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Supporting information

Hyper-branched Anion Exchange Membrane with High Conductivity and Chemical Stability

Qianqian Ge, Yazhi Liu, Zhengjin Yang*, Bin Wu, Min Hu, Xiaohe Liu, Jianqiu Hou and Tongwen Xu*

CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, PR China

Experimental section

Materials

N-Methyl-2-pyrrolidolone (NMP), methanol, chlorobenzene, tetrahydrofuran (THF), sodium hydroxide (NaOH), sodium chloride (NaCl), sodium bicarbonate ($NaHCO_3$) and sodium sulfate (Na_2SO_4), silver nitrate ($AgNO_3$), potassium chromate (K_2CrO_4), 2,2-azobisisobutyronitrile (AIBN), 2,2'-bipyridin (bipy) and methanol are of analytical purity and purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, PR China). All these reagents were used as received. 4-(Chloromethyl) styrene (VBC) and N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA) were purchased from Energy Chemical and were used as received. Copper(I) chloride (CuCl) was purchased from Sinopham Chemical Reagent Co., Ltd. (Shanghai, PR China) and was purified by washing with glacial acetic acid many times until the filtrate was colorless and then washed with diethyl ether twice, finally dried in the vacuum oven at 100 ^oC for 3 h.

Synthesis of hyper-branched PVBC (HB-PVBC) and linear PVBC (L-PVBC)

HB-PVBC and L-PVBC were synthesized according to the reference[1]. In a typical polymerization procedure of HB-PVBC, CuCl (0.1407 g, 1.4 mmol, 0.1 equiv) and bipy (0.4353g, 2.8 mmol, 0.2 equiv) were added to a long-necked reaction flask, followed by the addition of chlorobenzene (5 mL) and VBC (2 mL, 2.166g, 14mmol, 1 equiv). The flask was degassed by three freeze-pump-thaw cycles, then flame sealed under vacuum. It was finally placed in a thermostat-controlled oil bath at 115 °C. The deep red color of the catalyst slowly became green with the formation of a green precipitate. After 6 h, the flask was removed and cooled. THF (30 mL) was added, and the mixture was stirred at room temperature for several hours to dissolve the polymer and to oxidize the catalyst. The resulting solution was filtered through alumina column to remove the insoluble copper salts and the bipy. The resulting light yellow solution was concentrated and precipitated into methanol to give off-white precipitate. The crude product was re-dissolved in THF and precipitated into methanol. The purification was repeated three times and finally dried at 40 ^{o}C in the vacuum oven for 24 h. The synthesis of L-PVBC was based on radial bulk polymerization using AIBN as initiator (Scheme S1). The reaction was conducted at 70 ^{o}C under nitrogen atmosphere for 5 h and purified using the same procedure with HB-PVBC.

Synthesis of hyper-branched membrane (HB-QPVBC)

The preparation of hyper-branched membrane is based on the Menshutkin reaction between the primary benzyl chloride groups from HB-PVBC and tertiary groups from PMDETA. The typical procedure is as follows. To the HB-PVBC solution (0.2 g in 2 mL NMP), PMDETA solution (71 μL in 2 mL NMP) was added dropwise under vigorous stirring. After stirring at 25 ^{o}C for 0.5 h, the reaction solution was directly cast onto a clean glass plate and then dried at 60 ° C for 24 h. It is then peeled off to give a flexible light yellow membrane with thickness of around 56 μm. Membranes in OH^- form or HCO_3^- form were obtained by immersing the membranes in aqueous NaOH aqueous solution (1 M) or $NaHCO_3$ aqueous solution (1 M) at room temperature for 24 h. They were then washed thoroughly and immersed in deionized (DI) water for 48 h to remove residual NaOH or $NaHCO_3$.

Synthesis of the standard membrane quaternized poly(2,6-dimethy l-1,4-phenylene oxide) (QPPO)

Membrane QPPO was synthesized according to our previous work[2] and the titrated ion exchange capacity is 1.84 mmol/g.

Characterization

Nuclear magnetic resonance (NMR)

The synthesized HB-PVBC and L-PVBC were identified by ^{1}H NMR (Bruker AvanceIII 400 MHz) using Chloroform-d ($CDCl_3$) as solvents.

Gel Permeation Chromatography (GPC)

Molecular weight (Mn, Mw) and polydispersitie (PDI= Mw/Mn) of HB-PVBC was determined by GPC using a PL 120 Plus (Agilent Technologies co., Ltd, China) equipped with differential refractive index detector. The PL Gel Mixed Carbon 18 SEC columns connected in series was maintained at 40 °C to achieve the separation. Samples were freshly prepared in THF (HPLC) and passed through a 0.45 μm polytetrafluoroethylene syringe filter prior to injection. HPLC grade THF containing 0.03 wt % LiCl was used as the eluent at a flow rate of 1.0 mL/min. The detection system was calibrated with a 2 mg/mL polystyrene standard (Mw = 110K).

Fourier transform infrared (FTIR)

FTIR analysis was performed on KBr pellet using a Nicolet iS10 FTIR Spectrometer under ambient conditions with a resolution of 5 cm^{-1} and a wide spectral range of 4000-400 cm^{-1}.

Thermogravimetic analysis (TGA) and derivative thermogravimetric (DTG)

Thermal stability test of HB-QPVBC was conducted with a Shimadzu TGA-50H analyzer at a heating rate of 10 ° C/min from 30 to 700 ° C under nitrogen atmosphere.

Dynamic mechanical analyzer (DMA)

The mechanical property including tensile strength (TS) and elongation at break (Eb) of fully hydrated membrane was recorded on a Q800 dynamic mechanical analyzer (TA Instruments) at a stretch rate of 0.5 N/min.

Ion exchange capacity (IEC)

The IEC was measured by Mohr's method. Typically, the membrane sample was firstly immersed in NaCl aqueous solution (1 M) for 24 h. Then, the membrane was washed with DI water to remove the absorbed NaCl and dried to a constant mass and weighed (denoted as W_{dry}). Finally, the membrane was soaked in Na_2SO_4 aqueous solution (0.5 M) for 24 h to exchange Cl^- with SO_4^{2-}. The Cl^- ions released from the membrane were then titrated with $AgNO_3$ aqueous solution (0.05 M) using K_2CrO_4 as a colorimetric indicator. *IEC* value is calculated from the amount of $AgNO_3$ consumed during titration and the mass of the dry membrane in Cl^- form (W_{dry}) as shown in Eq. (1).

$$IEC\ (mmol/g) = \frac{V(AgNO_3) \times C(AgNO_3)}{W_{dry}}$$

(Eq. 1)

Water Uptake (WU) and Linear Swelling Ratio (LSR)

WU and *LSR* are calculated by measuring the change of weight and length of membrane samples before and after being immersed in water at certain temperature for 24 h according to Eqs. (2) and

(3), respectively.

$$WU = \frac{W_{dry} - W_{wet}}{W_{dry}} \times 100\% \qquad \text{(Eq. 2)}$$

$$LSR = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100\% \qquad \text{(Eq. 3)}$$

where W_{dry} and L_{dry} are the weight and length of dry membrane, while W_{wet} and L_{wet} are those of wet membrane.

Hydroxide Conductivity and Bicarbonate Conductivity

The conductivity of membrane was measured following a standard four-point probe technique[3] using an Autolab PGSTAT 302N (Eco Chemie, Netherland) equipped with a Teflon cell with an a.c. current amplitude of 0.1 mA over frequencies ranging from 1 MHz to 100 Hz. The testing procedure was carried out in galvanostatic mode monitored by a Bode plot to determine the frequency region over which the magnitude of the impedance was constant. During the measurement, the membrane sample was set into the Teflon cell where it was in contact with 2 current-collecting electrodes and 2 potential-sensing electrodes. Then the cell was immersed in DI water at given temperature and the impedance spectrum was collected. The ionic resistance of membrane was then obtained from a Nyquist plot and the conductivity was calculated according to the following Eq. 4:

$$\sigma = L/RWd \qquad \text{(Eq. 4)}$$

Where R is the absolute ohmic resistance of membrane sample, L is the distance between two potential-sensing electrodes (here 1 cm), W (1 cm for the test cell) and d are the width and thickness of the membrane, respectively.

Atomic Force Microscopy (AFM)

Tapping mode AFM (veeco diInnova SPM) observations were conducted using micro-fabricated cantilevers with a force constant of approximately 20 N/m.

Transmission electron microscopy (TEM)

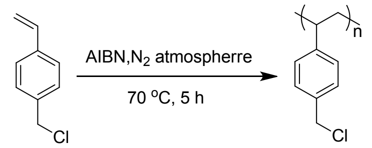
The sample for TEM was prepared as follows: membranes were stained by soaking in 1 mol/L potassium iodide aqueous solution for 24 h, then washed with DI water for many times and dried under vacuum at room temperature. The stained membrane was sectioned to yield slices with 60-100 nm thickness using a LEICA UC6+UC7 ultramicrotome and coated on a copper grid. The electron micrograph was taken with a JEM-2100 transmission electron microscope operated at 200 kV.

Alkaline Stability

To assess the alkaline stability, membrane samples were immersed in NaOH aqueous solutions (1 M) at 80 °C for 20 days. They were then thoroughly washed with DI water and immersed in DI water prior to measurements (such as ionic conductivity, IEC and mechanical property). The bicarbonate conductivity was obtained by exchanging OH^- with HCO_3^- thoroughly.

Table S1 Reagents used for the synthesis of HB-PVBC and GPC analysis of HB-PVBC.

Reaction condition					GPC analysis of HB-PVBC			
Solvent	VBC	n(VBC):n(CuCl):n(bpy)	T (°C)	t (h)	Mn (g/mol)	Mw (g/mol)	PDI	Molar Ratio (2°-BCl) /(1°-BCl)
Chlorobenzene 5 mL	2mL	10:1:2	115	6	9452	36925	3.91	0.33



Scheme S1. Synthesis of linear polymer L-PVBC via radical polymerization.

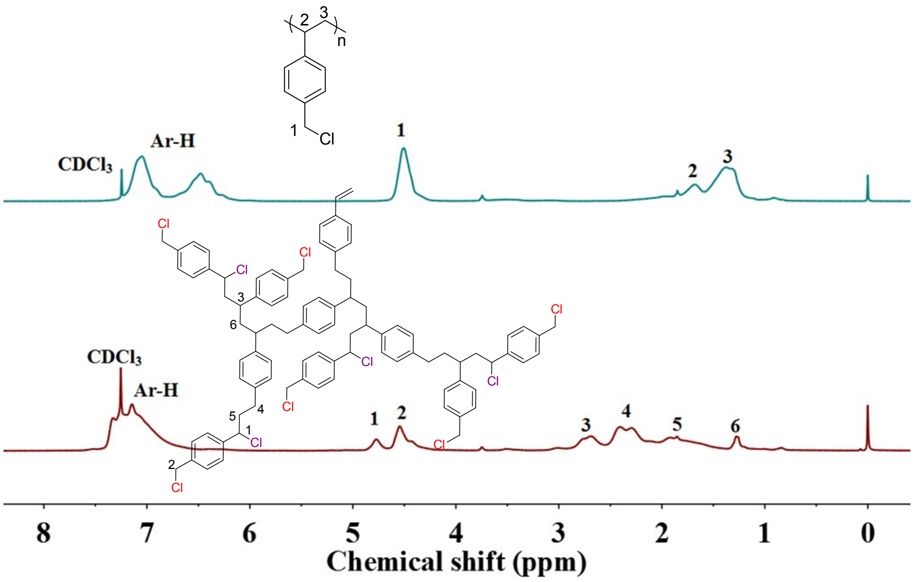


Fig. S1 ^{1}H NMR spectra of HB-PVBC and L-PVBC.

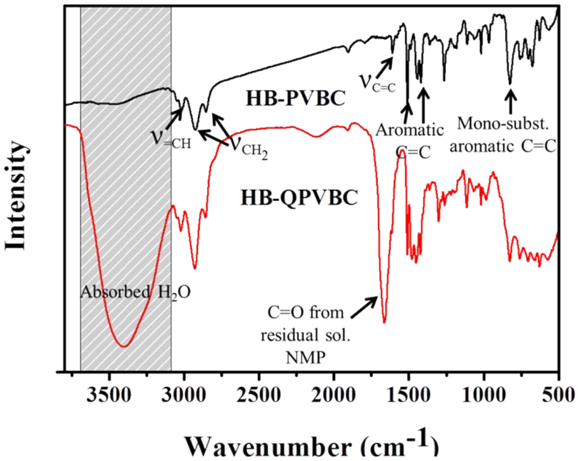


Fig. S2 FTIR spectra of HB-PVBC and HB-QPVBC.

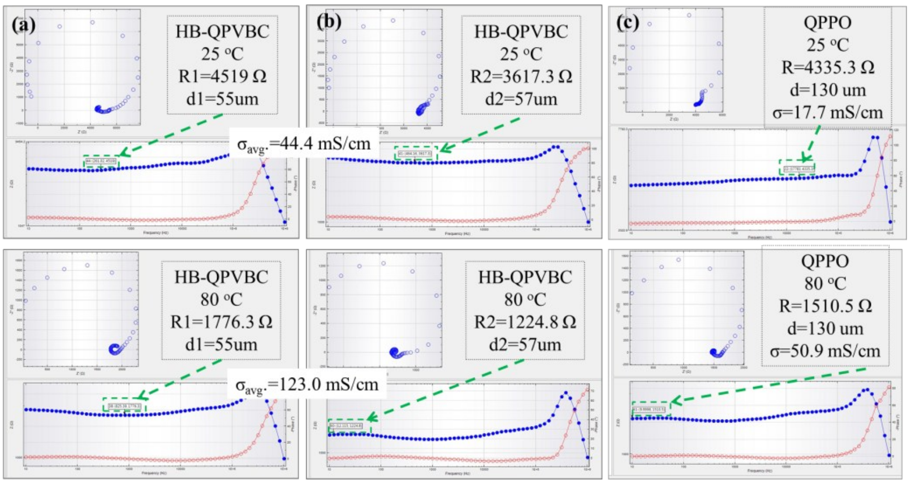


Fig. S3 Nyquist plots and Bode plots of membranes HB-QPVBC (sample 1, OH^- form) (a); HB-QPVBC (sample 2, OH^- form) (b); and QPPO (OH^- form).

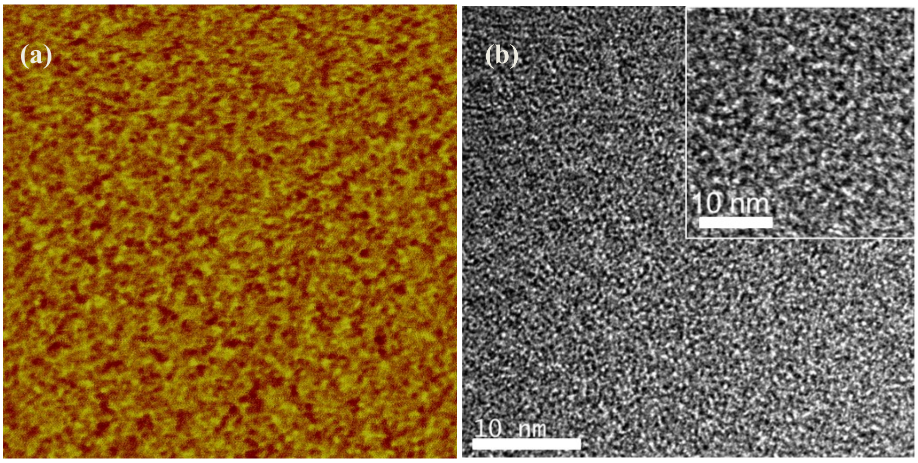


Fig. S4 AFM image (the scan box is 500 × 500nm) (a) and TEM micrograph of ionomer HB-QPVBC (b).

Table S2 IEC, WU, and OH⁻ conductivity of different AEMs reported in the literature compared with those of HB-QPVBC

Membrane	IEC (mmol/g)	Configuration	σ (mS/cm)	WU (wt %)	Ref
PAES-Q-90	1.68	Side chain type Mono-function	80.5 (60 °C)	68.9	4
gQAPPO	1.78	Side chain type Mono-function	52.5 (60 °C)	53.6	5
C6D40	2.08	Side chain type Mono-function	12.0 (60 °C)	25.6	6
PPO-TQA-3	1.50	Side chain type Multi-function	72.1 (60 °C)	20.4	3
CS-6	2.89	Side chain type Multi-function	64.0 (20 °C)	62.0	7
HB-QPVBC	2.36	Hyper-branched	84.7 (60 °C)	35.2	This Work

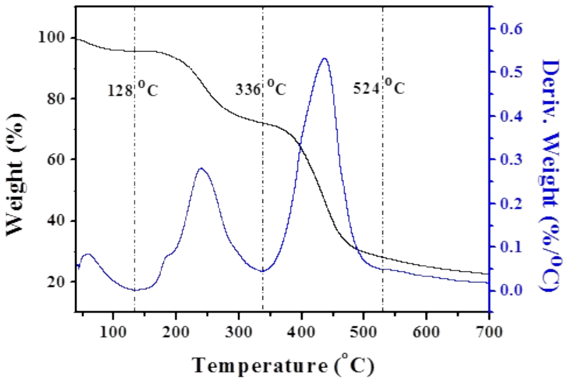


Fig. S5 TGA and DTG curves of membrane HB-QPVBC.

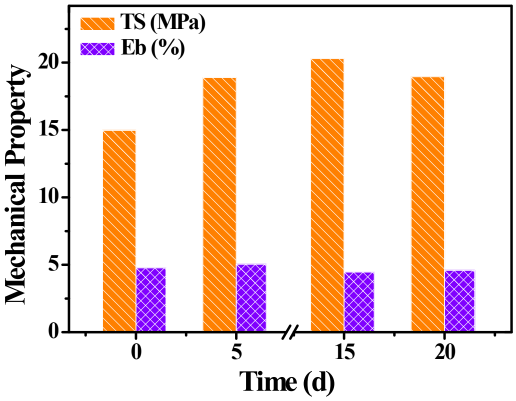


Fig. S6 The variation in TS and Eb of membrane HB-QPVBC during the prolonged alkaline treatment.

References

1 M. W. Weimer, F. Jmj and I. Gitsov, *J. Polym. Sci., Part A: Polym. Chem.*, 1998, **36**, 955-970.

2 J. Ran, L. Wu, B. Wei, Y. Y. Chen and T. W. Xu, *Sci. Rep.*, 2014, **4**, 6486.

3 Q. Li, L. Liu, Q. Q. Miao, B. K. Jin and R. K. Bai, *Chem. Commun.*, 2014, **50**, 2791-2793.

4 X. Li, G. Nie, J. Tao, W. Wu, L. Wang and S. Liao, *ACS appl. Mate. & interfaces*, 2014, **6**, 7585-7595.

5 Z. Yang, J. Zhou, S. Wang, J. Hou, L. Wu and T. Xu, *J. Mater. Chem. A*, 2015, **3**, 15015-15019.

6 N. W. Li, Y. J. Leng, M. A. Hickner and C. Y. Wang, *J. Am. Chem. Soc.*, 2013, **135**, 10124-10133.

7 J. Wang, S. Gu, R. Xiong, B. Zhang, B. Xu and Y. Yan, *Chemsuschem*, 2015, **8**, 4229-4234.