Electronic Supplementary Information (ESI)

Hypersulfonated Polyelectrolytes: Preparation, Stability and Conductivity

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Figure S1. FTIR spectra (full wavenumber width) corresponding to Fig. 2.
Figure S2. $^{19}$F NMR spectra (DMSO-$d_6$) of reaction products with incomplete substitution of the fluorine atoms during the thiolation of FPAS2 with NaSH. Reactions were carried out in DMAc at (a) room temperature, (b) 50 °C, (c) 80 °C, (d) 120 °C, (e) 140 °C and (f) 175 °C, respectively.
Figure S3. TGA traces of (a) S125, (b) S142 and (b) S220 under nitrogen at 10 °C min⁻¹ and under air at 1 °C min⁻¹, and (d) TGA trace of S125 at 200 °C under nitrogen as a function of time.
Preparation of the hypersulfonated polymer S107

**Synthesis**

*Polycondensation:* 10F (1.965 g, 5.881 mmol) and Li$_2$S (0.2706 g, 5.889 mmol, 99.9% trace metal basis, Alfa Aesar) were charged to a one-neck 50 mL round-flask with NMP (8.7 mL) in a Glove box filled with Argon. The polymerization was carried out at 165 °C in a closed system. After 17 h, the viscous solution was poured into deionized water to precipitate a white powder. The product was washed several times in deionized water and 2-propanol, and was collected via filtration. The product was dried under vacuum at 30 °C overnight (yield: 1.91 g, 98.9%).

*Sulfonation via thiolation:* The same procedure as for S142 was carried out for preparation of S107, except that the reaction temperature was 250 °C and the solvent used was sulfolane (yield: 79.8%).

**Discussion**

Several attempts were made to fully oxidize the thioether bridges to form the corresponding polysulfone, using either a conventional route involving hydrogen peroxide, as used for S142, or by using a route specifically suitable for hydrophobic compounds involving $m$-chloroperoxybenzoic acid (K. Matsumoto; T. Higashihara; M. Ueda, *J. Polym. Sci., Part A, Polym. Chem.* 2009, 47, 3444). However, no successful oxidation was confirmed by FTIR spectroscopy ([Fig. S5b, S5c](#)). This was most probably due to poor accessibility of the peroxide because of the perfluorinated structure of the polythioether. The thiolation method optimized for S142 was then used to substitute the fluorine atoms. However, this resulted in incomplete substitution. Finally, a reaction at 250 °C in sulfolane produced full substitution, and no fluorine was detectable by $^{19}$F NMR spectroscopy after the reaction ([Fig. S4b](#)). In the subsequent oxidation of the thiolated polymer, the remaining thioethers bridges were seemingly oxidized to sulfone bridges, as indicated by FTIR spectroscopy ([Fig. S5a, S5b](#)). In contrast to S142, the hypersulfonated polymer S107 was thermally unstable, as confirmed after exposure to air at 200 °C ([Fig. S5a](#)). Furthermore, TG-MS analysis under nitrogen was carried out to investigate the thermal stability difference between S142 and S107 ([Fig. S6](#)). After drying at 120 °C, the S107 sample became less soluble in water, resulting in a titrated IEC of 4.00 meq. g$^{-1}$ compared to the theoretical value of 9.70 meq. g$^{-1}$. Unfortunately, these findings indicated that the polymer was significantly degraded.
**Scheme S1.** Synthetic route to prepare the *hypersulfonated* aromatic polymer S107: (i) Li$_2$S, NMP, 165 °C, 17 h; (ii-1) NaSH, K$_2$CO$_3$, sulfolane, toluene, 160 °C, 4 h; (ii-2) NaSH, K$_2$CO$_3$, sulfolane, 250 °C, 20 h; (iii-1) H$_2$O$_2$, H$_2$O, 40 °C, 24 h; (iii-2) ion-exchange to H$^+$ form.

**Table S1** Molecular and thermal data of S107.

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<th>$M_w$</th>
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<th>$T_{d10%}^e$</th>
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<td>4.00$^b$</td>
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</table>

$^{a}$ measured in DMSO with LiBr (1 g L$^{-1}$) at 60 °C; $^{b}$ partly insoluble and unstable in water; $^c$: measured with a helium gas pycnometer; $^d$: measured under nitrogen at 10 °C min$^{-1}$; $^e$: measured under air at 1 °C min$^{-1}$; $^f$: measured by SAXS at 75% RH and room temperature. $d = 2\pi \times q^{-1}$. 
Figure S4. $^{19}$F and $^1$H NMR spectra of (a) the fluorinated precursor poly(arylene thioether) for S107 (recorded in CDCl$_3$) and (b) S107 (recorded in DMSO-$d_6$).
Figure S5. FTIR spectra of (a) S107 (the thin line is the spectrum of the sample after exposure to air at 200°C for 2 h) and the fluorinated precursor poly(arylene thioether) for S107 (b) after and (c) before oxidation.
Figure S6. TG-MS analysis of S107 under nitrogen at 10 °C min⁻¹: (a) weight loss and evolved (b) H₂O, (c) SO₂, and (d) CO₂ gas.
**Figure S7.** SAXS data of S107 at 75% RH and room temperature.