resulting solution was filtered off and the filtrate was evaporated. The resulting product **3a** was washed 3 times with 10 mL of acetonitrile and dried under vacuum overnight (10^{-2} mbar).

Structural characterization of 3a:

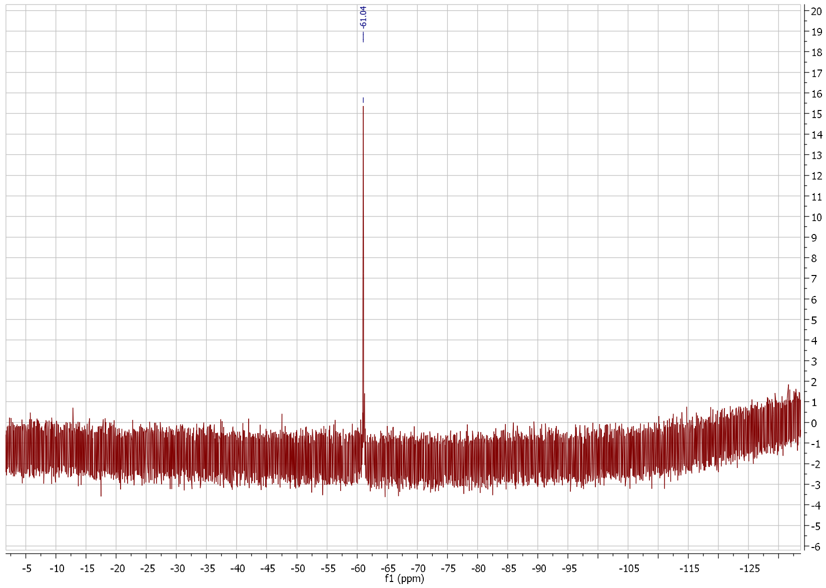


3a

^{1}H NMR (200 MHz, DMSO) δ 8.01 – 7.69 (m, 4H), 7.68 – 7.47 (m, 2H), 7.46 – 6.67 (m, 9H)

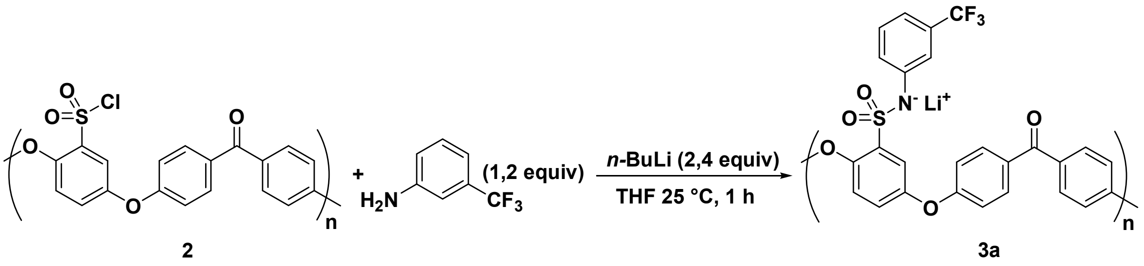


^{19}**F NMR** (188 MHz, DMSO-d$_6$) δ -61.04 (s, 3F)



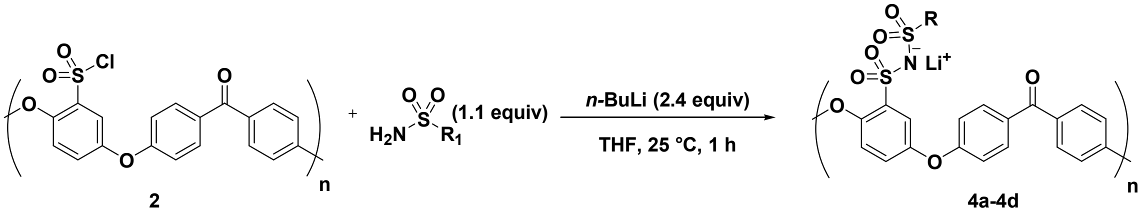
IR ν (cm^{-1}) : 2948, 1644, 1595, 1471, 1328, 1218,1159, 1082, 1026, 928, 864, 767

Preparation of polymeric sulfonimide lithium salts (method 2)



3-(Trifluoromethyl)aniline (100 mg, 0.62 mmol) was added to 10 mL of THF in a 50 mL flask under nitrogen. *n*-BuLi was slowly added to this solution (0.50 mL, 2.5 M in hexane, 1.24 mmol). A solution of **2** (200 mg, 0.52 mmol) in 20 mL of THF was prepared and stirred for 15 min and was added to the amine/*n*-BuLi solution and stirred at room temperature for 1 h. A yellow precipitate was formed. This precipitate was filtered off and washed 3 times with 10 mL of acetonitrile. The resulting solid **3a** was dried under vacuum overnight (10^{-2} mbar).

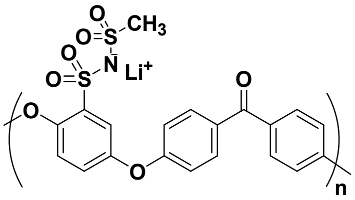
Preparation of polymer of bis(sulfonyl)imides lithium salts



Methanesulfonamide ($CH_3SO_2NH_2$, 0.054 g, 0,57 mmol), 10 mL of THF and *n*-BuLi (2 M in hexane, 0.62 mL, 1.24 mmol) were successively introduced in a 50 mL flask under nitrogen. The solution was stirred at room temperature for 15 h. A solution of **2** (200 mg, 0.52 mmol) in 20 mL of THF was slowly added and the mixture was stirred at room temperature for 1 h. A white precipitate was formed and filtered off. The solvent was concentrated for the re-precipitation. The resulting solid **4a** was washed 3 times with 10 mL of THF. The polymer was dried overnight under vacuum (10^{-2} mbar).

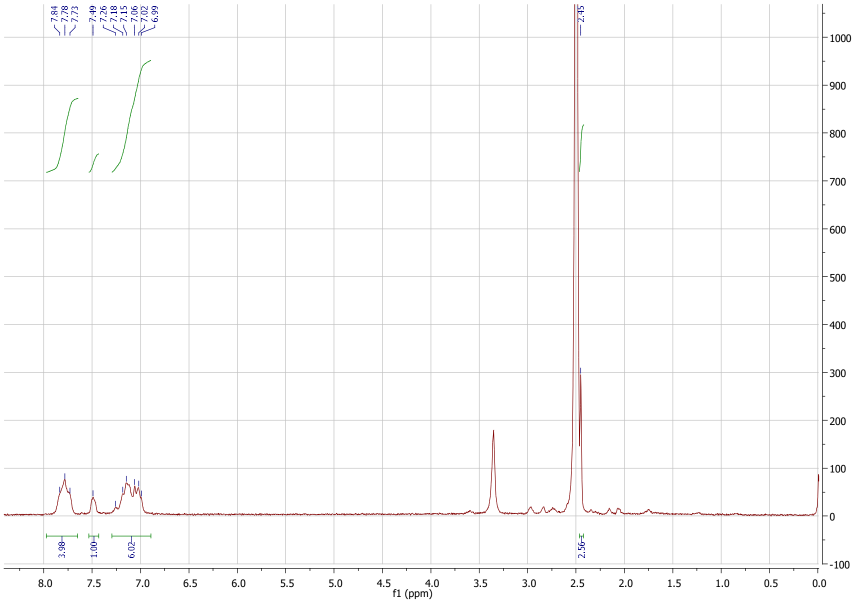
The same protocol was applied to the preparation of **4b**, **4c** and **4d**

Structural characterization of 4a:



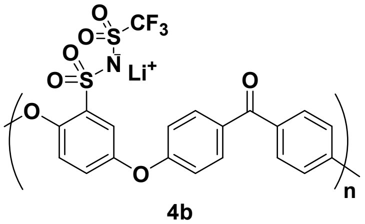
4a

^{1}H NMR (200 MHz, DMSO) δ 7.97 – 7.66 (m, 4H), 7.50 (s, 1H), 7.37 – 6.97 (m, 6H), 2.45 (s, 3H).



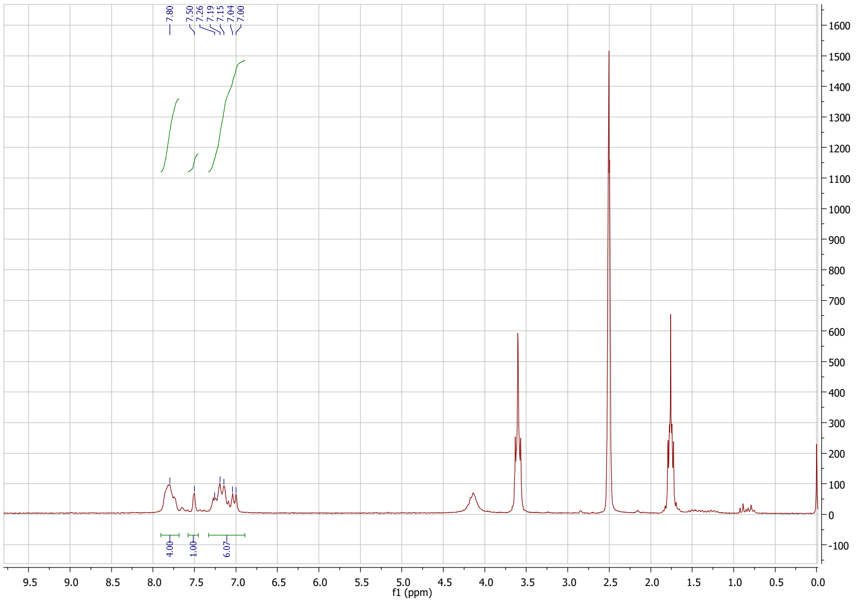
IR ν (cm^{-1}): 2957, 1644, 1595, 1470, 1217, 1149, 1082, 1025, 929, 863

Structural characterization of 4b:

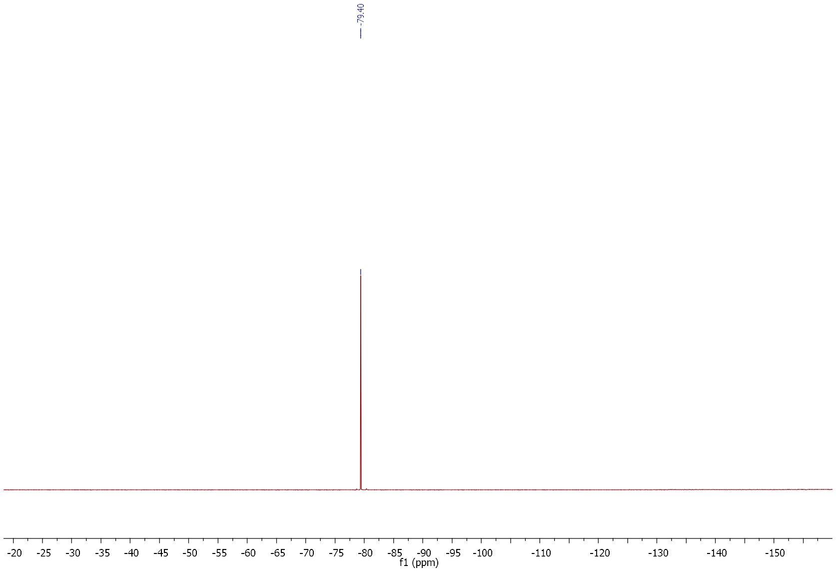


4b

^{1}H NMR (200 MHz, DMSO) δ 7.91 – 7.69 (m, 4H), 7.50 (s, 1H), 7.33 – 6.89 (m, 6H).

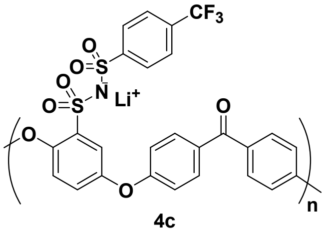


^{19}F NMR (188 MHz, DMSO) δ -79.40 (s).



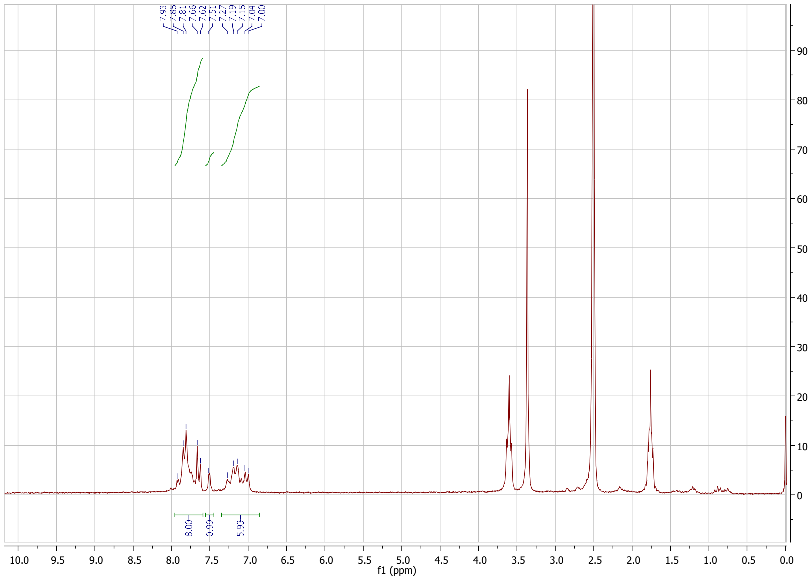
IR ν (cm^{-1}): 2922, 2852, 1626, 1595, 1470, 1417, 1309, 1218, 1187, 1159, 1026, 928, 863

Structural characterization of 4c:

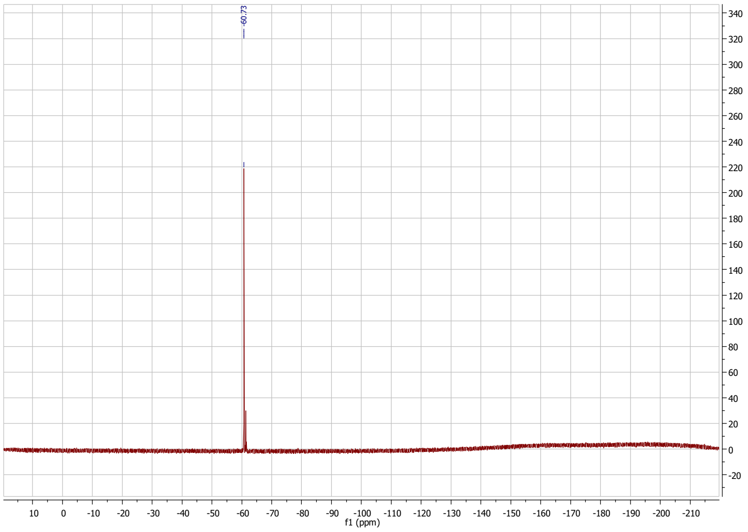


4c

^{1}H NMR (200 MHz, DMSO) δ 7.96 – 7.59 (m, 8H), 7.51 (s, 1H), 7.35 – 6.85 (m, 6H).

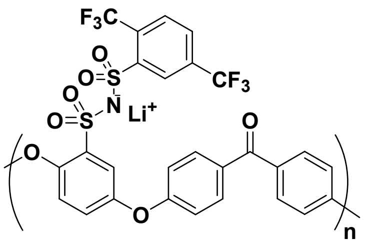


RMN ^{19}F (188 MHz, DMSO-d_6) δ -60,73 (s, 3F)



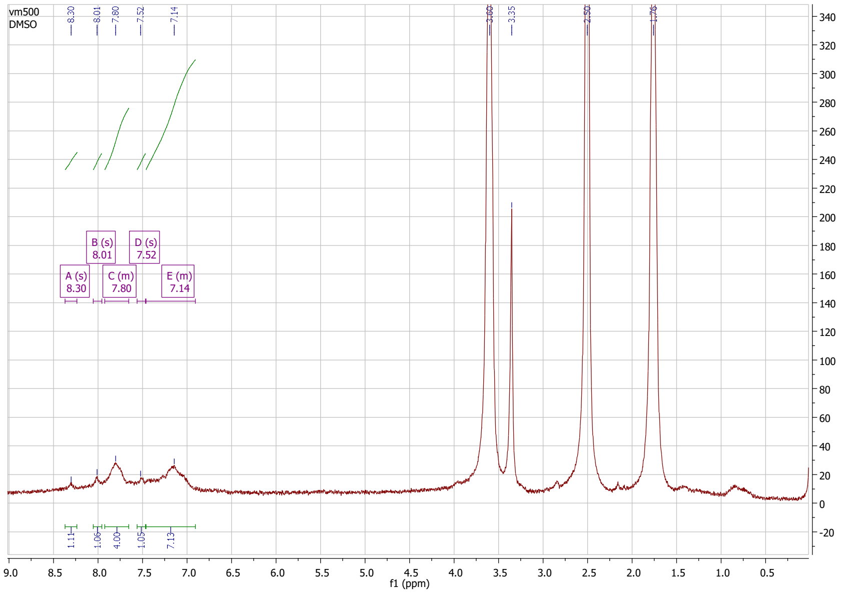
IR ν (cm^{-1}) : 2951, 2871, 1641, 1595, 1471, 1322, 1220, 1158, 1028, 928, 840

Structural characterization of 4d:

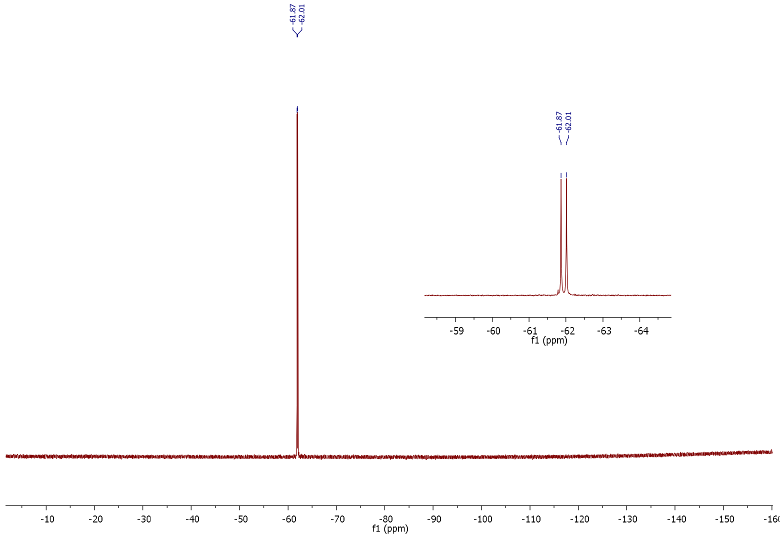


4d

^{1}H NMR (200 MHz, DMSO) δ 8.30 (s, 1H), 8.01 (s, 1H), 7.92 – 7.65 (m, 4H), 7.52 (s, 1H), 7.46 – 6.90 (m, 7H).



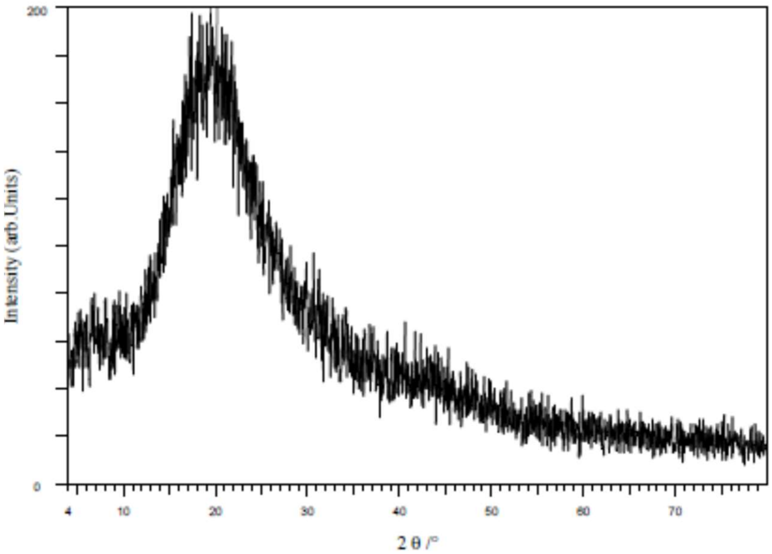
RMN ^{19}F (188 MHz, DMSO) δ -61.87 (s), -62.01 (s).



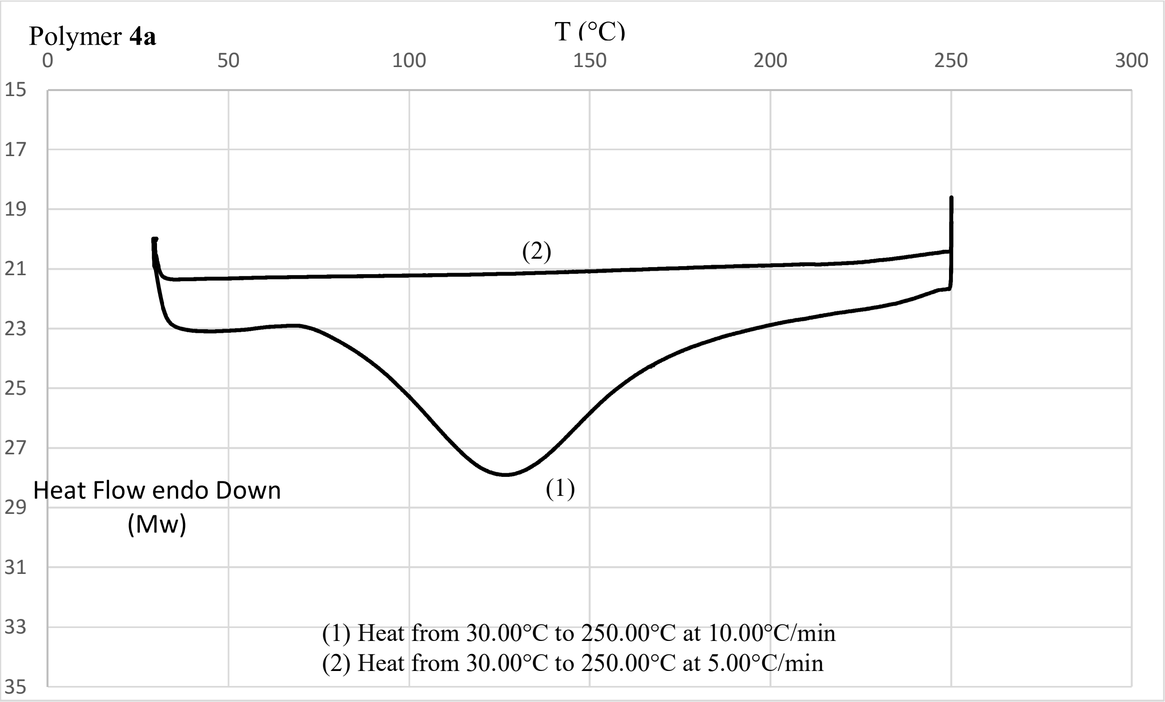
IR ν (cm^{-1}): 2941, 2899, 1631, 1595, 1470, 1323, 1232, 1156, 927, 842.

X-Ray Diffraction pattern of polymer 4a

The XRD pattern (Siemens D5000 diffractometer using CuKα radiation) shows a fully amorphous polymer.



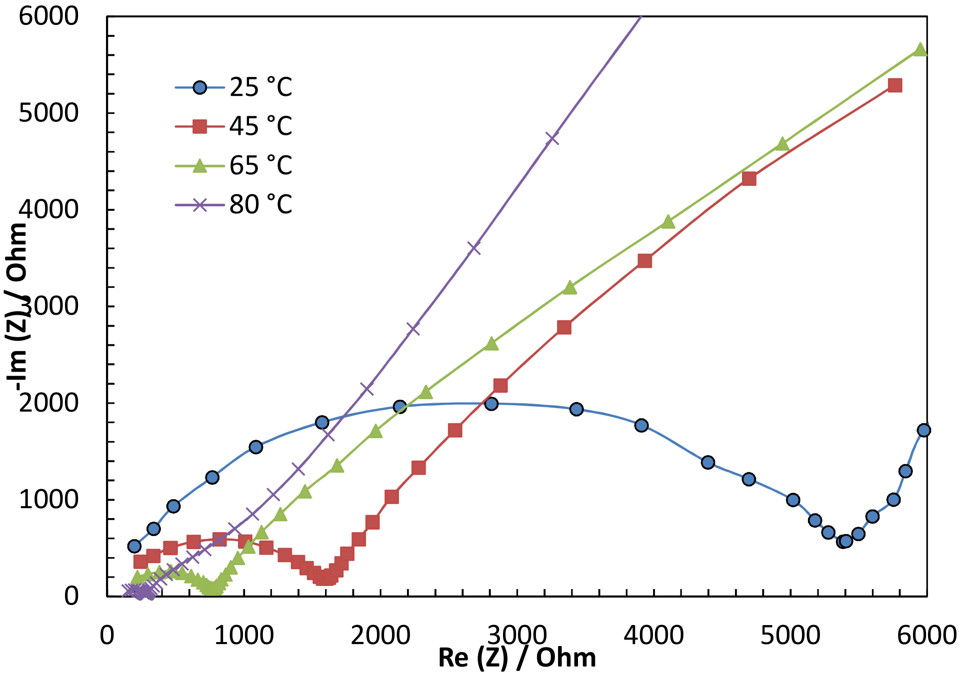
Differential Scanning Calorimetry (DSC) of **4a** was performed with a Perkin Thermal Analyzer in the temperature range of 30-250 °C at 10°C/min ramping scheme (1). After performing a hardening with liquid nitrogen,the polymer was heated in the temperature range of 30-250 ° at 5°C/min ramping scheme (2). About 15 mg of polymer **4a** was used.



Tensile stress-strain tests were performed using an ADAMEL Lhomargy DY30 traction machine at 25°C at a constant crosshead speed of 5 mm/min. Particular attention was given to the macroscopic homogeneity of membranes made by casting and only apparently homogeneous membranes were used for the mechanical tests. The clamping pressure was determined according to a preliminary tensile stress-strain test: it was about 40% of the apparent elasticity limit, corresponding to the linear part of the tensile curve. The membrane samples had a thickness of 30-70 μm, 5 mm width and 25 mm length. The border of the membranes, where composition may be inhomogeneous, was eliminated by cutting carefully the specimens. The selected tensile curves corresponded only to tests with a final rupture in the central part of the specimens. The other cases of rupture (<20%), e.g., near or under grips, were systematically eliminated. Prior to the measurements, the polymer samples were stabilized at 25 °C and humidity (40±10)% RH. The measurement time was below 5 min.

Electrochemical impedance spectroscopy

The **ionic conductivity** was measured between 25 and 80 °C by impedance spectrometry (Parstat model 4000) in Swagelok cells with stainless steel electrodes. The Swagelok cells were assembled in a glove box under residual humidity less than 4 ppm. The ac voltage amplitude was 10 mV and the frequency range between 10 and 6.10^6 Hz. The through-plane membrane resistance R was determined from the high frequency intersection of the impedance arc with the real axis in a Nyquist plot. The ion conductivity σ was calculated from the membrane thickness d, which was determined before and after the measurements by a micrometer, and the electrode area, which was $A = 0.28$ cm^2, using the equation: $\sigma = \frac{d}{R \cdot A}$



Nyquist plots for polymer **4a** containing 5 w% of PC/EC-DEC 50/50% between 25 and 80 °C