

Supplementary Information

“Synthesis and Characterization of Novel Sulfonated Poly(arylene thioether) Ionomers for Vanadium Redox Flow battery Application”

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1. Synthesis of monomers and polymers

Materials

9, 9-Bis(4-hydroxyphenyl)fluorene (purity > 98%) was purchased commercially from Tokyo Kasei Kogyo Co. Ltd., Japan (TCI). *N, N'*-dimethyl thiocarbamoyl chloride and benzophenone were purchased from Aldrich. *N, N'*-dimethylacetamide (DMAc), toluene, chloroform, dichloromethane, methanol, chlorosulfonic acid, hydrochloric acid, potassium hydroxide and anhydrous potassium carbonate were obtained from commercial sources. DMAc and toluene were dried with 4 Å molecule sieves prior to use. Dichloromethane was dried with anhydrous CaCl₂ and anhydrous potassium carbonate was dried at 120 °C for 10 h prior to use. Other chemicals were used as received. 1, 4-bis(4-fluorobenzoyl) benzene was synthesized according to the method reported by Hergenrother et al.¹

Monomer Synthesis

Monomer **1** and monomer **2** were synthesized by the following procedures according to the literature.²

To a 500 mL round bottom flask, 200 mL methanol and 14.6 g KOH (0.26 mol) were introduced. The mixture was stirred at 0 °C for 0.5 h. 40.0 g of 9, 9-bis (4-hydroxyphenyl) fluorene (0.114 mol) was then added and keep stirring for another 0.5 h. 31.0 g of *N, N'*-dimethylthiocarbamoyl chloride (0.25 mol) was added and reacted for 3 h. The precipitate was collected by filtration and washed with 200 mL solution of methanol and water (1 : 1). After recrystallization from ethanol / CHCl₃ twice, monomer **1** was obtained. Yield: 81%. M. p. 239-241 °C. ¹H-NMR (400 MHz, CDCl₃, ppm): 3.30 (s, 6H), 3.45 (s, 6H), 6.94 (d, 4H, J = 8.8 Hz), 7.24 (t, 4H, J = 8.8 Hz), 7.29 (d, 2H, J = 7.2 Hz), 7.36 (t, 2H, J = 7.2 Hz), 7.43 (d, 2H, J = 7.2 Hz), 7.77 (d, 2H, J = 7.2 Hz).

To a 150 mL three neck round bottom flask equipped with a N₂ inlet and a condenser, monomer **1** (40.0 g) and diphenyl ether (15.0 g) were introduced. The mixture was heated at 260 °C for 3 h. After cooling down, the mixture was washed with methanol (300 mL), dried at 80 °C under vacuum for 24 h. The crude product was recrystallization from ethanol / CHCl₃ twice to give birth of monomer **2**. Yield: 95 %. M. p. 279-281 °C. ¹H-NMR (400 MHz, CDCl₃,

ppm): 3.08 (s, 12H), 7.26 (d, 4H, $J = 6.8$ Hz), 7.30 (d, 2H, $J = 6$ Hz), 7.38-7.42 (8H), 7.79 (d, 2H, $J = 6$ Hz).

Polymerization and Sulfonation

The typical polymerization procedure is as follows: to a 25 mL three neck flask equipped with a magnetic stirrer, a N₂ inlet, a Dean-Stark trap and a condenser, monomer **2** (0.5247g, 1 mmol), 1, 4-Bis(4-fluorobenzoyl) benzene (0.3223g, 1 mmol), cesium carbonate (0.16g, 0.5 mmol), calcium carbonate (0.3g, 3 mmol) and 3.5 g of benzophenone were charged. The mixture was first heated at 200 °C for 3 h, and then brought up to 240 °C and reacted at that temperature for another 3 h. After cooling down, the viscous mixture was poured into ethanol to precipitate out the polymer which was collected by filtration. The polymer was purified by redissolving it in CHCl₃ and precipitate out for three times. The product was dried at 120 °C in vacuum for 24 h.

Poly(arylene thioether ketone) (PTK): Yield: 55%. ¹H-NMR (400 MHz, CDCl₃, ppm): 7.22 (d, 8 H, $J = 20$ Hz), 7.33 (t, 6 H, $J = 20$ Hz), 7.40 (d, 4 H, $J = 18$ Hz), 7.61 (d, 4 H, $J = 19$ Hz), 7.78 (d, 2 H, $J = 18$ Hz).

Poly(arylene thioether ketone ketone) (PTKK): Yield: 62%. ¹H-NMR (400 MHz, CDCl₃, ppm): 7.22 (d, 8 H, $J = 14$ Hz), 7.29 (t, 2 H, $J = 15$ Hz), 7.34 (d, 4 H, $J = 17$ Hz), 7.38 (d, 4 H, $J = 16$ Hz), 7.66(d, 4 H, $J = 17$ Hz), 7.78 (s, 6 H).

The typical sulfonation procedure is as follows: to a 150 mL round bottom flask, 75 mL dichloromethane and 0.4035 g (0.5 mmol repeat units) polymer PTK were introduced. After polymer PTK was dissolved completely, 25mL of 0.2 M solution of chlorosulfonic acid (5 mmol) in dichloromethane was added dropwise under the vigorously stirring over 3 h. The reaction was continued for another 5 h. The resulting pale purple product precipitated out from the solution during the course. The precipitates were washed with hexane many times and dissolved in 20 mL DMAc. To the solution 20 mL of 3 wt.% potassium hydroxide aqueous solution was added to react for 5 h, then the reaction mixture was acidified with 50 mL of 5 vol.% hydrochloric acid for another 5 h. The resulting solution was dialyzed for 3 days and the solvent was removed by rotary evaporator.

Sulfonated poly(arylene thioether ketone) (SPTK): Yield: 93%. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , ppm): 7.33 (d, 8 H, $J = 21$ Hz), 7.42 (d, 2 H, $J = 16$ Hz), 7.56 (s, 1-2 H), 7.69 (d, 1-2 H, $J = 19$ Hz), 7.89-7.97 (m, 8 H), 8.06 (d, 4 H, $J = 20$ Hz).

Sulfonated poly(arylene thioether ketone ketone) (SPTKK): Yield: 91%. $^1\text{H-NMR}$ (400 MHz, DMSO- d_6 , ppm): 7.20 (t, 4 H, $J = 17$ Hz), 7.37 (d, 4 H, $J = 17$ Hz), 7.48 (d, 4 H, $J = 17$ Hz), 7.65 (s, 2 H), 7.65-7.74 (m, 6 H), 7.83 (s, 4 H), 7.91 (d, 2 H, $J = 15$ Hz).

2. Spectral data for PTK, PTKK, SPTK and SPTKK

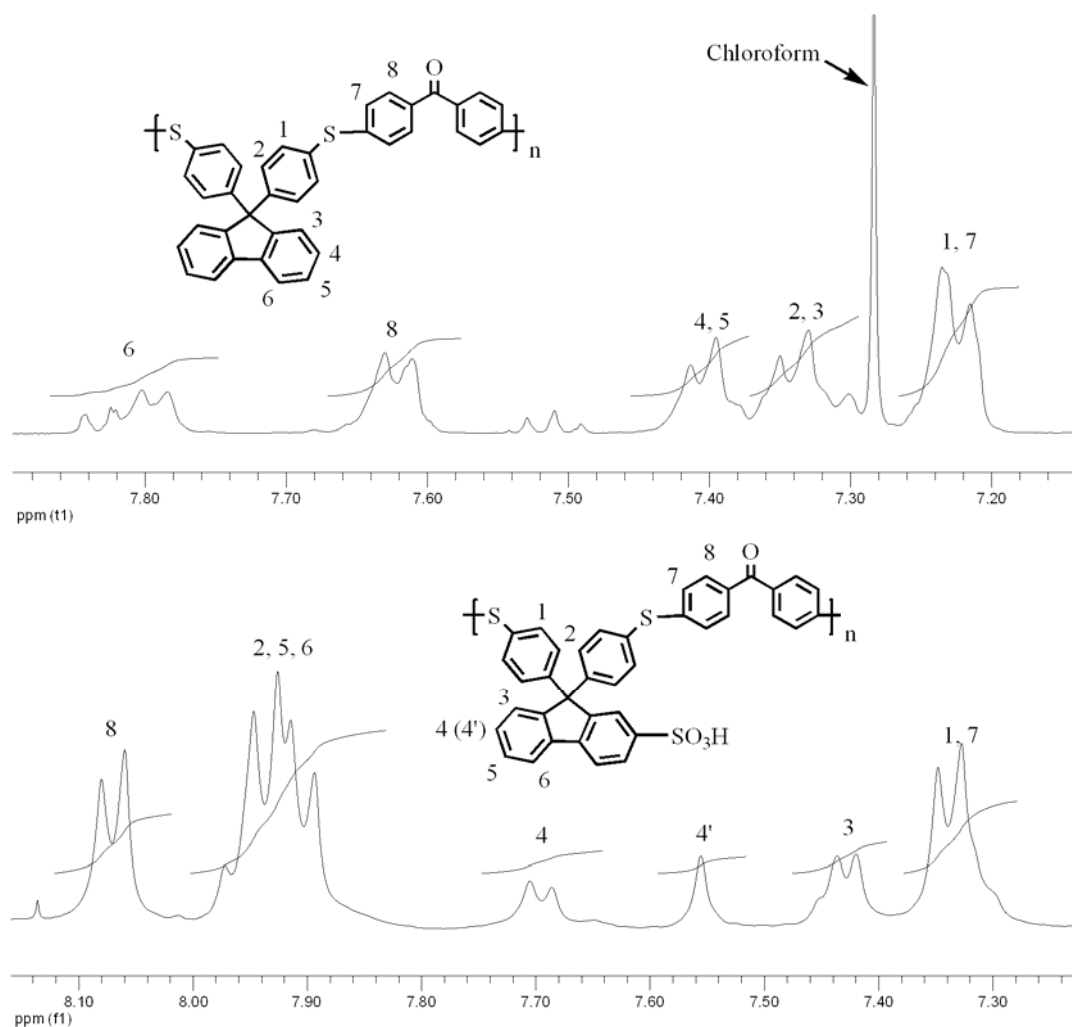


Figure 1S. ¹H-NMR spectra of PTK (CDCl₃) and SPTK (DMSO-d₆).

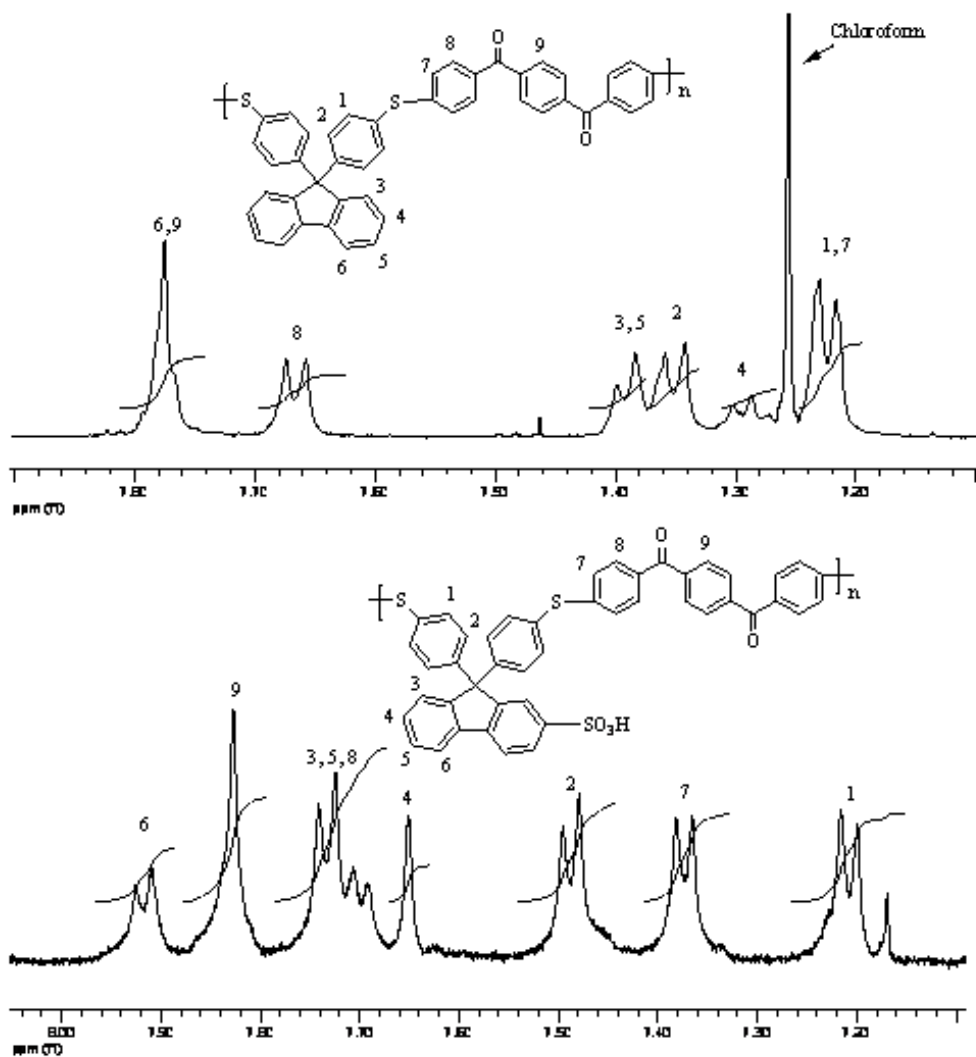


Figure 2S. ¹H-NMR spectra of PTKK (CDCl₃) and SPTKK (DMSO-d₆).

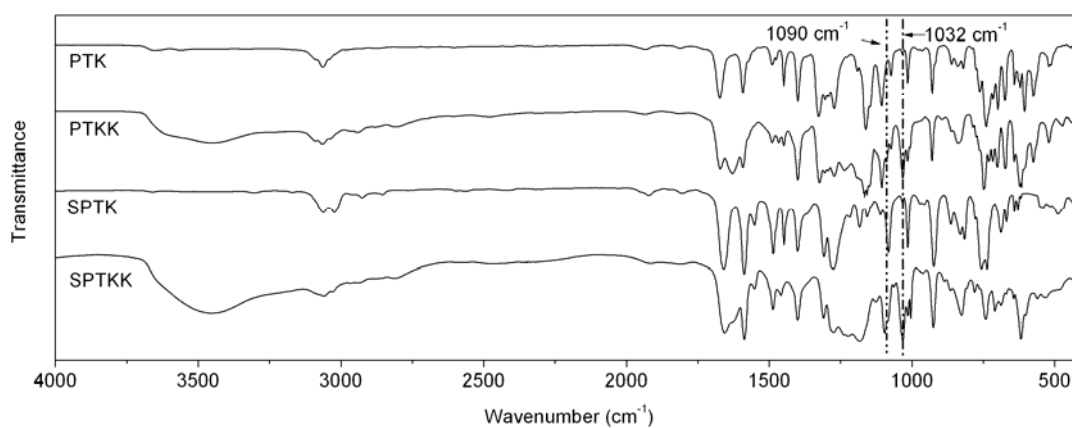


Figure 3S. FT-IR spectra of PTK, PTKK, SPTK and SPTKK.

REFERENCES:

1. Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* 1988, 29, 358.
2. Ding, Y.; Hay, A. S. *Tetrahedron* 1997, 53, 15237.