A novel guanidinium grafted poly(aryl ether sulfone) for high-performance hydroxide exchange membranes

Electronic Supplementary Information

Materials and Measurements

1. Materials

All reagents were purchased from Aldrich and used without purification, except for NMP, which was dried over CaH_2 and distilled under reduced pressure before use.

2. Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity spectrometer at 300 M Hz at 30°C with DMSO-d_6 as the solvent. The thermogravimetric analyses (TGA) were obtained under nitrogen using a PerkinElmer TGA-2 thermogravimetric analyzer (Inspiratech 2000 Ltd., UK) at a heating rate of 10°C/min. The ion-exchange capacity, defined in this study as mol (OH^-) g^{-1} (dry HEMs), was determined using the standard back-titration technique reported previously.[1]

The ionic conductivity in the longitudinal direction was measured by the four-electrode method using an AC impedance analyzer under water-immersed conditions. The equipments used were an impedance/gainphase analyzer (Solartron SI 1260) and a potentiostat (Solartron SI 1287), and the measurements were carried out over the frequency range 1 Hz–100 kHz. All membrane samples were immersed in DI water for at least 24 h before testing. The conductivity of the membrane was

calculated using the equation

$$\sigma = \frac{L}{WdR}, \qquad (1)$$

Where σ is the ionic conductivity, L is the distance between the two reference electrodes, and W and d are the width and thickness of the membrane samples, respectively. R is the resistance of the membrane.

Eq. (2) was used to calculate the water uptake (W)

$$W = \frac{W_s - W_d}{W_d}, \qquad (2)$$

where W_d and W_s are the weights of the dry and water-swollen membranes, respectively.

The water swelling ratio of the membranes was investigated by immersing circular membrane samples in water at room temperature for a given time, and the swelling ratio (sr) was calculated from

$$sr = \frac{l_w - l_d}{l_d}, \qquad (3)$$

where l_d and l_w are the lengths of the dry and wet samples, respectively.

3. Monomer, polymer synthesis and membrane preparation

3.1 Monomer synthesis

3,3-bis(4-hydroxyphenyl)-2-(3-(methylamino)propyl)isoindolin-1-one (PPH-MPDA)

The monomer PPH-MPDA was synthesized according to the following procedure (Scheme 1). A 500 mL, three-necked, round-bottom flask equipped with a mechanical stirrer, gas inlet, and condenser was charged with 100.0 g (0.31 mol) PPH, 26.0 mL

(0.31 mol) concentrated hydrochloric acid and 150 g (1.7 mol) N'-methylpropane-1,3-diamine. This solution was refluxed for 24 h. Subsequently, the solution was poured into deionized water, and a white precipitate was obtained by filtration. The crude product was recrystallized from a mixture of ethanol and water. The yield was 85%. ^{1}H NMR (DMSO-d_6-ppm): 0.90 (m, 2H), 2.07 (s, 3H), 2.16 (t, 2H), 6.71 (d, 4H), 6.93 (d, 4H), 7.39 (d, 1H), 7.44 (t, 3H), 7.54 (t, 3H), 7.68 (d, 1H).

Vilsmeier salt

The Vilsmeier salt (C-chloro-N,N,N,N-tetramethylformamidine) was obtained by reaction of 1,1,3,3-tetramethylurea with oxalyl chloride in toluene.[2]

3.2 Polymer synthesis

PES-A

A typical example of polymerization is as follows: 4,4'-dichlorodiphenylsulfone (2.8716 g, 0.01 mol), PPH-MPDA (3.8846g, 0.01 mol), and K_2CO_3 (2.76 g, 0.02 mol) were charged into the flame-dried three-necked flask, which was equipped with a mechanical stirrer, nitrogen inlet, and a Dean-Stark trap. NMP was introduced to afford a concentration of 20% solids, and toluene (NMP/toluene 2/1v/v) was used as an azeotropic agent. The reaction mixture was heated under reflux at 140°C for 4 h to remove the water. The bath temperature was subsequently raised slowly to 160°C and reacted for an additional 10 h. The viscous solution was cooled to room temperature then diluted with NMP. The copolymer solution was filtered to remove the salt from the product, then isolated by precipitation in deionized (DI) water. The polymer was separated by filtration and dried in a vacuum oven at 120^{o}C for 24 h.

PES-G-Cl

A solution of PES-A (2.87 g, 0.05 mol) in anhydrous NMP was cooled to 0°C under argon, and the Vilsmeier salt (1.02 g, 0.06 mol) and triethylamine (0.51 g, 0.05 mol) were added. Following addition, the reaction mixture was stirred for an additional 2 h, warmed to 25°C, and stirred for 8 h. The polymer was recovered by precipitation, washed, and dried in an oven.

3.3. Membrane preparation

Polymer membrane was prepared by solution casting from NMP. Membranes were prepared by dissolving the polymer in NMP and casting on a levelled Teflon sheet. Polymer films were dried at 60°C for 12 h then at 120 ^{o}C under vacuum overnight. To replace the Cl^- anions in the membrane with OH^- anions, the PES-G-Cl membrane was immersed in a KOH solution (1 mol L^{-1}) for 48 h, then rinsed and soaked for 48 h at room temperature in deionized water.

(1) R. C. T. Slade, J. R. Varcoe, *Solid State Ionics*, 2005, **176**, 585-597.

(2) H. Xie, S. Zhang, H. Duan, *Tetrahedron Lett*., 2004, **45**, 2013-2015.

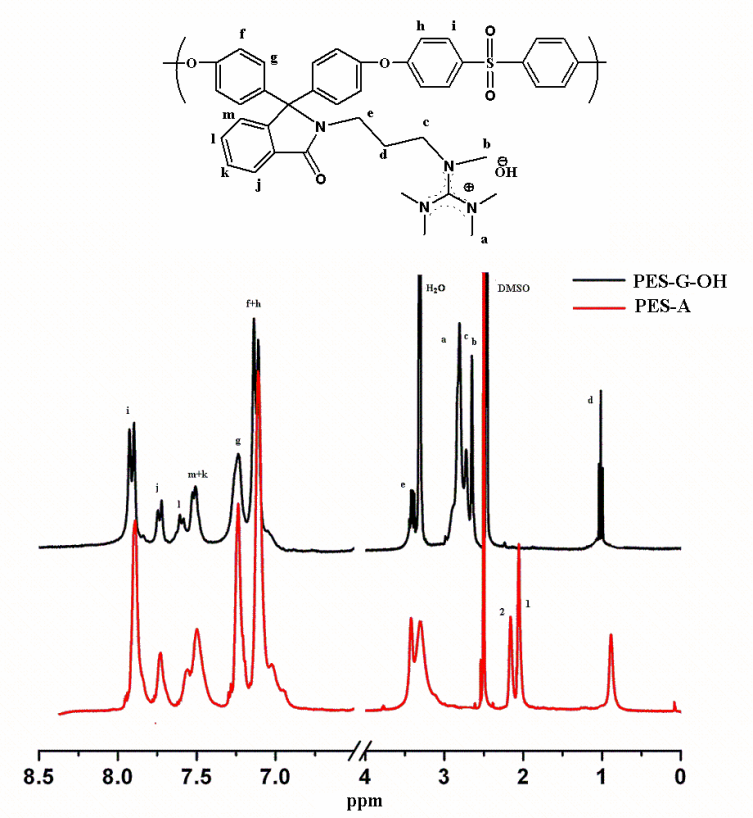

Fig. S1 ^{1}H NMR spectra of PES-G-OH and PES-A.

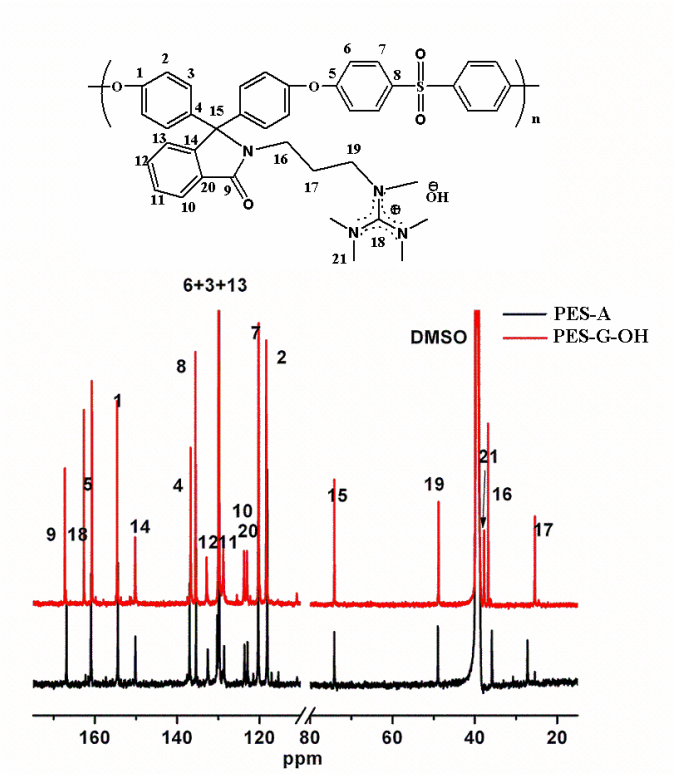

Fig. S2 ^{13}C NMR spectra of PES-G-OH and PES-A.

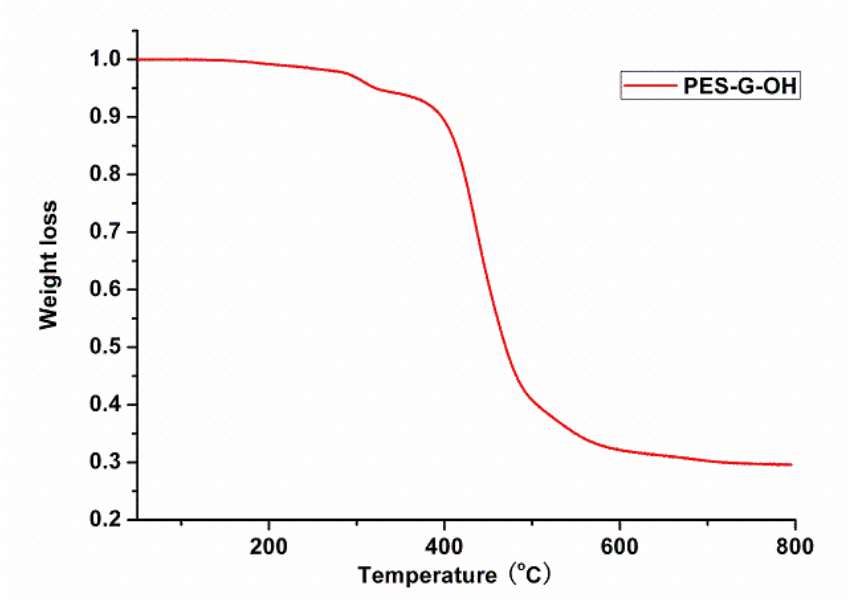

Fig. S3 TGA trace for PES-G-OH (under N_2).

Table S1 Solubility of PES-G-OH.

Water-soluble solvent	Boiling-point / ^{o}C	PES-G-OH
Water	100.0	--
Methanol	64.7	++
Ethanol	78.3	+
Acetone	58.1	-
Ethyl acetate	77.1	--
n-praponal	97.2	+-
Chloroform	61.7	+-
Dichloromethane	39.7	-
DMF	152.8	++
DMAc	166.2	++
DMSO	189.3	++
NMP	202.5	++

The solubilities were determined at 10% solid content; ++, soluble at room temperature, the solid polymer was completely dissolved in the solvent to afford a clean, homogeneous solution; +, soluble upon heating; +-, swelling; -, partially soluble; -, insoluble; the solid polymer did not dissolve in the solvent.

Table S2 IEC, water uptake and swelling ratio of the membrane.

Poymers	**IEC (mmol/g)**	**Water uptake (%)**		**Swelling ratio (%)**	
		20 ^{o}C	**60 ^{o}C**	**20 ^{o}C**	**60 ^{o}C**
PES-G-OH	**1.39**	**31.5**	**35.8**	**10.6**	**15.2**

Table S3 Alkaline stability of PES-G-OH membrane after immersion in NaOH solution for 24 h.

Concentration of NaOH (mol/L)	Temperature (°C)	Ionic conductivity (S/cm)	Swelling ratio (%)
1	25	0.024	10.6
2	25	0.024	10.8
4	25	0.025	10.3
6	25	0.023	10.5
8	25	0.022	10.1
10	25	0.022	9.9
2	40	0.024	10.6
2	60	0.023	10.7
2	80	0.021	10.0
2	100	Can't measure (brittle)	9.5