Supporting Information for

Novel self-crosslinked poly(aryl ether sulfone) for high alkaline stable and fuel resistant alkaline anion exchange membranes

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1. Experimental

Synthesis of Diallyl bisphenol S based poly(ether sulfone) (SPES) and Diallyl bisphenol A based poly(ether sulfone) (APES): The synthesis procedures of SPES and APES were almost the same. The only difference between them was the monomers they prepared from. The diallyl bisphenol S was used in the preparation of SPES whilediallyl bisphenol A was used in the preparation of APES. Here we described the synthesis procedure of SPES for illustration. Diallyl bisphenol S (6.60g, 0.02mol), K_2CO_3 (2.898g, 0.021mol), 4,4'-difluorodiphenyl sulfone (5.08g, 0.02mol) were added to a three neck bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap. NMP/toluene (38ml/20ml) solvent system was used in this reaction. The reaction bath was heated to 140^{o}C and kept at this temperature for at least 3h to remove water. Then the temperature was proceeded to 170^{o}C for 6h. Before being put in vacuum, the product was washed with deionized water to remove the residual salts and solvent.
^{1}HNMR (500 MHz, DMSO-d6, δ, ppm): SPES: 1.65 (-CH_3 of propenyl groups), 6.45 (HC=CH of propenyl groups), 7.09 (ArH ortho to –O–), 8.18 (ArH ortho to propenyl groups), 7.79-7.88 (other ArH). APES: 1.12, 1.62 and 2.04 (-CH_3 of propenyl groups and -CH_3 of bisphenol A), 5.83-6.26 (HC=CH of propenyl groups), 6.92 (ArH ortho to –O–), 7.51 (ArH ortho to propenyl groups), 7.79 (ArH ortho to -SO_2-), 7.18 (other ArH).

Bromination of SPES and APES: To be brief, we take APES as an example in turn and the APES-Br was synthesized as follows. APES (1.044g, 2mmol) was first dissolved in 100ml chloroform in a three neck bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a condenser. Then proper content of NBS was added in the flask and reflux for 16h. The mixture was poured into 75% ethanol solvent to make the crude product precipitate. After wash the product several times with acetone, APES-Br was obtained.
^{1}H NMR (500 MHz, DMSO-d6, δ, ppm): SPES-1Br: 1.76 (-CH_3 of propenyl groups), 6.47 (HC=CH of propenyl groups), 7.12 (ArH ortho to –O–), 8.19 (ArH ortho to propenyl groups), 7.81-7.90 (other ArH). APES-2Br: 1.63-1.84 (-CH_3 of propenyl groups and -CH_3 of bisphenol A), 4.84-5.74 (HC=CH of propenyl groups), 6.97 (ArH ortho to –O–), 7.52 (ArH ortho to propenyl groups), 7.89 (ArH ortho to -SO_2-).

Preparation of the Anion Exchange Membranes: The bromic membranes were prepared by the simple solution casting method. Dried APES or SPES powder was dissolved in N-methyl-2-pyrrolidone (NMP) at room temperature to prepare a 10wt% solution. The resulting solution was cast onto a glass plate and heated at 60°C for 24h in a vacuum oven. Then the temperature was raise to 80^{o}C for 12h to induce and complete the cross-linking reaction. After peeled off from the glass, the bromic membranes were immersed in Trimethylamine (TMA) solutions for 24h. The result membranes were then immersed in 1M NaOH solution to replace the Br^- in the membranes with OH^-. Finally,

the OH^- type membranes were washed with deionized water until the pH of residual water was neutral.

2. Measurements

^{1}H NMR spectroscopy: ^{1}H NMR (500 MHz) analysis was performed on a Bruker Avance 510 spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the internal reference.

Thermogravimetric analysis: (TGA): TGA was performed on a Pyris TGA (Perkin-Elmer) thermal analyzer system to investigate the thermal stabilities of the SPES membranes in both Br^- form and OH^- form under nitrogen gas. About 3-5mg samples of the membranes were heated to 120°C and kept at this temperature until constant weight was obtained to remove the residual water and solvent, and then cooled to 80°C and reheated to 700°C at a heating rate of 10°C min^{-1}.

Mechanical Strength: The mechanical properties of the membranes were measured by SHIMADZU AG-I 1KN. The size of the specie is 15mm×4mm while the test speed is 10mm min^{-1}. For each testing report, three measurements at least were recorded and average value was calculated.

Water and Methanol Swelling Ratio: The swelling ratio of membranes was determined by measuring the change in the thickness between the dry and swollen membranes. In particular, the membranes were dried at 80°C under vacuum until constant weight was obtained. To make the membrane equilibrium in the water or methanol, the membranes were immersed into deionized water or anhydrous methanol at desired temperature for 24 hours. Then the membranes were taken out, wiped with tissue paper, and quickly measured their thickness.

The swelling ratio was calculated by the following equation:

$$\text{swelling ratio}(\%) = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100\% \quad (1)$$

where T_{dry} and T_{wet} are the thickness of dry and corresponding swollen membranes, respectively.

Ionic Conductivity: The ionic conductivity of the membranes were measured using a modified four-probe AC impedance method from 0.1 Hz to 100 kHz, 10mV AC perturbation and 0.0V DC rest voltage using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. To eliminate the potential interference caused by the presence of dissolved carbon dioxide, the membranes were pretreated. The membranes were first immersed in a diluted sodium hydroxide aqueous solution for 12 h, then extensively washed with deionized water several times, set on the four-probe cell holder and sealed in the vessel filled with deionized water for at least 48 hours. During the measurement, the cell was completely immersed in deionized water pre-equilibrated to the desired temperature and then immediately measured. The ionic conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (2)$$

where σ is the ionic conductivity, L is the distance between the electrodes used to measure the potential (L=1cm), R is membrane resistance and A is membrane area.

Methanol Diffusion Coefficient: The methanol permeability was measured by using a diffusion cell described in the literature[1,2]. The cell was consisted of two reservoirs that were separated by a membrane. The methanol concentrations in the water cell were determined by using a SHIMADZU GC-8Achromatograph. Methanol permeability was calculated as follows:

$$C_B(t) = \frac{A}{V_B}\frac{D_K}{L}C_A(t-t_0) \quad (3)$$

where A (in cm^2), L (in cm) and V_B (in ml) are the effective area, the thickness of the membranes and the volume of

permeated reservoirs, respectively. C_A and C_B (in mol m^{-3}) are the methanol concentration in feed and in permeate, respectively. D_K (in cm^2s^{-1}) denotes the methanol permeability. Here we chose 10M as the feed methanol concentration.

3. Figures

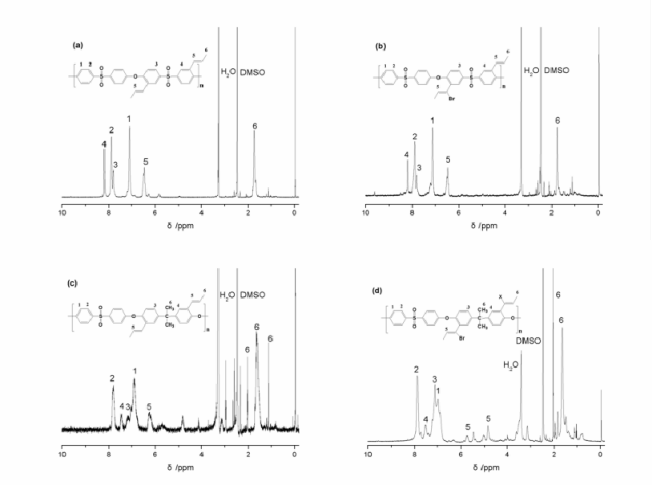

Figure S1. **^{1}H NMR spectra of (a) SPES, (b) SPES-1Br, (c) APES, (d) APES-2Br**

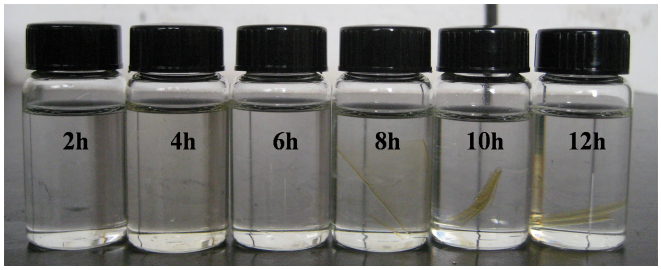

Figure S2. **Membranes treated for different time after immersing in NMP for 24h at 60^{o}C**

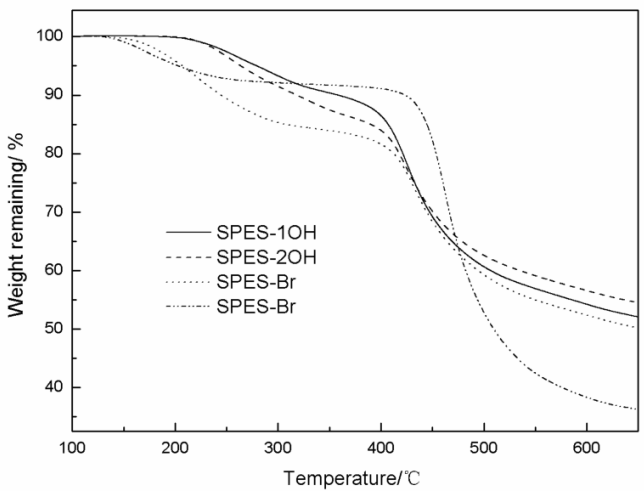

Figure S3. **The TGA curves of SPES membranes in both Br form and OH^- form under N_2.**

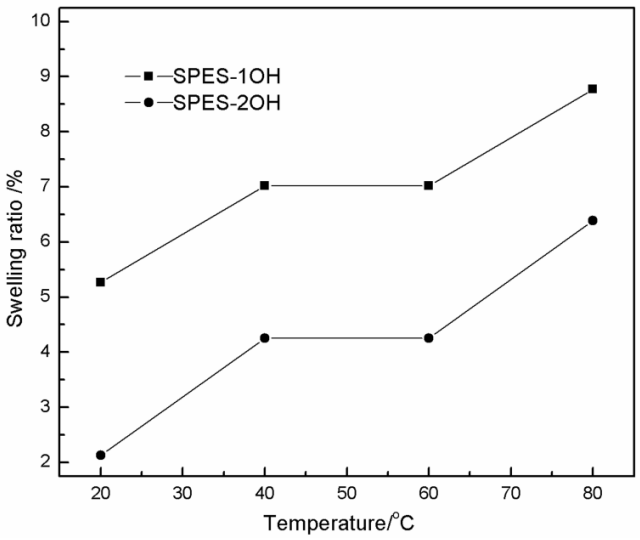

Figure S4. **Swelling ratio of the membranes in deionized water**

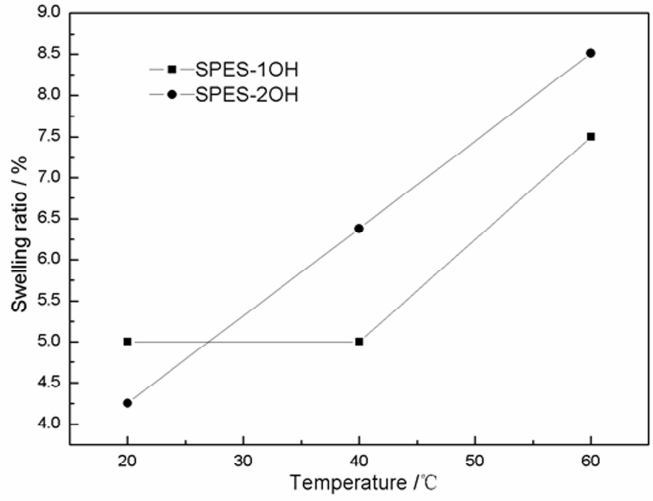

Figure S5. **Swelling ratio of the membranes in anhydrous methanol**

4. Tables

Table S1. Solubility[a] of SPES-Br

Solvent	Boiling Point(°C)	SPES-Br(Powder)	SPES-Br(Membrane)
Chloroform	62	+	-
Tetrahydrofuran	66	+	-
N,N-Dimethylformamide (DMF)	153	+	-
Dimethylacetamide (DMAc)	166	+	-
Dimethyl sulfoxide (DMSO)	189	+	-
N-Methyl-2-pyrrolidone (NMP)	204	+	-

[a]+: Soluble, −: Insoluble.

Table S2. Properties of the membranes

HEMs	σ (mS cm^{-1})		D_k	$T_{d0.05}$ (°C)		Young's Modulus	Elongation at break
	20 °C	80 °C	(cm^{2}s^{-1})	Br^- form	OH^- form	(MPa)	(%)
SPES-1OH	13.4	31.3	2.07×10^{-9}	207	279	1429	7.40
SPES-2OH	18.8	45.5	1.92×10^{-9}	203	264	1358	7.26

References

(1) M. Gil, X. L. Ji, X. F. Li, H. Na, J. E. Hampsey and Y. F. Lu, J. Membr. Sci., 2004, 234, 75–81.

(2) X. F. Li, C. P. Liu, H. Lu, C. J. Zhao, Z. Wang, W. Xing and H. Na, J. Membr. Sci., 2005, 255, 149–155.