Supporting Information

Development of Novel Polymer Electrolyte Membranes Based on a Benzothiadiazole Unit

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1. Materials

4,4′-Biphenol (BP) and 4,4′-dichlorodipheyl sulphone (DCDPS) were purchased from Tokyo Chemical Industry Co. and used after drying in a vacuum oven for 24 h at 80°C. 3,3′-Disulphonated-4,4′- dichlorodiphenyl sulphone sodium salt (SDCDPS) were purchased from NARD Institute Ltd. and used after drying in a vacuum oven for 24 h at 80°C. p-Fluorophenylboronic acid (FPB), 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) and 4,7-dibromo-2,1,3- benzothiadiazole (DBBTD), potassium carbonate (K_2CO_3), palladium(II) acetate ($Pd(OAc)_2$), tripotassium phosphate (K_3PO_4), *N*-methylpyrrolidone (NMP), tetrahydrofuran (THF), and toluene were purchased from Wako Pure Chemical Industries, Ltd. K_2CO_3 was used after drying in a vacuum oven at 80°C for 24 h.

2. General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker model AVANCE-500 spectrometer, operating at 500 MHz for ^{1}H and 125 Hz for ^{13}C, respectively, where chemical shifts (δ in ppm) were determined with respect to non-deuterated solvent residues as internal references. Degree of sulphonation and ion exchange capacity (IEC) of the products were estimated from the integral intensity of ^{1}H NMR. The calculation method is given in a previous study.[S1] Thermogravimetric analysis (TGA) was performed on a PerkinElmer model Pyris 1 TGA, where the heating profile was recorded and analyzed using a PerkinElmer Pyris software system. Gel permeation chromatography (GPC, L-7100 Hitachi Co. Ltd.; Shodex Oven A0-30, Showa Denko K.K.; Shodex RI-71, Showa Denko K.K.; UV L-7400, Hitachi Co. Ltd.; Shodex Asahipak GF-7MHQ columns, Showa Denko K.K) was employed to determine the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the product. The standard curve used to determine the molecular weight was created from a polystyrene standard solution (TSK, Tosoh Corp.).

3. Synthesis

Hydrophobic monomer based on benzothiadiazole unit

FPB (4.53 g, 32.3 mmol), DBBTD (4.53 g, 15.4 mmol), $Pd(OAc)_2$ (0.692 g, 3.08 mmol), SPhos (1.27 g, 3.09 mmol), K_3PO_4 (16.4 g, 77.1 mmol), 95 ml of THF and 40 ml of water were added to a two-necked 300 ml round-bottom flask with a reflux condenser and stirring bar. The atmosphere in the flask was changed from air to argon (Ar) gas. The reaction was carried out for 6 h at 80°C. After the reaction, the flask was cooled to room temperature. The reaction mixture was poured into a large amount of water. Heated chloroform was added to the crude product. The solution was distilled to remove the solvent. The obtained solid was sublimated at 250°C overnight. After that, the product was dried in a vacuum oven at 80°C for 24 h to remove the solvent completely. Yield: 68%. ^{1}H NMR (500 MHz, DMSO *d6*): (ppm) 8.09–8.06 (H_b), 7.97 (H_c), 7.43–7.39 (H_a). ^{13}C NMR (125 MHz, DMSO *d6*): (ppm) 163.68, 161.72, 153.74, 133.67–133.65, 131.72–131.64, 128.75, 116.06–15.89.

Another research group has already synthesized the BT-based monomer using a different catalyst and reaction conditions.[S2]

SPES-0.1%BT

SDCDPS (5.1083 g, 10.4 mmol), BP (3.8723 g, 20.8 mmol), DCDPS (2.9794 g, 10.4 mmol), BT (0.0068 g, 0.021 mmol), K_2CO_3 (5.2108 g, 37.7 mmol) and 90 ml of NMP were added to a three-necked 300 ml flask equipped with a reflux condenser, a dean–stark trap, a nitrogen inlet and a mechanical stirrer. The solution was heated at 135°C for 3 h to dissolve the monomer in NMP. To this solution, 30 ml of toluene was added and the mixture was heated at 155°C until toluene was completely removed. The resulting solution was kept at 185°C for 12 h. After cooling to room temperature, the mixture was filtered to remove K_2CO_3. The filtered solution was placed on a molecular porous membrane and dialysed while replacing the outside solvent for 1 day. The solution was poured into a large amount of 2-propanol. The crude product was washed with hot methanol several times and dried in a vacuum oven at 80°C for 24 h. Yield: 85%. ^{1}H NMR (500 MHz, DMSO *d6*): (ppm) 8.30 (H_e), 8.12 (H_n), 7.96–7.94 (H_i, H_m), 7.85 (H_d), 7.74–7.70 (H_b, H_g, H_k), 7.22–7.11 (H_a, H_f, H_h, H_j, H_l), 7.01 (H_c). ^{13}C NMR (125 MHz, DMSO *d6*): (ppm) (ppm) 161.39–161.30 (H_s, H_z) 158.26 (H_e) 155.59–155.29 (H_k, H_v), 154.12–153.93 (H_a, H_o), 139.22–134.21 (H_d, H_h, H_j, H_n, H_r, H_t, H_y, $H_{b'}$, $H_{c'}$), 129.94 (H_g), 128.61–128.22 (H_c, H_i, H_m, H_q, H_u, H_x), 120.79–119.41 (H_b, H_f, H_l, H_p, H_w), 118.01 ($H_{a'}$).

SPES-1%BT

SDCDPS (2.5504 g, 5.19 mmol), BP (1.9338 g, 10.4 mmol), DCDPS (1.4610 g, 5.09 mmol), BT (0.0336 g, 0.104 mmol), K_2CO_3 (3.3743 g, 24.4 mmol) and 60 ml of NMP were added to a three-necked 200 ml flask equipped with a reflux condenser, a dean–stark trap, a nitrogen inlet and a mechanical stirrer. The solution was heated at 135°C for 2 h to dissolve the monomer in NMP. To this solution, 30 ml of toluene was added and the mixture was heated at 155°C until toluene was completely removed. The resulting solution was kept at 185°C for 24 h. After cooling to room temperature, the mixture was filtered to remove K_2CO_3. The filtered solution was placed on a molecular porous membrane and dialysed while replacing the outside solvent for 1 day. The solution was poured into a large amount of 2-propanol. The crude product was washed with hot methanol several times and dried in a vacuum oven at 80°C for 24 h. Yield: 71%. ^{1}H NMR (500 MHz, DMSO *d6*): (ppm) 8.30 (H_e), 8.12 (H_n), 7.96–7.94 (H_i, H_m), 7.85 (H_d), 7.74–7.70 (H_b, H_g, H_k), 7.22–7.11 (H_a, H_f, H_h, H_j, H_l), 7.01 (H_c). ^{13}C NMR (125 MHz, DMSO *d6*): (ppm) 161.39–161.30 (H_s, H_z) 158.26 (H_e) 155.59–155.29 (H_k, H_v), 154.12–153.93 (H_a, H_o), 139.22–134.21 (H_d, H_h, H_j, H_n, H_r, H_t, H_y, $H_{b'}$, $H_{c'}$), 129.94 (H_g), 128.61–128.22 (H_c, H_i, H_m, H_q, H_u, H_x), 120.79–119.41 (H_b, H_f, H_l, H_p, H_w), 118.01 ($H_{a'}$).

4. Structural Analysis

Tapping-mode atomic force microscope (AFM, Cypher S, Oxford Instruments) analysis was used to investigate the membrane surface morphology. AFM was performed using micro-fabricated cantilevers. All samples were dried at 50°C for 24 h under vacuum before AFM measurements.

5. Water Content Measurements

The water content was measured by measuring the amount of water adsorbed at 80°C as a function of relative humidity (30%–95%). The membranes were dried at 60°C in vacuum oven for 15 min to get the dry weight (W_{dry}). The swollen membranes were swollen at 80°C suspended in an atmosphere of each relative humidity condition to obtain the wet weight of membrane (W_{wet}). The water content of the membranes was calculated using Eq. 1.

$$\text{Water content} = (W_{swallen} - W_{dry})/W_{dry} \times 100\% \qquad (1)$$

where W_{dry} is the membrane's weight in the dry state and $W_{swollen}$ is the swollen weight of the membrane.

6. Swelling Ratio Measurements

The swelling ratio was measured by the change in the volume of the membranes. The membranes were dried at 80°C in vacuum oven for 24 h to obtain the dry volume (V_{dry}). The swollen membranes were swollen in water for 1 h at 80°C to obtain the wet volume of membrane (V_{wet}). The swelling ratio of the membranes was calculated using Eq. 2.

$$\text{Swelling ratio} = (V_{swallen} - V_{dry})/V_{dry} \times 100\% \qquad (2)$$

where V_{dry} is the dry volume of the membrane and $V_{swallen}$ is the swollen volume of the membranes after hot water treatment.

7. Proton Conductivity Measurements

The proton conductivity σ (S/cm) of the membranes was measured by an AC impedance method using a Solatron 1260 impedance analyzer, as reported in the previous study.[S1] Four platinum electrodes were placed on a membrane on a glass plate. Another glass plate was placed on the platinum electrode to hold both the membrane and the electrodes. The measurement conditions were controlled by a bench-top-type temperature and humidity chamber (SH-221, ESPEC). The impedance spectra were then measured using ZPlot/ZView software (Scribner Associates) under an AC perturbation signal of 10 mV for in the frequency range of 1 Hz to 10000 KHz. The proton conductivity σ (S/cm) of the membranes was calculated using Eq. 3.

$$\text{Proton conductivity } \sigma = D/(R \times L \times T) \times 10^4 \text{ S/cm} \qquad (3)$$

where R is the membrane resistance, D is the distance between two platinum electrodes, L is the membrane width, and T is the membrane thickness.

8. Supporting Reference

S1. N. Hara, H. Ohashi, T. Ito and T. Yamaguchi, *J. Phys. Chem. B*, 2009, **113**, 4656–4663.

S2. F. S. Mancilha, B. A. D. Neto, A. S. Lopes, P. F. Moreira, F. H. Quina, R. S. Goncalves and J. Dupont, *Eur. J. Org. Chem.*, 2006, **21**, 4924–4933.

9. Supplementary Figures

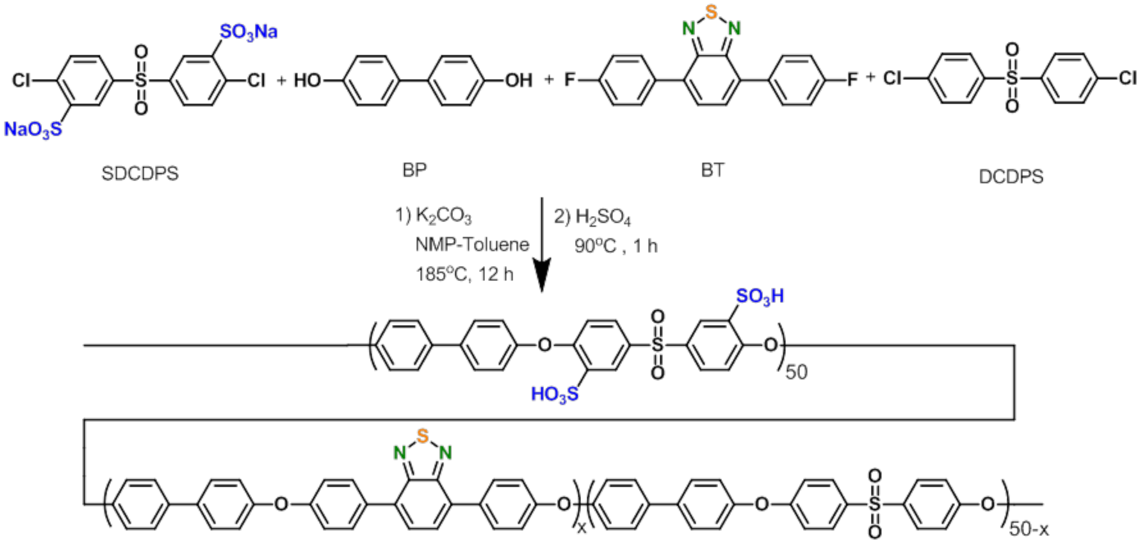

Fig. S1 Schematic representation for the synthesis of BT-based copolymers (x = 0.1, 1).

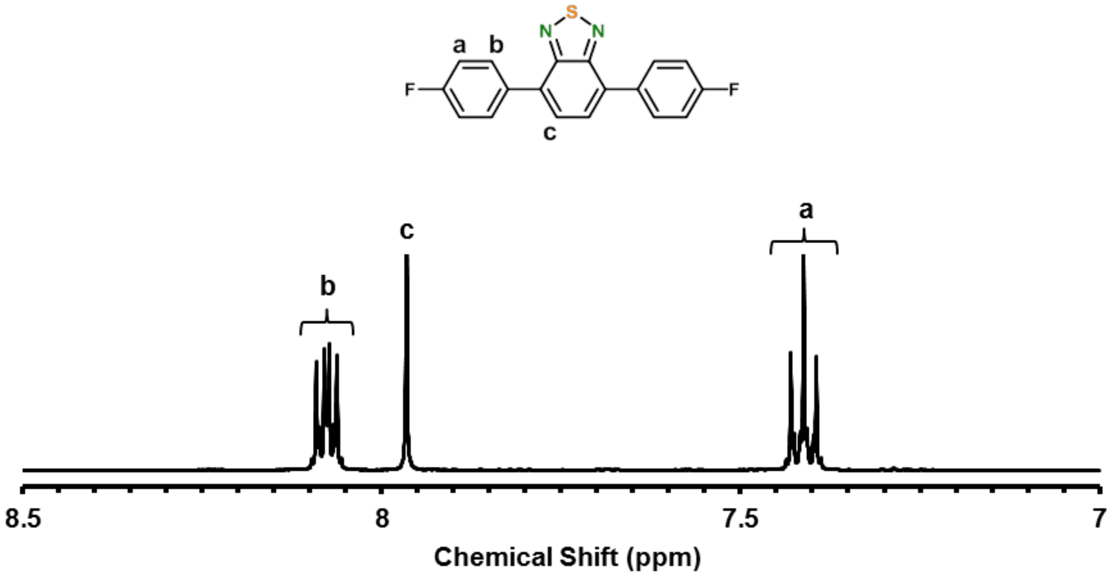

Fig. S2 ^{1}H NMR spectra of hydrophobic BT-based monomer.

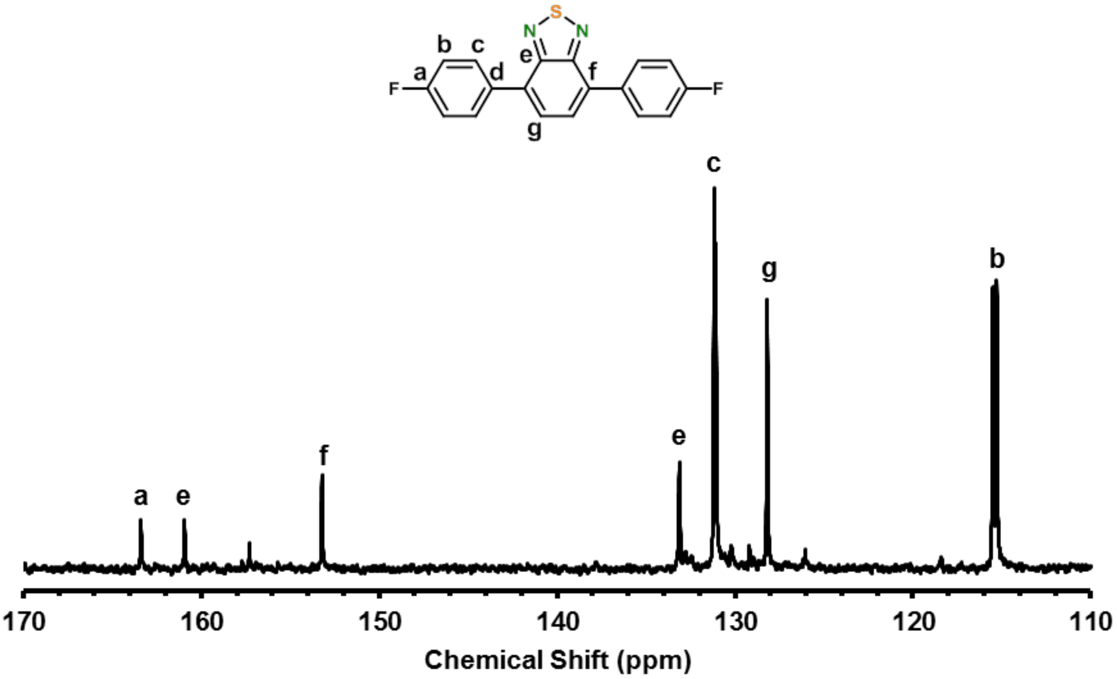

Fig. S3 ^{13}C NMR spectra of hydrophobic BT-based monomer.

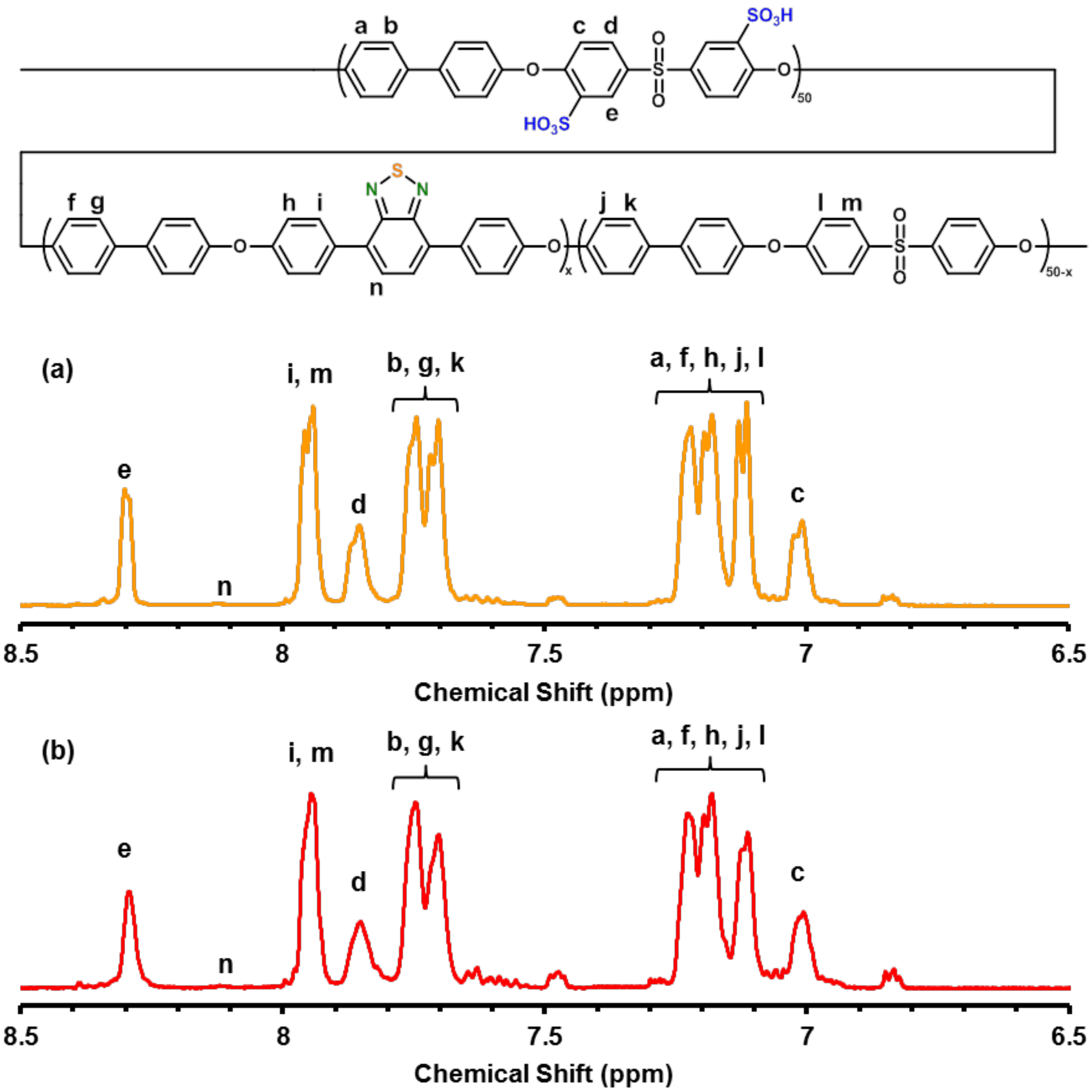

Fig. S4 ^{1}H NMR spectra of an aromatic random polymer based on BT units. (a) SPES-0.1%BT (x = 0.1), (b) SPES-1%BT (x = 1).

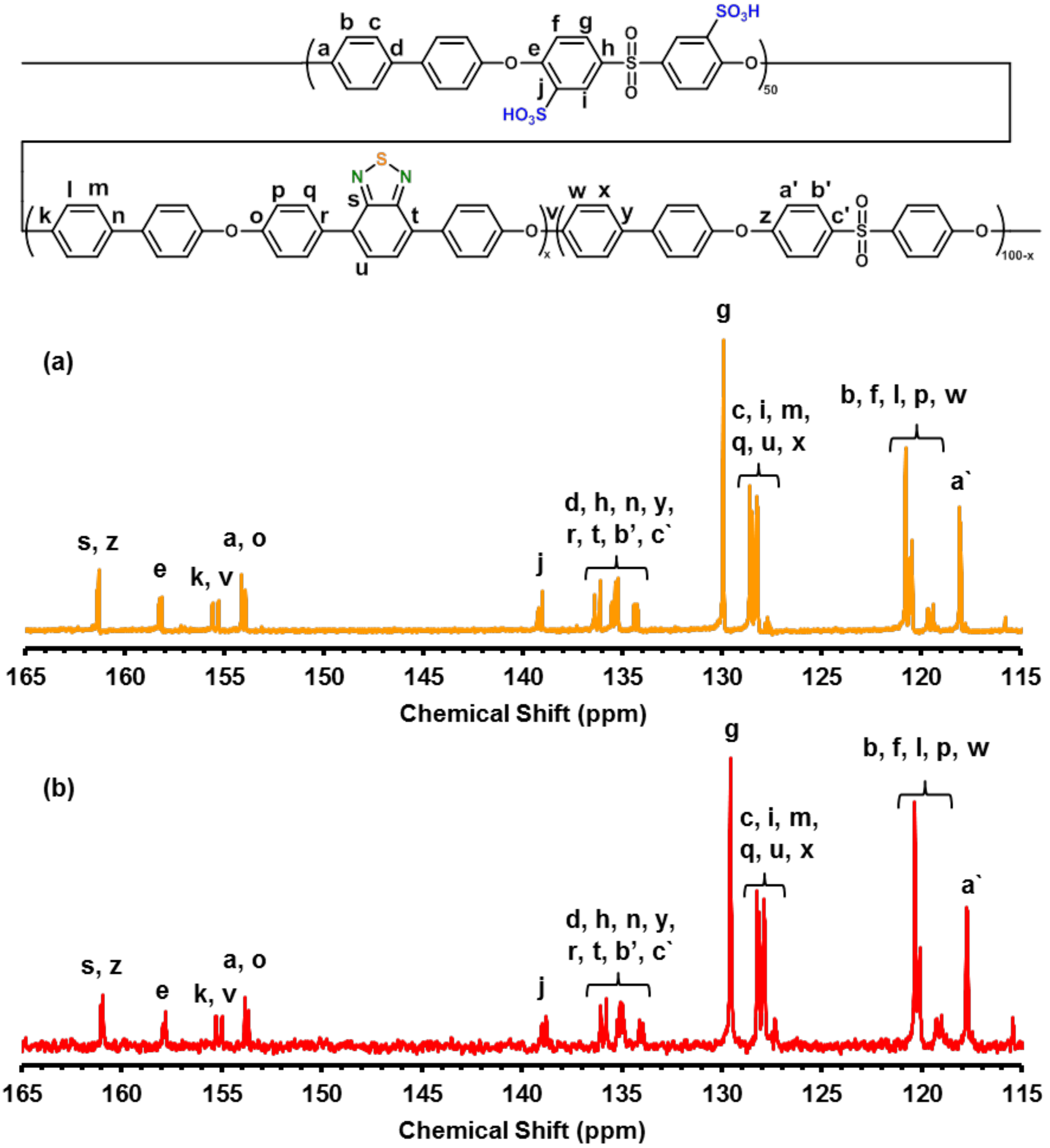

Fig. S5 ^{13}C NMR spectra of aromatic random polymer based on BT units. (a) SPES-0.1%BT (x = 0.1) and (b) SPES-1%BT (x = 1).

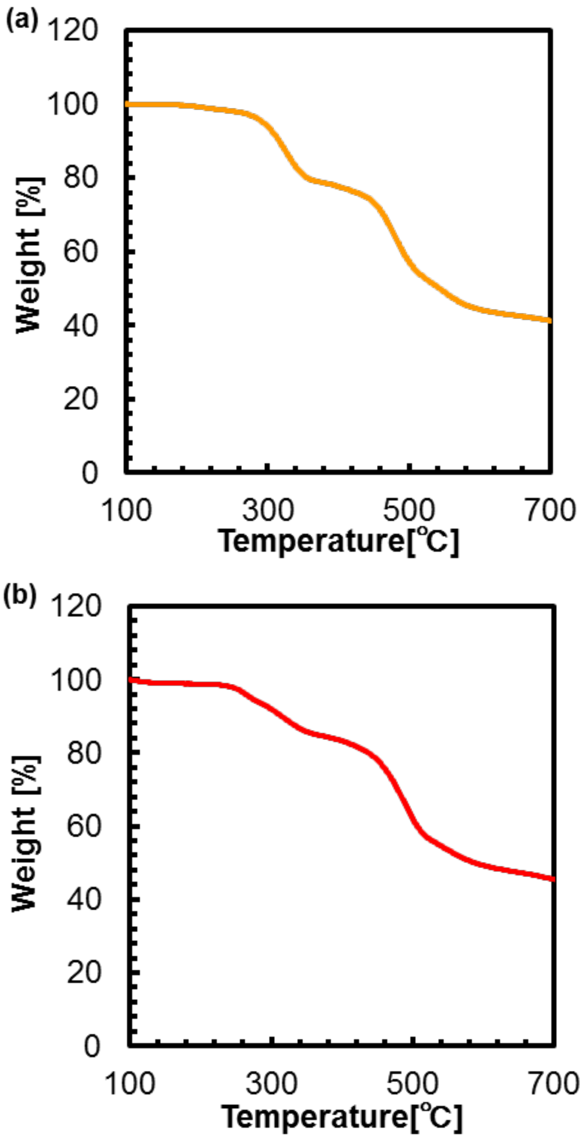

Fig. S6 TG-curves of (a) SPES-0.1%BT (x = 0.1) and (b) SPES-1%BT (x = 1).

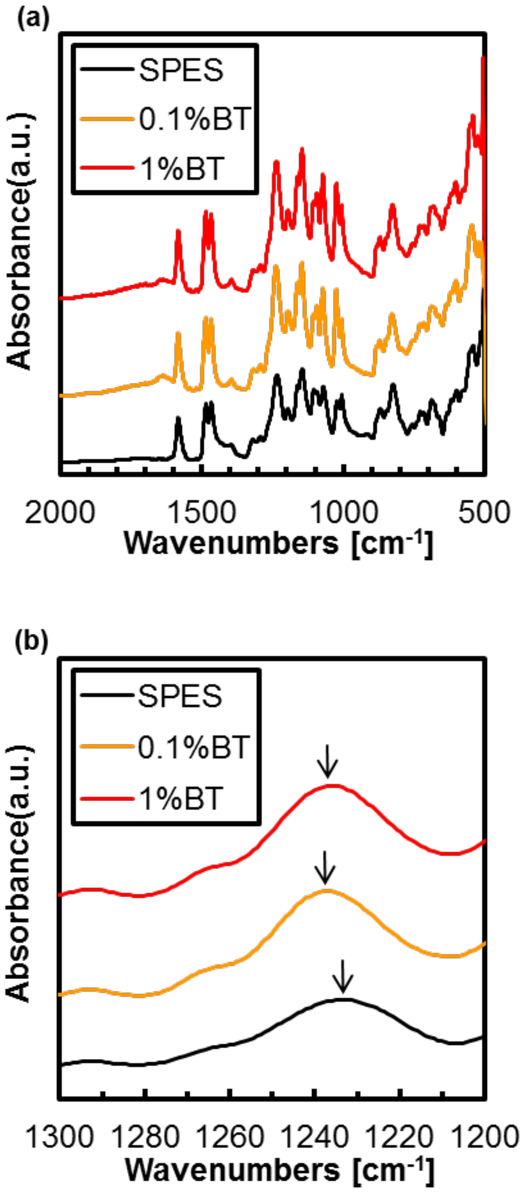

Fig. S7 IR spectra in the (a) 2000–500 cm^{-1} and (b) 1300–1200 cm^{-1} range of SPES membrane; 0.1%BT membrane; 1%BT membrane.

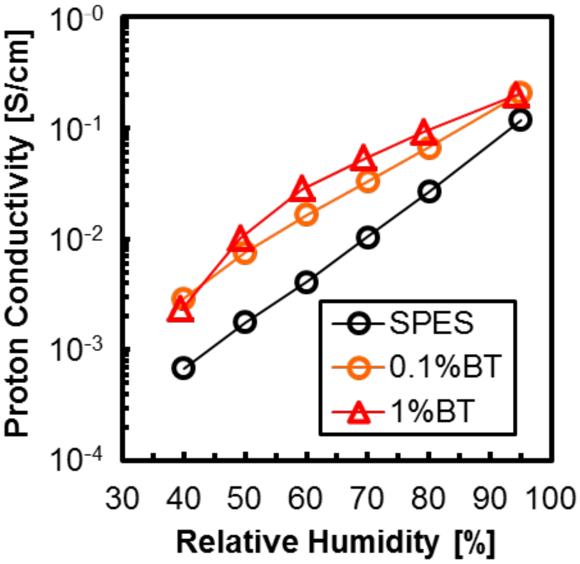

Fig. S8 Proton conductivity as a function of relative humidity at 80°C.