

Supporting Information

Polymer Electrolyte Membranes Based on Multiblock Poly(phenylene ether ketone)s with Pendant Alkylsulfonic Acids: Effects on the Isomeric Configuration and Ion Transport Mechanism

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Synthetic procedure

Synthesis of 2-Chloro-4-fluoro-4'-methoxybenzophenone (CFMB). To a 250 mL flask equipped with a magnetic stirrer, 2-chloro-4-fluorobenzoic acid (20.00 g, 114.6 mmol) and 100.0 mL of thionyl chloride was added. The solution was kept at 85 °C for 10 h and the excessive thionyl chloride was evaporated under atmosphere. The 2-chloro-4-fluorobenzoyl chloride (CFBC) was obtained by evaporating under reduced pressure to afford a colorless liquid; 20.30 g (yield: 92%).

To a fully dried 250 mL three-necked flask, AlCl₃ (15.20 g, 114.0 mmol) and anisole (60.00 mL) were charged. After cooling to 0 °C by an ice-water bath, CFBC (20.00 g, 103.6 mmol) was added dropwise to the mixture through a pressure-equilibrium drop funnel and the reaction mixture was then heated to 50 °C for 3 h. The solution was poured into ice water with a few drops of HCl, and the product was extracted with chloroform. After drying over MgSO₄, evaporation, and recrystallization from ethanol, CFMB (20.85 g) was obtained; yield: 76%. FTIR (KBr): ν 2960-2870 (C-H), 1647 (C=O), 1597 (C=C), 1180 cm⁻¹ (C-O-C). ¹H NMR (CDCl₃, ppm): δ = 7.78-7.76 (*d*, 2H, *J* = 10.0 Hz), δ = 7.38-7.35 (*m*, 1H), δ = 7.22-7.19 (*m*, 1H), δ = 7.10-7.06 (*m*, 1H), δ = 6.95-6.93 (*d*, 2H, *J* = 10.0 Hz), δ = 3.88 (*s*, 3H, -OCH₃). ¹³C NMR (CDCl₃, ppm): δ = 191.94 (1C, C7), 163.22 (1C, C11), 163.05, 161.04 (1C, C3), 134.18 (1C, C6), 131.52 (2C, C9), 129.62 (1C, C1), 129.54 (1C, C5), 128.37 (1C, C8), 116.63, 116.44 (1C, C2), 113.22 (1C, C4), 112.96 (2C, C10), 54.59 (1C, C12). LCMS/MS: 265.68 (*m/z*)⁺.

Synthesis of Bis[5-fluoro-2-(4'-methoxybenzoyl)]biphenyl (*m*-BFMBP). To a 100 mL two-necked flask equipped with a magnetic stirrer, were charged with CFMB (10.00 g, 37.78 mmol), Ni(PPh₃)₂Cl₂ (1.240 g, 1.890 mmol), and zinc dust (6.180 g, 94.45 mmol). After being exchanged with argon three times, 60.0 mL of anhydrous DMAc was added. The reaction mixture underwent a color change from green to yellowish brown and finally dark red at 50

°C for 24 h. After filtration, the product was separated by a silica column using EtAc/*n*-Hex as eluents. By recrystallization from ethanol, *m*-BFMBP (7.360 g) was obtained as white needle-like crystals; yield: 85%. FTIR (KBr): ν 2960-2870 (C-H), 1647 (C=O), 1600 (C=C), 1180 cm^{-1} (C-O-C). ^1H NMR (CDCl_3 , ppm): δ = 7.59-7.57 (*d*, 4H, J = 10.0 Hz, Ar-H), δ = 7.36-7.33 (*m*, 2H, Ar-H), δ = 7.12-7.09 (*m*, 2H, Ar-H), δ = 7.04-7.01 (*m*, 2H, Ar-H), δ = 6.69-6.67 (*d*, J = 10.0 Hz, 4H, Ar-H), δ = 3.79 (*s*, 6H, -OCH₃). ^{13}C NMR (CDCl_3 , ppm): δ = 193.61 (2C, C7), 162.97, 160.96 (2C, C3), 162.41 (2C, C11), 140.96 (2C, C1), 133.67 (2C, C6), 131.75 (4C, C9), 130.24 (2C, C8), 128.93 (2C, C5), 117.60, 117.42 (2C, C2), 113.07, 112.90 (2C, C4), 112.29 (4C, C10), 54.37 (2C, C12). LCMS/MS: 459.45 (m/z)⁺.

Characterization

Ion Exchange Capacity (IEC). *IECs* of the membranes were determined by a titration method. The proton-type samples were ion-exchanged by a 15 wt% NaCl solutions and titrated with a 0.02 M NaOH solution with phenolphthalein as the indicator. *IEC* was calculated from Equation (1):

$$IEC = C_{\text{NaOH}} \times V_{\text{NaOH}} / W_d \quad (1)$$

where C_{NaOH} and V_{NaOH} are the concentration of NaOH solution and the consumed volume of NaOH solution, respectively. W_d refers to the weight of a dry membrane sheet.

Water Uptake. Water uptake (WU) was measured by soaking a sample sheet in water at 80 °C, 95% RH for 2 h. Then the membrane was taken out and weighed on a microbalance. Water uptake was calculated from Equation (2):

$$WU = (W_s - W_d) / W_d \times 100\%$$

where W_s is the weight of the water-absorbed membrane.

Proton Conductivity. Proton conductivity in plane direction of the membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 10 Hz to 1 MHz (Hioki 3532-80). A two-point probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed in a thermo-controlled humid chamber at 80 °C for 2 h before the measurement. Proton conductivity (σ) was calculated from the following Equation (3):

$$\sigma = \frac{d}{t_s w_s R} \quad (3)$$

where d is the distance between the two electrodes, t_s and w_s are the thickness and width of the membrane, and R is the resistance measured.

Atomistic simulation methods

All molecular simulations were done using the Materials Studio software package of Accelrys, Inc. (San Diego, CA). Atomistic construction models were generated using the Amorphous Cell module and were subsequently equilibrated using molecular dynamics (MD) simulations with the Forcite module, which was also applied for the diffusion simulations. The COMPASSII force field was used during each stage of the simulations. In all cases, the non-bond interactions were calculated up to a cut-off distance of 18.5 Å, which was truncated using a cubic spline function with a width of 1 Å. For this, a Ewald representation for the summation of the electrostatic interactions, and an atom-based representation for the summation of the van der Waals interactions were used during construction model generation, equilibration and subsequent production runs. The respective Andersen temperature, and Berendsen pressure control algorithms were used throughout, and the Smart minimization algorithm as implemented in the Amorphous Cell and Forcite modules of Materials Studio was used for all geometry optimizations. A collision ratio of 1.0 was used for the external Andersen thermostat; while a decay constant of 0.1 ps was applied for the Berendsen barostat.

Free volume calculation method. The FFV value of **bSPPEK** membranes can be estimated using the Equations (4):

$$FFV = \frac{V_f}{V_{sp}} = \frac{V_{sp} - 1.3V_w}{V_{sp}} \quad (4)$$

where V_f (cm³/g) is the free volume, or void volume, of the polymer, and V_{sp} (cm³/g) the specific volume (reciprocal of polymer density). The free volume is frequently calculated by subtracting the volume occupied by the polymer chains per unit mass from the polymer specific volume, or total volume. The occupied volume is then calculated from the total van der Waals volume, V_w (cm³/g), of the participating functional groups in the polymer repeat units that is in turn calculated with the Bondi group contribution method,¹ which uses a so-called “universal packing constant” of 1.3. Thus, the total occupied volume $V_{oc}=1.3V_w$.

Radial distribution function (RDF). An RDF was adopted to analyze the microstructure of the material characteristic. This function counts the number of two-atom species within specific distances and is defined as Equations (5):

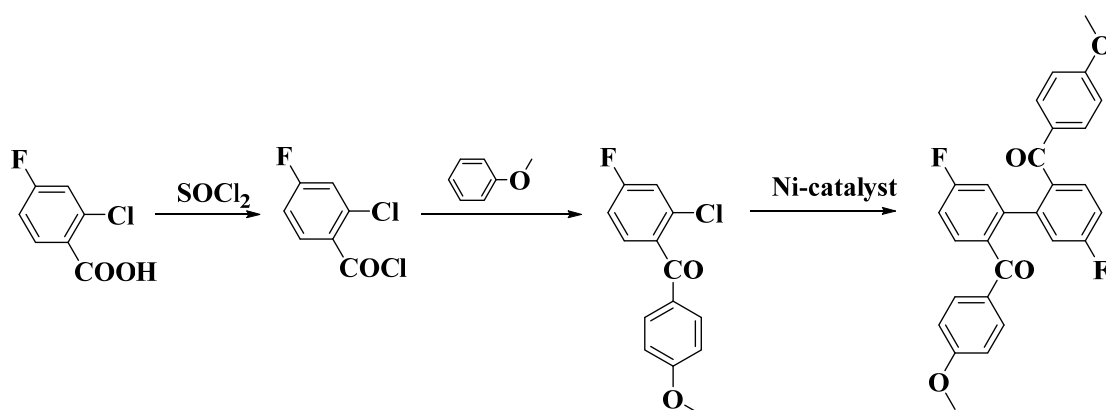
$$g_{\alpha,\beta}(r) = \frac{V_0}{N_\beta} \frac{N_\beta(r)}{4\pi r^2 \Delta r} \quad (5)$$

where V_0 is the cell volume, N_β is the total number of β atoms, and $N_\beta(r)$ is the number of β atoms found within a spherical shell with radius r to $r+\Delta r$, which corresponds to α atoms.

Diffusion simulations. Mean squared displacement (MSD) of functional groups and water molecules can be analyzed using the Einstein relationship (6):

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_i^{N_a} |R_i(t) - R_i(t_0)|^2 \quad (6)$$

where N_α is the total number of atoms, $R_i(t_0)$ and $R_i(t)$ are the initial and final positions of the centre of mass of particle i over the simulation time t that was used, and the term in brackets is the mean square displacement (MSD) averaged over the total number of molecules of penetrant α . In this study, a certain amount of water molecules were randomly inserted into the membrane matrix to calculate their MSD diagrams and self-diffusivities.



Scheme S1 Synthetic route of *m*-BFMBP.

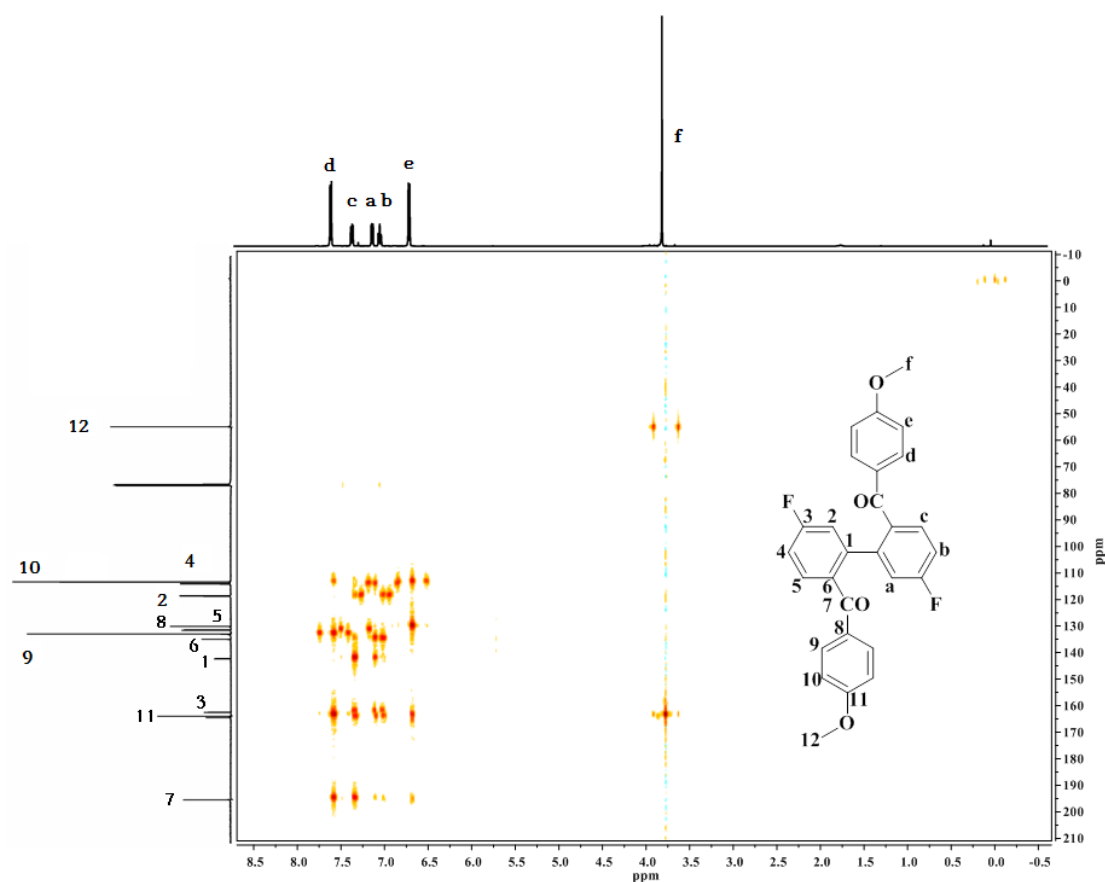


Figure S1. ^{13}C - ^1H COSY NMR spectrum of *m*-BFMBP in CDCl_3 .

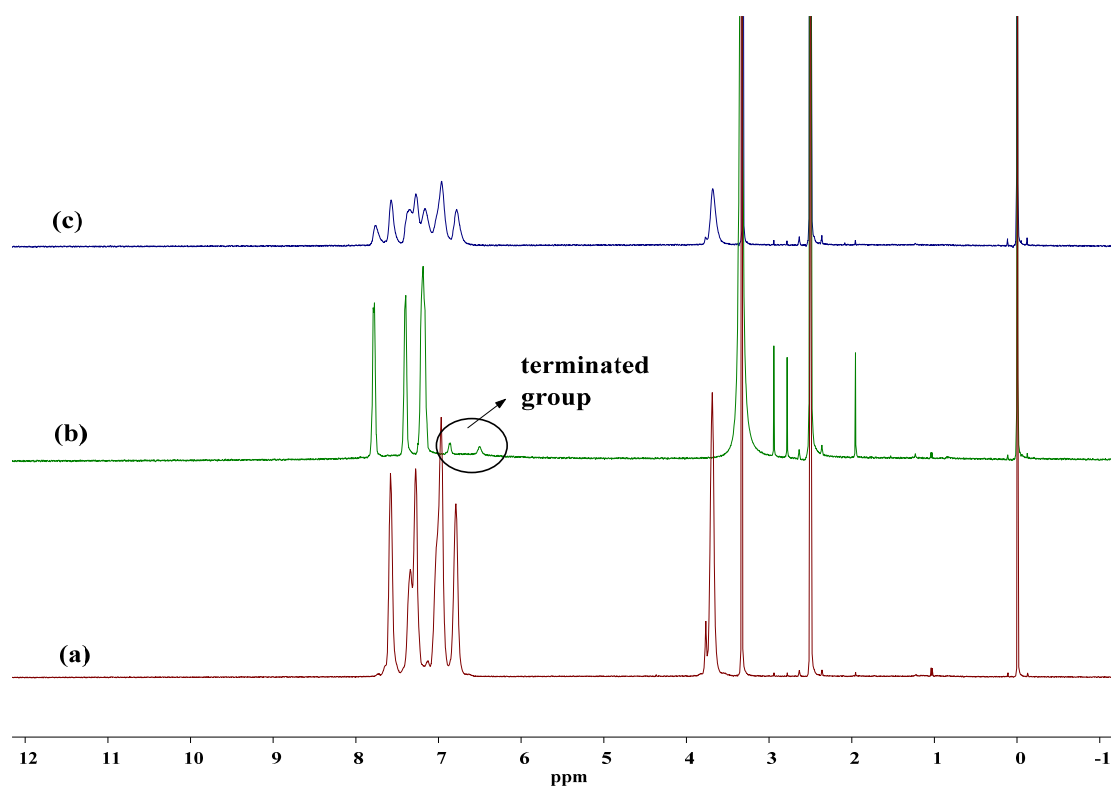


Figure S2. ^1H NMR spectra of (a) oligomer O1; (b) oligomer O2; and (c) polymer P3.

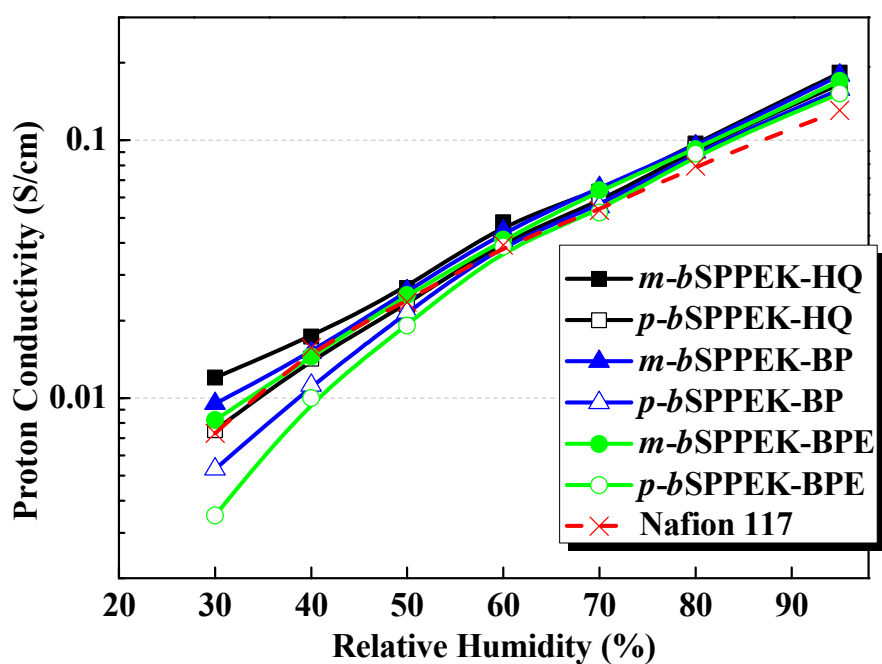


Figure S3. Proton conductivities of bSPPEKs and Nafion 117 membranes as a function of relative humidity condition.

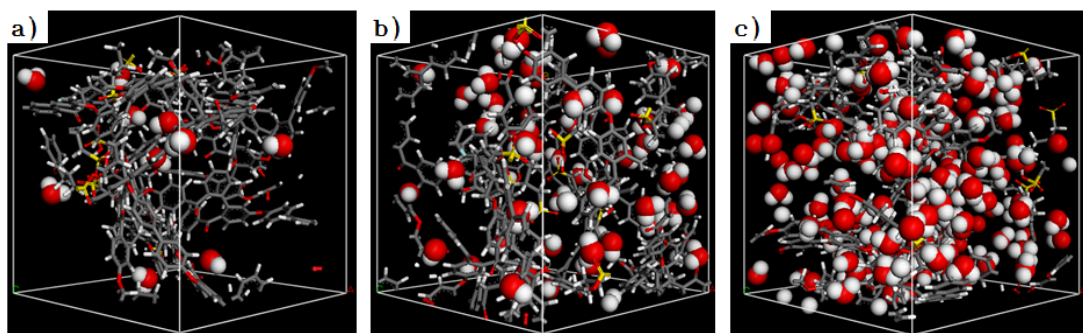


Figure S4. Illustrative example of a relaxed bSPPEK and water molecules construction model in the cubic simulation cell (In-cell style). Carbon atoms are colored grey, sulfur atoms are colored yellow, and H₂O molecules are displayed as CPK type. a) $\lambda=1$; b) $\lambda=5$; c) $\lambda=15$.

Table S1 Equilibration and dynamic steps.

Step	Task	Ensemble	Pressure	Temperature	Simulation time
1	Annealing	NVT	-	300-1000 K	10.0 ns
2	Dynamics	NPT	0.1 MPa	400 K	5.0 ns
3	Dynamics	NPT	1.0 MPa	353 K	5.0 ns
4	Dynamics	NVT	-	353 K	10.0 ns

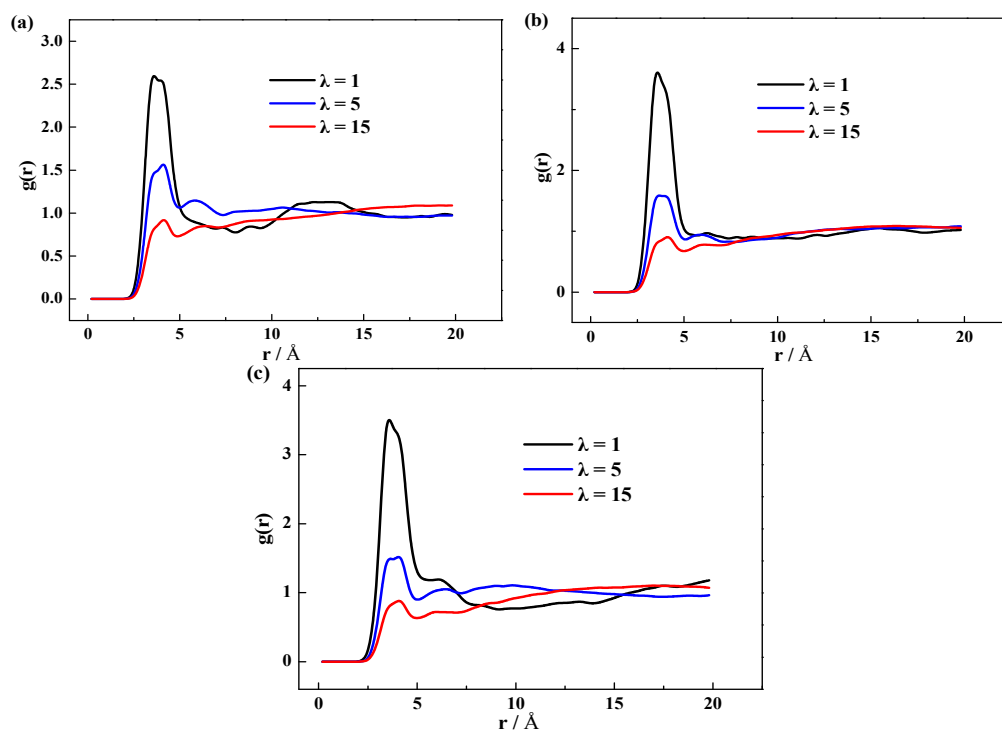


Figure S5. RDF for *p*-bSPPEK between sulfonate sulfur and water molecules as a function of λ values at 353 K.

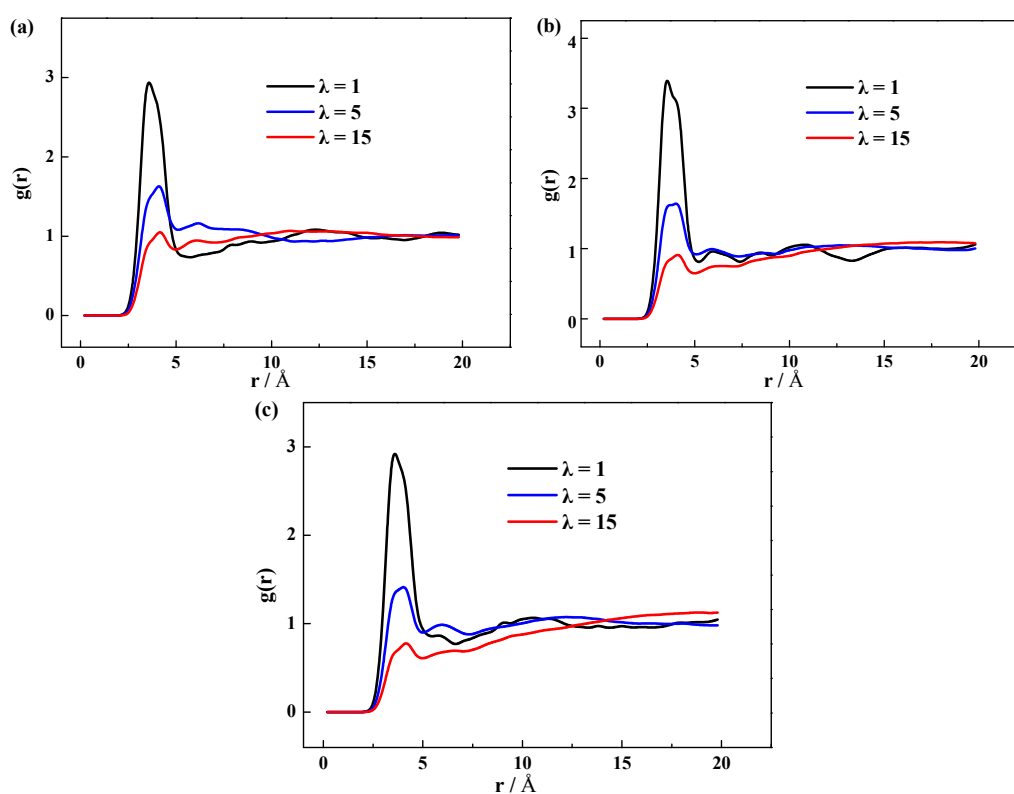


Figure S6. RDF for *m*-bSPPEK between sulfonate sulfur and water molecules as a function of λ values at 353 K.

REFERENCE

- (1) Bondi, A. van der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, *68*, 441–451.