Materials Chemistry Frontiers

Supporting Information

High conductivity and alkaline stability of anion exchange membrane containing multiple flexible side-chain piperidinium ions

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Contents

1. Experimental Section

1.1 Materials

4,4′-Difluorodiphenyl sulfone (DFDPS), boron tribromide (BBr_3) and sodium hydride (NaH) were purchased from Shanghai Macklin Biochemical Co., Ltd. (3,5-Dimethoxyphenyl)boronic acid, Tetrakis(triphenylphosphine)palladium(0) was provided from Shanghai Aladdin Reagent Co., Ltd. Hexafluorobisphenol A (BPAF), 1,6-Dibromohexane and *N*-Methylpiperidine were purchased from TCI Co., Ltd.

1.2 Synthesis of 3,3′,5,5′-tetra(3″,5″-Dimethoxyphenyl)-4,4′-difluorodiphenyl sulfone

The monomer, 3,3′,5,5′-tetra(3″,5″-Dimethoxyphenyl)-4,4′-difluorodiphenyl sulfone (**TDMPDPS**), was synthesized by the method previously reported in the laboratory [1]. The ^1H NMR spectrum of **TDMPDPS** was shown in Figure S1a.

1.3 Synthesis of (6-bromohexyl)-1-methylpiperidinium bromide

(6-Bromohexyl)-1-methylpiperidinium bromide (**BrC_6mPip**) was synthesized according to the literature [2]. 97.60 g (0.40 mol) 1,6-dibromohexane and 200 mL acetonitrile to a 500 mL three-neck flask equipped with a reflux condenser and an electric stirrer. After stirring well at 60 ºC, a mixture of *N*-methylpiperidine (0.04 mol, 3.97 g) and acetonitrile (20 mL) was added slowly through a constant pressure titration funnel. The mixture was stirred vigorously at 60 °C for 24 h. Then, the solvent with low boiling point was removed by vacuum distillation. The product was precipitated in 1000 mL ethyl acetate for 48 h. After filtering, the solid was washed 3 times with ethyl acetate and dried under vacuum at room temperature for 24 h to obtain 10.41 g of white powder with a yield of 75.8%. The ^1H NMR spectrum of **BrC_6mPip** was shown in Figure S1b.

1.4 Synthesis of poly(aryl ether sulfone)s containing methoxybenzene

The poly(aryl ether sulfone)s containing methoxybenzene (PAES-$8OCH_3$-x, where x is the molar ratio of TDMPDPS in the total difluorodiphenylsulfone monomers) was synthesized by the report [3]. The synthesis of copolymer via a nucleophilic polycondensation reaction was described in Scheme 1. Take the synthesis of PAES-$8OCH_3$-0.35 as an example: added 2.7938 g (3.5 mmol) of TDMPDPS, 1.6525 g (6.5 mmol) DFDPS, 3.3623 g (10.0 mmol) hexafluorobisphenol A, 3.3170 g (24.0 mmol) anhydrous potassium carbonate, 15 mL N-methylpyrrolidone, 6 mL toluene to a 100 mL three-necked round bottom flask equipped with an electric stirrer, water separator, reflux condenser and nitrogen inlet and outlet. Pre-react at 140 ℃ for 1 h, steam the generated water molecules and toluene through a water trap, and then heat up to 160 ℃ to react for about 4 to 8 h. Add an appropriate amount of N-methylpyrrolidone to reduce the viscosity, settle in 500 mL ethanol/water solution (V: V = 1:1) to obtain a white product poly(aryl ether sulfone)s PAES-8OCH$_3$-0.35, and soak the product several times with hot water, then dried at 80 ℃ in vacuum for 24 h.

1.5 Synthesis of hydroxyl-contained poly(aryl ether sulfone)s

Hydroxyl-contained poly(aryl ether sulfone)s (PAES-8OH-x) can be obtained via demethylation reaction [4]. 3.5 g of PAES-8OCH$_3$-x was completely dissolved in 100 mL of chloroform at room temperature. A mixture of 4 mL BBr$_3$ and 50 mL CHCl$_3$ was added slowly through a constant pressure titration funnel at 0 ºC. The solid polymer continuously precipitated during the reaction was filtered, washed with methanol, and dried at 80 °C to obtain PAES-8OH-x.

1.6 Synthesis of poly(arylene ether sulfone)s functionalized with locally dense side-chain-type piperidinium ions

The poly(arylene ether sulfone)s functionalized with locally dense side-chain-type piperidinium (PAES-8mPip-x) was synthesized via Williamson reaction. 1.00 g (3.99 mmol –OH) of PAES-8OH-0.35 was completely dissolved in 15 mL of NMP. Then, 0.32 g (9.98 mmol) NaH was added at 0 ºC. Next, 2.74 g BrC6mPip (7.98 mmol) was added after stirring for 30 min. The reaction solution was reacted at 90 ºC for 12 h. After cooling, the reaction solution was slowly poured into 300 mL of isopropanol for precipitation, filtered, washed and dried in vacuum at 80 ºC for 10 h to obtain PAES-8mPip-0.35.

1.7 Preparation of Membrane

The preparation of the membrane refers to our previous work [5]. PAES-8mPip-x in the bromide form was dissolved in DMAc to prepare a 5 wt% solution. The polymer solution was filtered through a 0.45 μm PTFE filter. Then cast onto a smooth glass mold. The solvent was evaporated at 70 °C for 24 h, followed by vacuum drying for another 24 h at 80 °C, to provide

PAES-8mPip-x membrane in the bromide form.

2 Characterization

The characterization of the polymer and the performance test of the membrane refer to our previous work [6]. The structure of the polymer was characterized by ^{1}H NMR spectra via Bruker AVANCE DMX-400 NMR instrument at 400 MHz, using DMSO-d6 as the solvent and tetramethylsilane (TMS) as the internal reference.

The molecular weights of the PES-8OCH$_3$-x copolymers were estimated by size exclusion chromatography. The eluent was tetrahydrofuran (THF), at a flow rate of 1.0 mL min^{-1}. PAES-8CH$_3$-x samples (25 mg) were dissolved in THF (4 mL), and filtered through a 0.45 μm PTFE syringe filter, and the copolymer molecular weights and polydispersity index (PDI) were tested at 30 ℃.

The morphology of the membrane was measured by Atomic force microscopic (AFM).

The mechanical properties of the anion conductive membranes were measured at 20 ℃ under conditions of complete hydration (Load of 5 kN, tensile rate of 5 mm min^{-1}.). Membrane samples were cut into strips of 5 cm × 1 cm, and the average value of the three measurements is reported.

Thermal stability of PAES-8mPip-x membrane was determined using a TG 209 F1 thermogravimetric analyzer (TGA) manufactured by Netzsch, Germany. The temperature was increased from 50 ℃ to 850 ℃ at a rate of 20 °C min^{-1} in nitrogen. Samples were dried in vacuum at 80 ℃ for 6 h before testing.

The ion exchange capacitys (IEC) of membrane in (Br$^-$ form) were determined by Mohr titration. About 0.15 g of membrane were ion exchanged in aqueous KCl (1 mol L^{-1}) solution for 24 h (the KCl solution was changed three times during this period) and then washed with deionized water thoroughly. Each AEM sample was dried at 60 ℃ in vacuum for 24 h and weighed. Then each AEM sample (Cl$^-$ form) was immersed in 50 mL of aqueous NaNO$_3$ (0.2 mol L^{-1}) solution for 8 h (three replacements of solution). The combined NaNO$_3$ solution was titrated with aqueous AgNO$_3$ (0.1 mol L^{-1}) solution using K$_2$CrO$_4$ as colorimetric indicator. IEC was calculated from dry mass of the membrane and the amount AgNO$_3$ consumed in titration (1:1 precipitation titration). The IEC values are calculated according to equation (1) as follows:

$$IEC_{\mathrm{tit}} = \frac{C_{\mathrm{AgNO_3}} \times V_{\mathrm{AgNO_3}}}{M_{\mathrm{dry}}} \times 1000 \quad (1)$$

The weight percentage of water uptake (WU) and swelling ratio (SR) of the PES-8mPip-x membrane were measured in the Br^- form and calculated based on the equations (2) and (3):

$$WU = \frac{M_{\mathrm{wet}} - M_{\mathrm{dry}}}{M_{\mathrm{dry}}} \times 100 \quad (2)$$

$$SR = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100 \quad (3)$$

First, a 1 cm × 5 cm membrane of regular size was immersed in deionized water at different temperatures for one day. The weight (W_{wet}), length (L_{wet}) and width (Wi_{wet}) of wet samples were measured after removing surface water with tissue paper. Then, the membrane was dried under vacuum at 80 ℃ and the weight (W_{dry}), length (L_{dry}) and width (Wi_{dry}) of dry samples were measured. $S = \sqrt{L \times Wi}$ refers to the area of the membrane. The hydration number (λ) refers to the number of water molecules associated with a single quaternary ammonium cation, and is calculated using equation (4):

$$\lambda = \frac{WU \times 10}{18.02 \times IEC} \quad (4)$$

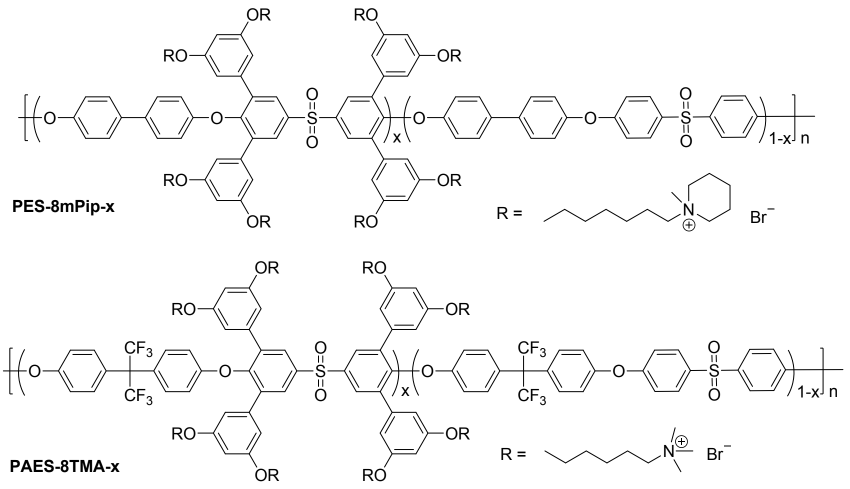
In-plane conductivities of AEM samples were tested using a GAMRY Reference 3000 electrochemical workstation (USA) at a frequency of 1 to 10^5 Hz and a temperature range of 20 to 80 ℃ using the four-electrode method. The OH^- exchanged membrane was washed several times with N_2 treated DI Water and sealed in a plastic bottle containing DI Water. The average value of the three measurements is reported. The hydroxide conductivity is determined using equation (5):

$$\sigma = \frac{d}{L \times W \times R} \quad (5)$$

Where d (cm) is the distance between the two electrodes, L (cm) and W (cm) are the width and thickness of the membrane, respectively, and R (Ω) is the test resistance.

The alkaline stabilities of AEM samples were determined from IEC values, hydroxide conductivities and NMR spectroscopy. AEM samples were cut into 5 cm × 3 cm strips and placed in 2 mol L^{-1} NaOH aqueous solution at different temperatures and test periods.

3 Structure of PES-8mPip-0.25 and PES-8TMA-0.27



Scheme S1 Structure of PES-8mPip-0.25 and PAES-8TMA-0.27.

4 GPC data of PES-8OCH3-x

Table S1 GPC data of PAES-8OCH_3-x.

Polymer	GPC		
	M_n	M_w	PDI
PAES-8OCH_3-0.15	6.42	14.32	2.23
PAES-8OCH_3-0.20	6.48	14.64	2.26
PAES-8OCH_3-0.25	6.14	14.24	2.32
PAES-8OCH_3-0.30	6.01	14.36	2.39
PAES-8OCH_3-0.35	5.89	14.61	2.48

5 IEC, WU, SR and λ values of PES-8mPip-x membrane

Table S2 IEC, WU, SR and λ values of PES-8mPip-x membrane.

Sample	Thickness	IEC / mmol g^{-1}			WU / %		SR / %		λ [d]
	µm	Theo [a]	NMR [b]	Tit [c]	30 °C	60 °C	30 °C	60 °C	60°C
PAES-8mPip-0.15	54±3	1.29	1.28	1.26	31.4	44.8	9.9	14.4	19.7
PAES-8mPip-0.20	53±2	1.51	1.52	1.49	41.6	56.8	10.6	15.9	21.1
PAES-8mPip-0.25	54±3	1.69	1.68	1.64	52.2	70.4	11.5	18.3	23.8
PAES-8mPip-0.30	54±2	1.83	1.81	1.78	63.6	86.2	12.4	21.4	26.9
PAES-8mPip-0.35	55±4	1.95	1.93	1.90	75.2	104.4	13.5	25.3	30.5
PAES-8TMA-0.27	56±4	1.93	1.90	1.91	56.4	88.6	10.1	14.7	25.7
PES-8mPip-0.25	56±3	1.94	1.92	1.91	61.2	93.8	13.2	26.4	27.3
Nafion 212	51±2	—	—	0.89	—	32.1	—	69.0	20.0
Cr-ASU-PSF	—	—	—	1.92	—	~86	—	~30	24.8
PPO-DMP-40	45–55	—	2.02	1.98	—	125.7	—	29.6	35.2
QH-1.89	40	—	—	1.89	—	~59	—	~38	17.3

[a] Calculated value based on monomer feed ratio; [b] Calculated value based on ^{1}H NMR; [c] The value measured by molar titration; [d] At 60 °C, the hydration number.

6 Mechanical properties and hydroxide conductivity of PAES-8mPip-x membrane

Table S3 Mechanical properties and hydroxide conductivity of PAES-8mPip-x membrane.

Sample	IEC	Tensile strength [a] (MPa)	Elongation at break [a] (%)	σ [b] (mS cm^{-1})		E_a
	mmol g^{-1}			30 °C	60 °C	kJ mol^{-1}
PAES-8OCH$_3$-0.35	—	58.7±2.1	4.8±0.5	—	—	—
PAES-8mPip-0.15	1.26	31.2±1.1	21.5±0.8	29.8±2.5	49.5±4.1	13.5
PAES-8mPip-0.20	1.49	26.5±0.9	24.2±0.7	38.4±2.3	60.9±4.2	12.9
PAES-8mPip-0.25	1.64	21.4±0.8	28.4±0.8	48.2±3.4	76.1±4.3	11.9
PAES-8mPip-0.30	1.78	17.5±0.6	34.4±0.9	62.3±3.5	93.3±4.4	11.4
PAES-8mPip-0.35	1.90	13.5±0.7	37.8±1.3	74.2±3.5	114.2±4.4	10.6
PAES-8mPip-0.35 [c]	1.73	9.7	22.4	52.2	—	—
PAES-8TMA-0.27	1.91	19.3±0.6	30.6±2.1	41.5±3.2	79.4±5.2	—
PES-8mPip-0.25	1.91	24.2±0.8	26.4±1.7	43.8±2.8	84.4±5.7	—

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[a] Measured at 100% RH.

[b] Calculated values from high frequency resistance in ultrapure water.

[c] Immersing in 2 mol L^{-1} NaOH solution at 80 ℃ for 480 h.

7 ^{1}H NMR spectrum of 3,3′,5,5′-tetra(3″,5″-Dimethoxyphenyl)-4,4′-difluorodiphenyl sulfone and (6-bromohexyl)-1-methylpiperidinium bromide

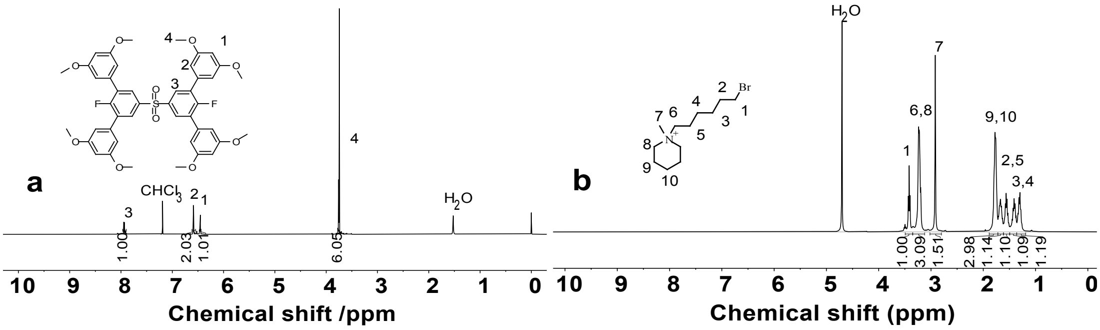

Fig. S1 ^{1}H NMR spectrum of 3,3′,5,5′-tetra(3″,5″-Dimethoxyphenyl)-4,4′-difluorodiphenyl sulfone and (6-bromohexyl)-1-methylpiperidinium bromide.

8 Appearance photos of PAES-8mPip-x (x=0.15 and 0.35)

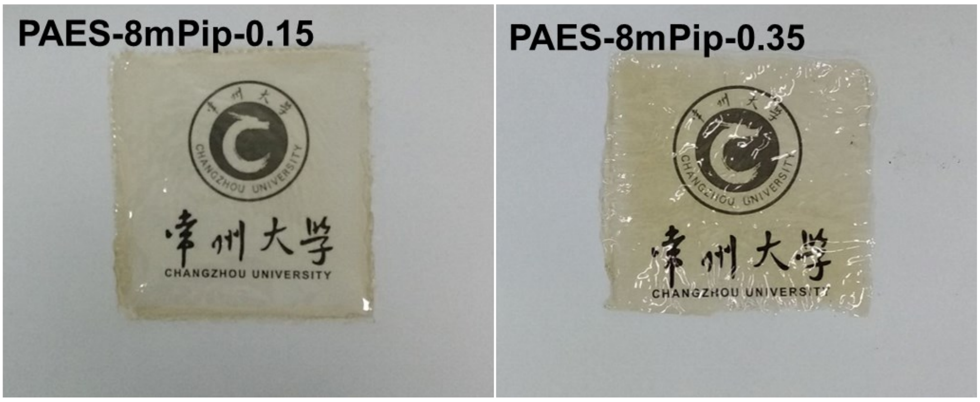

Fig. S2 Appearance photos of PAES-8mPip-x (x=0.15 and 0.35).

9 Mechanical strength of the PAES-8mPip-x

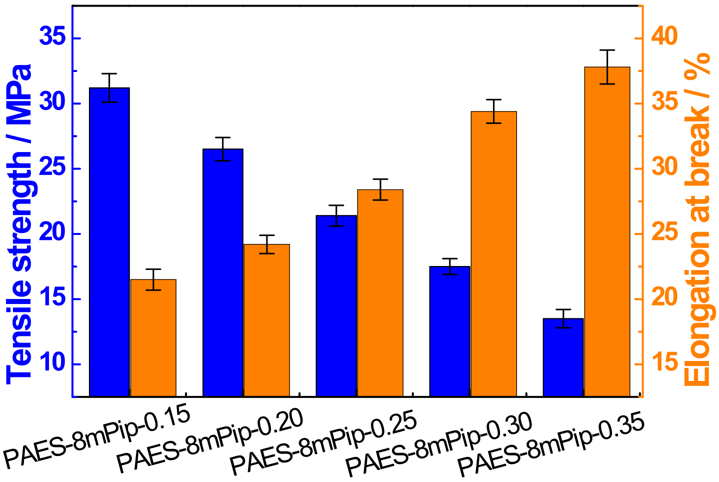

Fig. S3 Mechanical strength of the PAES-8mPip-x.

10 TGA curve of PAES-8OCH$_3$-0.35 and PAES-8mPip-0.35

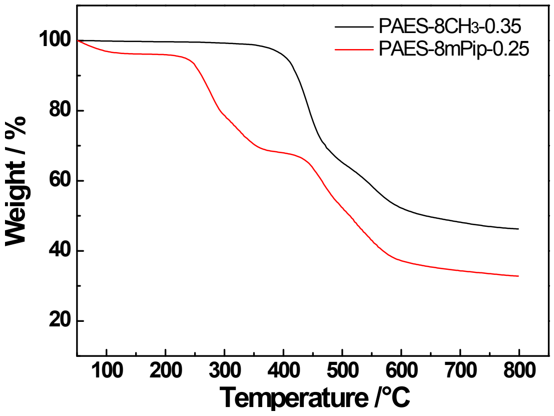

Fig. S4 TGA curve of PAES-8OCH$_3$-0.35 and PAES-8mPip-0.35.

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