

Supporting information

High Hydroxide-Conducting Polymer Electrolyte Membranes from Aromatic ABA Triblock Copolymers

Qing Li,^a Lei Liu,^a Qingqing Miao,^b Bangkun Jin^{*a} and Ruke Bai^{*a}

^a CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China.

^b CAS Key Laboratory of Soft Matter Chemistry, Department of Chemistry, University of Science and Technology of China, Hefei 230026, P. R. China.

E-mail: bairk@ustc.edu.cn

Experimental Section

Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was supplied by the Institute of Chemical Engineering of Beijing (China). 4,4'-Difluorodiphenyl sulfone (FPS), bisphenol A (BPA), dimethylamino pyridine (DMAP), CuCl, 2,2'-azobisisobutyronitrile (AIBN), N-bromosuccinimide (NBS), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), chlorobenzene, toluene, methanol, tetrahydrofuran (THF), chloroform and potassium carbonate (K₂CO₃) were used as purchased. AIBN was dissolved in boiled methanol, then recrystallized in an ice bath and dried at room temperature under vacuum. CuCl was dissolved in strong HCl, precipitated by dilution with water and filtered off. The precipitate was washed with ethanol and diethyl ether, then dried and stored in a vacuum desiccator.

Synthesis of OH-terminated poly(arylene ether sulfone)s (HO-PAES-OH)

Into a three-neck flask equipped with a magnetic stirrer, Dean–Stark trap, and an argon gas inlet were added 46 mmol of FPS, 48 mmol of BPA, and 60 mmol of K₂CO₃. Then, 60 mL of NMP and 30 mL of toluene were charged into the reaction flask under an argon atmosphere and the reaction mixture was heated to 140 °C. After dehydration and removal of toluene for 4 hours, the reaction temperature was increased to about 170 °C. The reaction was maintained at 170 °C for 20 h, then was cooled to room temperature and poured into a large excess of deionized water

acidified with HCl under vigorous stirring. The precipitate was washed thoroughly with water and ethanol several times, and dried under vacuum at 60 °C for 24 h. Yield: 97%.

Synthesis of triblock copolymers containing poly(2,6-dimethyl-1,4-phenylene oxide) and poly(arylene ether sulfone)s (PPO-PAES-PPO).

The following represents a typical procedure for the synthesis of PPO-PAES-PPO-0.38 (0.38 represents the weight ratio of PPO to PAES). HO-PAES-OH (2.11 g), PPO (0.8 g), DMAP (0.186 g) and CuCl (0.096 g) were added into the reaction flask under an argon atmosphere. The reaction was started by the addition of chloroform (60 mL). After reaction during 1 week at room temperature, the reaction mixture was poured into methanol. The obtained precipitate was washed thoroughly with methanol and water several times and dried in a vacuum oven at 60 °C for 24 h. Yield: 92%

Synthesis of brominated triblock copolymers (BPPO-PAES-BPPO)

A typical synthetic procedure for BPPO-PAES-BPPO-0.38 as follows: PPO-PAES-PPO-0.38 (1.5 g, ca. 3.4 mmol of PPO repeat units) was dissolved in chlorobenzene (40 mL) and then, NBS (1.6 g, 9 mmol) and AIBN (0.3 g) were added. The mixture was heated at reflux conditions (135 °C) for 4 h. After cooling, the reaction mixture was poured into methanol to precipitate the product. The polymer was filtered and washed with methanol, and the residue subsequently was redissolved in chloroform (120 mL) and precipitated into methanol. The polymer was collected and dried in a vacuum oven at 45 °C for 24 h, the degree of bromomethylation: 0.88. Yield: 94%.

Membrane preparation and quaternization

BPPO-PAES-BPPO polymers were dissolved in chlorobenzene to form 5 wt % solutions. The solutions were cast onto a glass dish and dried at 60 °C for 24 h to form transparent and tough membranes. The membranes were immersed in 30 wt % trimethylamine aqueous solution at room temperature for 48 h for the quaternization reaction. The quaternary ammonium triblock copolymer membranes were washed with water several times and immersed in 1 M NaOH at room temperature for 48 h to obtain the hydroxide conductive QPPO-PAES-QPPO membranes (thickness: 30 ± 5 μm). They were then washed thoroughly with deionized water and stored in a closed vessel filled with deionized water.

Characterization

NMR spectra were recorded on a Bruker AVANCE II spectrometer with TMS as an internal

standard. Thermal analysis was carried out on NETZSCH STA 449F3 thermogravimetric analyzer (TGA). Samples were heated from 50 to 800 °C at a heating rate of 10 °C /min under a nitrogen flow. Tensile measurements of fully humidified membranes were carried out using a Q800 dynamic mechanical analyzer (DMA, TA Instruments) at a stretch rate of 0.5 N/min at room temperature. The cross sectional area of the samples is about 0.40 mm². Stress-strain curves were recorded and tensile modulus was determined from the slope of the initial, linear portion of the stress-strain curve. Tapping mode atomic force microscopy (AFM) observations were performed with a veeco diInnova SPM, using micro-fabricated Cantilevers with a force constant of approximately 20 N/m.

Small-angle X-ray scattering (SAXS) was measured for the dry triblock copolymer membranes experiments at room temperature. SAXS experiments were performed at the beamline BL16B1 of Shanghai Synchrotron Radiation Facility (SSRF) (wavelength, $\lambda=0.124$ nm). Two-dimensional SAXS patterns were obtained using a Mar165 CCD detector (2048×2048 pixels with pixel size of 80 μ m). The effective scattering vector (q) were calculated from the scattering angles (θ) using ($q = 4\pi\sin 2\theta/\lambda$), where λ and 2θ are the incident wavelength and total scattering angle, respectively. Where λ is the wavelength and 2θ is the scattering angle. The Bragg distance d is related to q , $d = 2\pi/q$.

The molecular weight and molecular weight distribution of the polymers were measured on a Waters gel permeation chromatography (GPC) system, which was equipped with a Waters 1515 HPLC solvent pump, a Waters 2414 refractive index detector, and three Waters Styragel high-resolution columns at 40 °C using HPLC grade chloroform as eluent at a flow rate of 1.0 mL/min. Monodispersed polystyrenes were used to generate the calibration curve.

Hydroxide conductivity

The ionic conductivities of the membranes were measured using the commonly encountered four-point probe technique. The impedance was recorded using an Autolab PGSTAT 30 (Eco Chemie, Netherland) at galvanostatic mode with a current amplitude of 0.1 mA over frequencies ranging from 1 MHz to 50 Hz. Bode plots were used to determine the frequency region over which the the magnitude of the impedance was constant, and the ionic resistance was then obtained from the associated Nyquist plot (Fig. S5). The membrane being studied was set into a

Teflon cell where it was in contact with 2 current collecting electrodes and 2 potential sensing electrodes (the distance between the potential sensing electrodes was 1 cm). The cell was completely immersed in deionized water and the impedance spectrum was collected. This was done quickly to minimize the potential error caused by reaction of the hydroxide ions in the membrane with dissolved carbon dioxide (resulting in the formation of carbonate/bicarbonate anions and reduced membrane conductivity). The ionic conductivity was calculated according to the following equation:

$$\sigma = \frac{L}{RWd} \quad (1)$$

where R is the obtained membrane resistance, L is the distance between potential-sensing electrodes (here 1 cm), and W and d are the width (here 1 cm) and thickness of the membrane, respectively.

Ion exchange capacity (IEC)

IEC was measured using standard back titration methods. The membranes in OH⁻ form were immersed in 100 mL of 0.1 M HCl standard solution for 24 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator. The IEC value was calculated using the equation:

$$\text{IEC} = \frac{V_{0,\text{NaOH}} C_{\text{NaOH}} - V_{x,\text{NaOH}} C_{\text{NaOH}}}{m_{\text{dry}}} \quad (2)$$

where $V_{0,\text{NaOH}}$ and $V_{x,\text{NaOH}}$ are the volume of the NaOH consumed in the titration without and with membranes, respectively, C_{NaOH} is the mole concentration of the standardized NaOH solution, and m_{dry} is the mass of the dry membranes. Three replicates were conducted for each sample.

Water uptake and swelling ratio

The water uptake values were determined for all the membranes in their OH⁻ forms. The membranes were dried in a vacuum oven at 80 °C to obtain a constant dry weight. The dry membrane samples were soaked in the deionized water at a given temperature for 24 h. The hydrated polymer membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake values of membranes were calculated according to

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (3)$$

Where W_{dry} and W_{wet} are the weight of the dry and water-swollen membranes, respectively.

The number of absorbed water molecules per ammonium group (λ) was calculated according to

$$\lambda = \frac{\text{Water uptake}}{18 \times \text{IEC}} \times 1000 \quad (4)$$

The swelling ratio was characterized by linear expansion ratio, which was determined by the difference between wet and dry dimensions in the length or thickness direction of a membrane sample. The swelling ratio was calculated from

$$\text{Swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \quad (5)$$

Where l_{wet} and l_{dry} are the dimensions of wet and dry membranes, respectively.

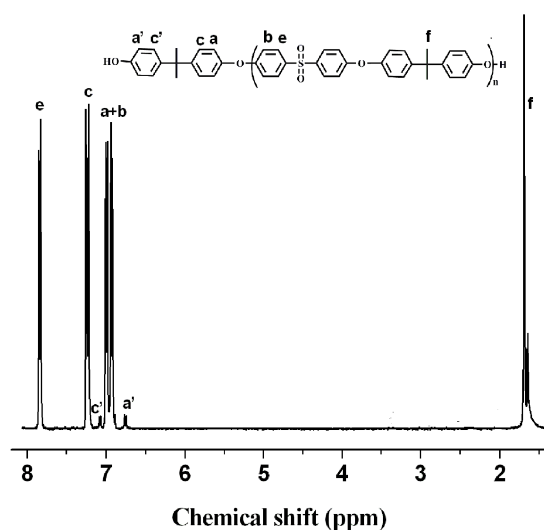


Fig. S1 ^1H NMR spectrum of HO-PAES-OH in CDCl_3 .

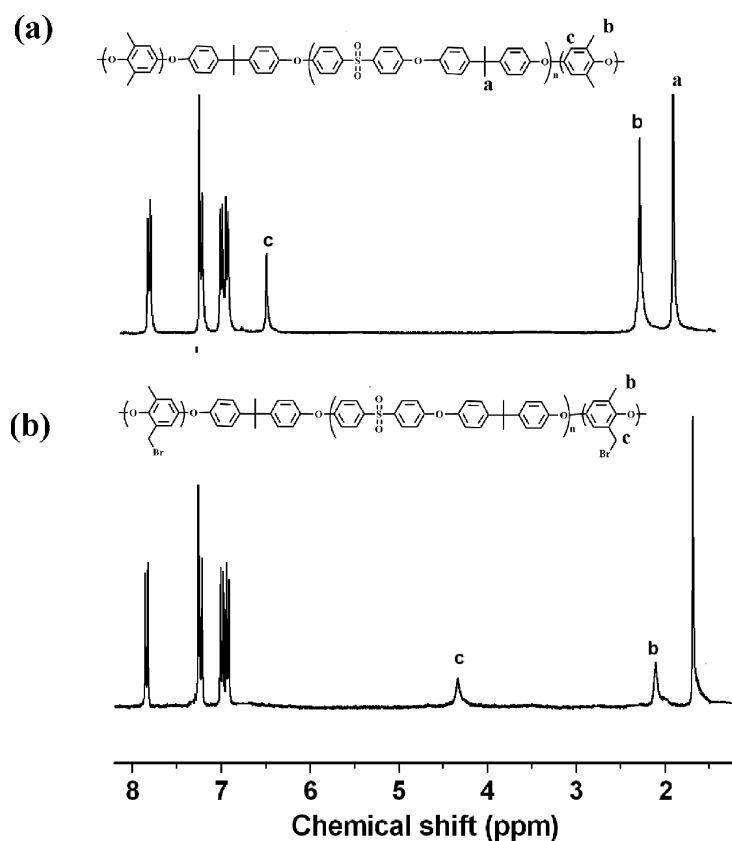


Fig. S2 ¹H NMR spectra of (a) PPO-PAES-PPO-0.38 and (b) BPPO-PAES-BPPO-0.38 in CDCl₃.

Table S1. Molecular weights and molecular weight distributions of triblock copolymers.

sample	M _{n, GPC} ^a (g/mol)	M _{w, GPC} ^a (g/mol)	M _{w, GPC} / M _{n, GPC}
HO-PAES-OH	16900	26500	1.56
PPO-PAES-PPO-0.38	22900	36500	1.59
PPO-PAES-PPO-0.76	30900	46700	1.51
PPO-PAES-PPO-1.14	37300	61200	1.64

^a Determined by GPC.

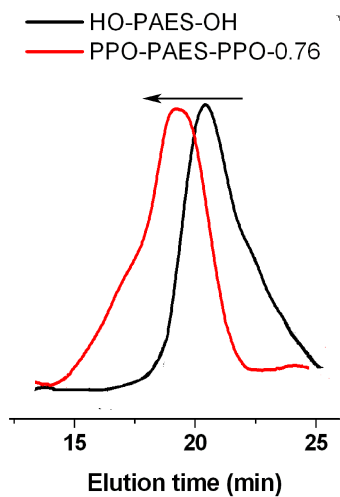


Fig. S3 Representative GPC traces of HO-PPO-OH and PPO-PAES-PPO-0.76.

Table S2. Solubility of HO-PAES-OH, PPO, PPO-PAES-PPO and BPPO-PAES-BPPO.

sample	H ₂ O	CHCl ₃	THF	DMF	chlorobenzene
HO-PAES-OH	–	+	+	+	–
PPO	–	+	+	–	+
PPO-PAES-PPO	–	+	+	–	+
BPPO-PAES-BPPO	–	+	+	+	+

+, soluble at room temperature; –, insoluble.

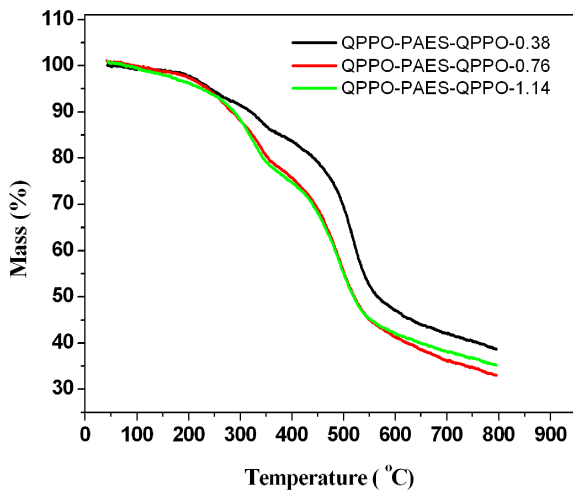


Fig. S4 TGA curves for the QPPO-PAES-QPPO membranes under N₂ atmosphere.

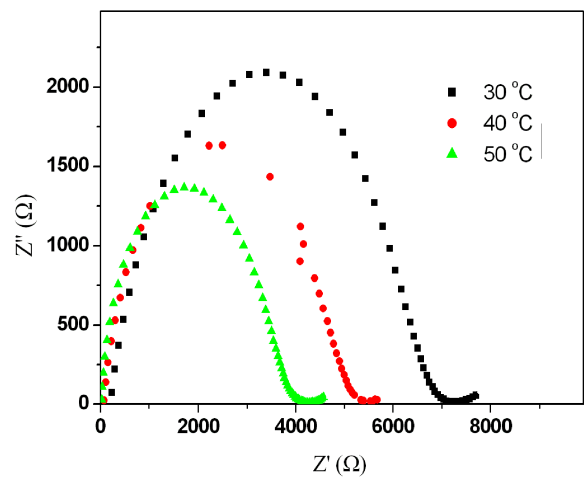


Fig. S5 Representative Nyquist plots of Z'' vs. Z' from AC impedance spectroscopy measurements of the QPPO-PAES-QPPO-0.76 membrane.

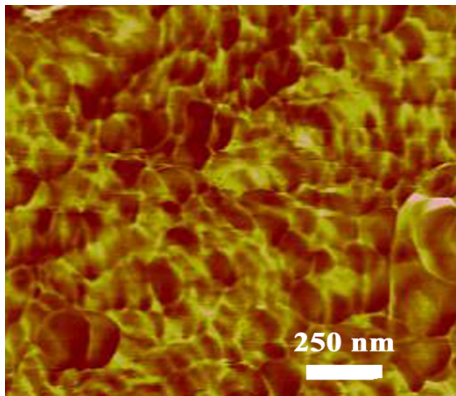


Fig. S6 The AFM tapping phase image of QPPO-PAES-QPPO-1.14

Table S3. Mechanical properties of the QPPO-PAES-QPPO membranes

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
QPPO-PAES-QPPO-0.38	36.7	480.0	17.5
QPPO-PAES-QPPO-0.76	24.2	269.3	25.3
QPPO-PAES-QPPO-1.14	21.5	243.8	9.6

Table S4. The alkaline stability of QPPO-PAES-QPPO-0.38 and QPPO-1 membranes in 1 M NaOH at 80 °C.

Sample	OH ⁻ conductivity (mS/cm) at 30 °C					
	0 days	1 day	3 days	5 days	7 days	10 days
QPPO-1	6.8	4.2	2.5	- ^a	- ^a	- ^a
QPPO-PAES-QPPO-0.38	32.1	24.3	20.2	18.2	16.8	15.7

^a The membrane was broken into small pieces, not to measure.

