Supporting Information

Polymer Electrolyte Membranes Based on Poly(phenylene ether)s with Sulfonic Acid via Long Alkyl Side Chains

Xuan Zhang, Li Sheng, Teruaki Hayakawa, Mitsuru Ueda*, and Tomoya Higashihara*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

Fax: +81-3-5734-2127, E-mail: mueda@kanagawa-u.ac.jp:thigashihara@yz-yamagata-u.ac.jp

^{1}H NMR and FTIR Spectra of the polymer 2, 3 and 4

2a: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.77-7.73 (bm, Ar-H), δ = 7.02-6.89 (bm, Ar-H), δ = 3.80 (s, -OCH_3). IR (KBr): *v* 2960-2870 (C-H), 1658 (C=O), 1597 (C=C), 1169 cm^{-1} (C-O-C).

2b: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.87-7.77 (bm, Ar-H), δ = 7.52 (bs, Ar-H), δ = 7.14-6.96 (bm, Ar-H), δ = 3.82 (s, -OCH_2-). IR (KBr): *v* 2960-2870 (C-H), 1658 (C=O), 1597 (C=C), 1169 cm^{-1} (C-O-C).

2c: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.83-7.72 (m, Ar-H), δ = 7.07-7.00 (m, Ar-H), δ = 6.92 (s, Ar-H), δ = 3.81 (s, -OCH_3). IR (KBr): *v* 2960-2870 (C-H), 1654 (C=O), 1593(C=C), 1188 cm^{-1} (C-O-C).

3a: ^{1}H NMR (DMSO-d_6, ppm): δ = 10.33 (s, -OH), δ = 7.81-7.67 (bm, Ar-H), δ = 7.04-6.62 (bm, Ar-H). IR (KBr): *v* 3500-3200 (-OH), 1643 (C=O), 1597 (C=C), 1169 cm^{-1} (C-O-C).

3b: ^{1}H NMR (DMSO-d_6, ppm): 10.36 (s, -OH), δ = 7.87-7.67 (bm, Ar-H), δ = 7.34-7.26 (bm, Ar-H), δ = 7.10-6.99 (bm, Ar-H), δ = 6.86-6.64 (bm, Ar-H). IR (KBr): *v* 3500-3200 (-OH), 1643 (C=O), 1597 (C=C), 1169 cm^{-1} (C-O-C).

3c: ^{1}H NMR (DMSO-d_6, ppm): δ = 10.18 (s, -OH), δ = 7.81-6.83 (bm, Ar-H), δ = 6.65 (bs, Ar-H). IR (KBr): *v* 3500-3200 (-OH), 1651 (C=O), 1601 (C=C), 1169 cm^{-1} (C-O-C).

4a: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.78-7.74 (bm, Ar-H), δ = 7.05-6.93 (bm, Ar-H), δ = 4.01 (s, -OCH_2-), δ = 2.54 (s, -CH_2-SO_3Na), δ = 1.81-1.73 (m, -CH_2-).IR (KBr): *v* 2960-2870 (C-H), 1654 (C=O), 1597 (C=C), 1169 cm^{-1} (C-O-C), 1115, 1045 cm^{-1} (O=S=O).

4b: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.77-6.80 (bm, Ar-H), δ = 3.91 (s, -OCH_2-), δ = 2.54 (s, -CH_2-SO_3Na), δ = 1.84-1.74 (m, -CH_2-). IR (KBr): *v* 2960-2870 (C-H), 1658 (C=O), 1600 (C=C), 1176 cm^{-1} (C-O-C), 1119, 1049 cm^{-1} (O=S=O).

4c: ^{1}H NMR (DMSO-d_6, ppm): δ = 7.78-7.57 (bm, Ar-H), δ = 7.16-6.81 (bm, Ar-H), δ = 3.89 (s, 6H, -OCH_2-), δ = 2.56 (s, -CH_2-SO_3Na), δ = 1.75 (bs, -CH_2-). IR (KBr): *v*

2960-2870 (C-H), 1662 (C=O), 1601 (C=C), 1169 cm^{-1} (C-O-C), 1119, 1049 cm^{-1} (O=S=O).

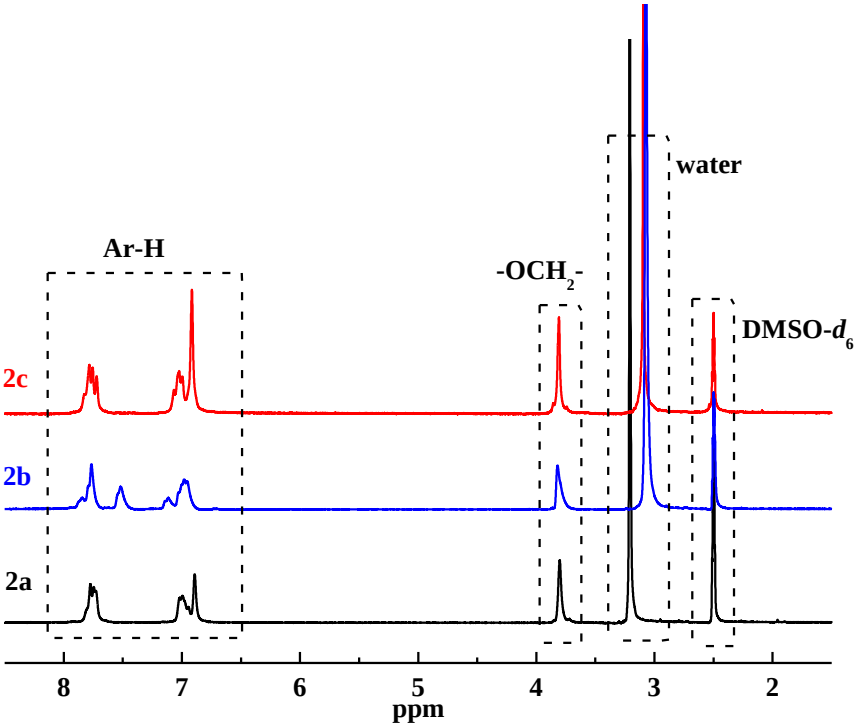

Figure S1. ^{1}H NMR spectra of the polymer **2** in DMSO-d_6.

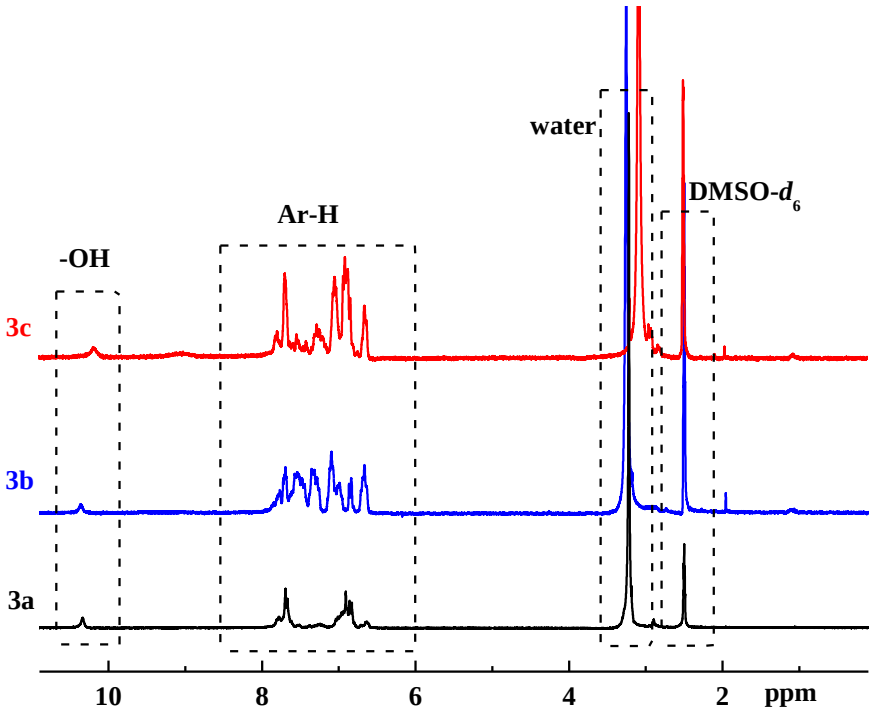

Figure S2. ^{1}H NMR spectra of the polymer **3** in DMSO-d_6.

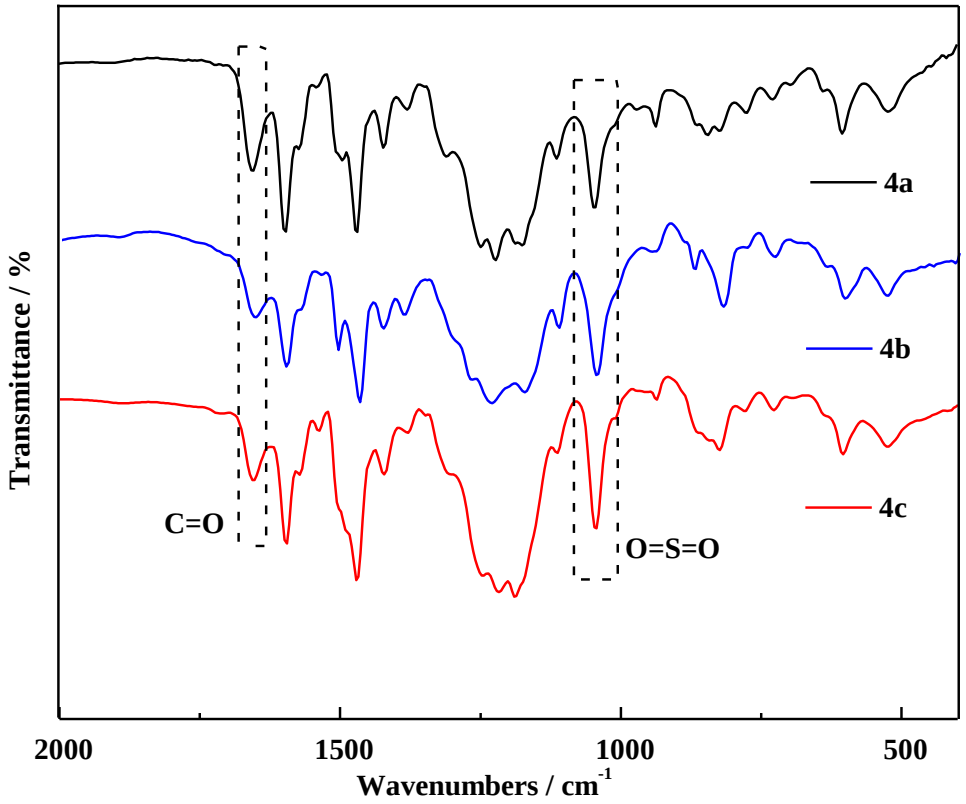

Figure S3. IR spectra of the polymer **4.**

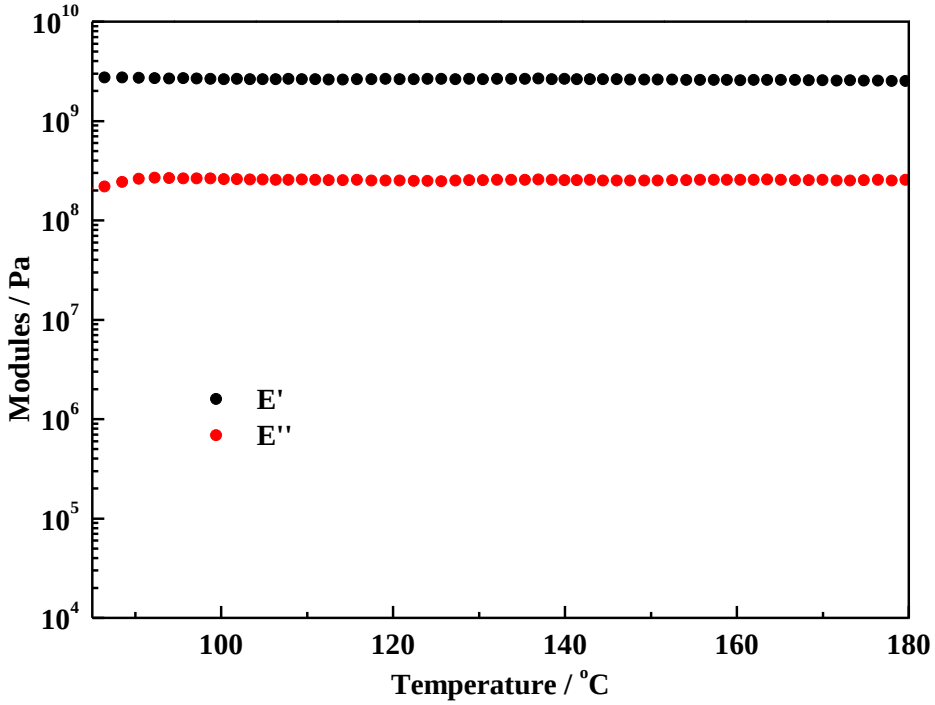

Figure S4. DMA curve of **4c**.

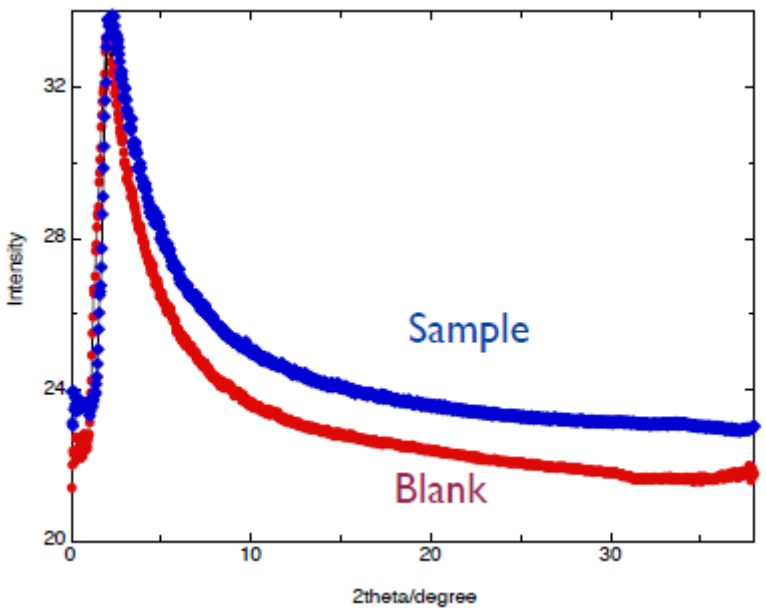

Figure S5. WAXD curves of polymer **4a**.

Table S1 *WU* and proton conductivities data of **SPPE** membranes as a function of relative humidity.

Code	WU / %				Proton Conductivity / mS/cm			
	30%	50%	70%	95%	30%	50%	70%	95%
4a	5.0	17.0	24.5	67.9	8.4	31.2	82.4	234.0
4b	4.5	12.0	19.5	55.2	5.6	24.6	64.6	187.9
4c	2.0	7.8	13.7	39.2	2.5	18.7	57.3	173.4
Nafion 117	2.4	4.1	6.4	12.5	7.3	25.6	57.0	130.7