Supporting information

Comb-shaped Polymers to Enhance Hydroxide Transport in Anion Exchange Membranes

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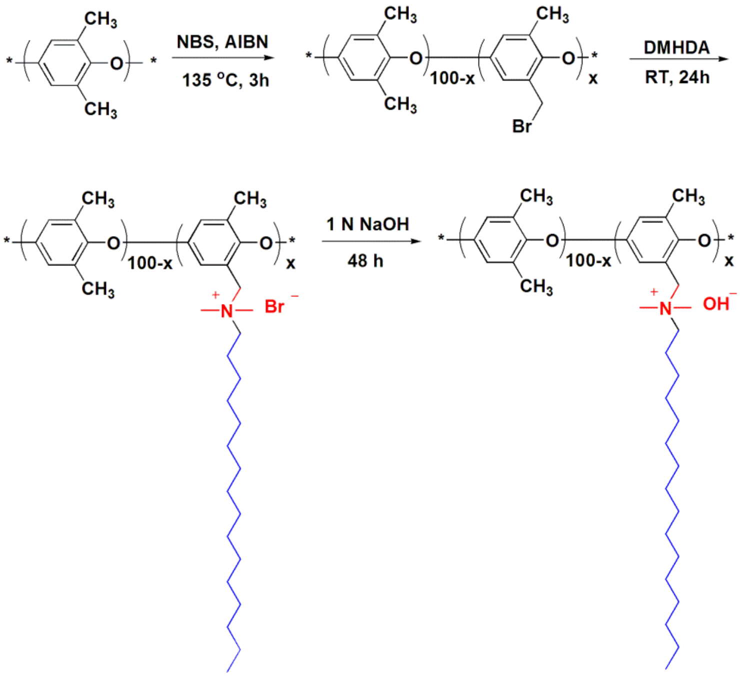
1. Synthesis and characterization of brominated poly(phenylene oxide) (Br-PPO).

A typical synthetic procedure (target degree of substitution of 0.5, is described (Scheme S1) as follows: To a stirred solution of 12 g PPO (100 mmol) in chlorobenzene(100 mL) was added *N*-bromosuccinimide(NBS) (8.9 g, 50mmol),and 2,2'-azobis-isobutyronitrile (0.5 g, 3mmol). The mixture was heated at reflux conditions (135 ^oC) for 3 h. After cooling, the reaction mixture was poured into a 10-fold excess of ethanol to precipitate the product. The polymer was filtered and washed with ethanol, and the residue subsequently redissolved in chloroform (120 mL) and precipitated into a 10-fold excess of ethanol solution. The polymer was collected as a light yellow powder and dried under vacuum for overnight to get Br-PPO with a yield of 92 %, bromination ratio: 39 % (DS=0.39).

All of the other Br-PPO polymers with different DS were prepared by using different amount of NBS according to the above procedure. The bromination ratio was determined by ^1H NMR and the results were shown in Table S1.



Scheme S1. The synthesis of comb-shaped PPO-DMHDA-*x* polymers.

Table S1. Degree of bromination substitution (DS) and IEC values of PPO-DMHDA-*x*polymers.

sample	DS (%) (target)	DS (%) (^{1}H NMR)	Bromination yields (%)	IEC (^{1}H NMR)	IEC (titration)
PPO-DMHDA-20	30	21	70	1.15	1.08
PPO-DMHDA-30	40	32	80	1.52	1.48
PPO-DMHDA-40	50	39	78	1.74	1.67
PPO-DMHDA-55	65	55	85	2.04	1.92
PPO-TMA-20	30	21	70	1.48	1.39

Basically, bromination can take place either at the benzylic position or at the aromatic rings of PPO, depending on the reagents and reaction conditions. Various reagents have been used to perform the a bromination of alkyl benzenes under heating or light irradiation, such as bromine and NBS, and some relevant concerns are the effects of solvents, catalysts, and the selectivity between radical substitutions on the side chain or electrophilic substitutions on the aromatic ring. Because NBS is a popular reagent employed mostly in free-radical allylic and benzylic bromination, we focused on the use of NBS. Generally, bromine radicals were generated by the irradiation of NBS in a refluxing chlorobenzene solution with AIBN as initiator. The partially methyl-brominated polymers were obtained in excellent selectivity at high yields, and hardly any phenyl-brominated or methyl-dibrominated derivatives were found after isolation. As shown in Fig. S1, the ^{1}H NMR spectrum of Br-PPO exhibited a singlet at4.3 ppm and multiplets at6.5–6.7 ppm, which corresponded to the bromobenzylic region and the correlated aromatic proton resonances, respectively. There is no any peak at about 6.1 ppm which is the shift of Br-substituted aromatic proton was found. Thus, the bromination ratio(%)Br-PPO could be determined by the comparison of the integration of methlyene at 4.3 ppm with methyl. Br-PPO polymers with various bromination ratio were accessible by the use of different amounts of NBS under similar reaction conditions.

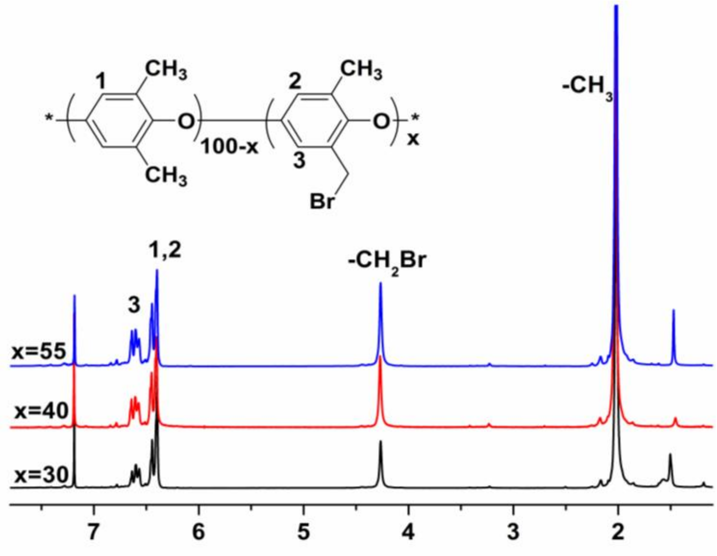


Fig. S1.^{1}H NMR spectra of Br-PPO in $CDCl_3$.

2. Synthesis and characterization of comb-shaped PPO in the bromine ion form.

Br-PPO with a DS of 0.39 (1.5 g, 10 mmol) was dissolved in 20 mL of NMP. Subsequently, *N*,*N*-dimethyl-1-hexadecyamine (DMHDA) (3.6 g, 15mmol) was added. The mixture was stirred for 48 h at room temperature. Then, the reaction mixture was poured to a 10-fold excess of toluene or water to precipitate the product. The polymer was filtered and washed with toluene three times and hexane three times. The polymer was collected as a light yellow powder and dried under vacuum for overnight to obtain the comb-shaped PPO in the bromine ion form with a yield of 90 %.

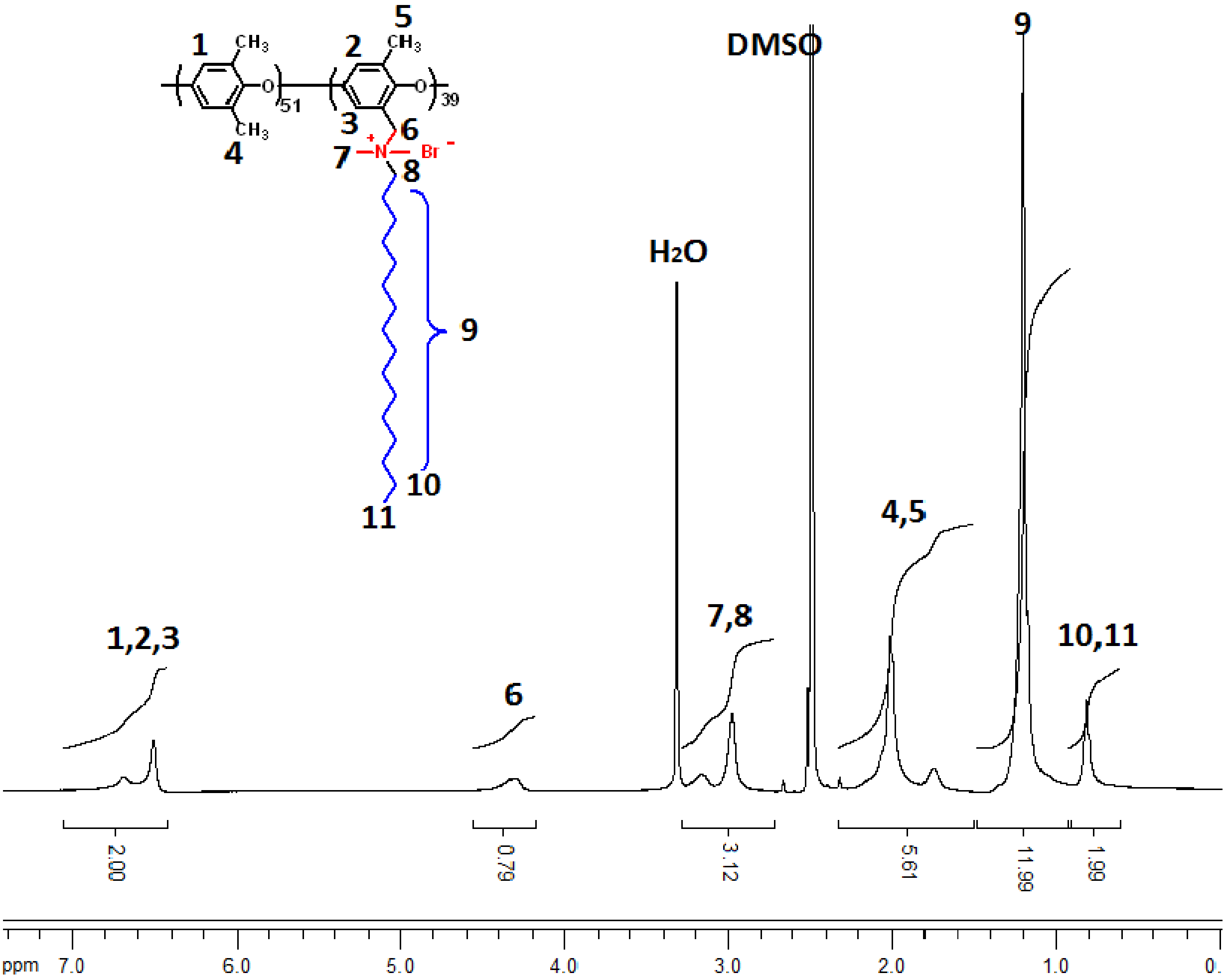


Fig. S2. ^{1}H NMR of comb-shaped PPO-DMHDA-40 in the bromine form in DMSO-d_6.

The PPO ammonium bromine salts were isolated and characterized by ^{1}H NMR spectroscopy.

The disappearance of the bromo benzylic peak at4.3 ppm along with the concomitant appearance of peaks for *N*,*N*-dimethyl-1-hexadecyamine (DMHDA) salts at0.5-1.5ppm indicated that the quaternary ammonium formed successfully. A broad hump from4.32 ppm to4.51 ppm was seen, which could be assigned to the two benzylic protons H6, probably because of the deshielding effect from quaternary ammonium salts.

3. Membrane casting and ion exchange.

The PPO-DMHDA-*x* polymers in the bromine form with cyan color were cast from NMP solutions (5 wt %) in a custom-built flat glass dish. The membranes were first dried at 80 ^{o}C for 12 h and then vacuum dried at 100 ^{o}C for 24 h. The membranes in the bicarbonate form were achieved by exchanging the bromine form membranes with sodium bicarbonate followed by extensive rinsing to remove the excess salt. The PPO-DMHDA-*x* membranes were treated in 1 N NaOH at room temperature for 48 h to obtained the hydroxide conductive PPO-DMHDA-*x* membranes. They were then washed thoroughly and immersed in deionized water that was degassed and blanketed with flowing Ar to remove residual NaOH. As shown in Fig. S3, the ^{1}H NMR spectrum of the hydroxide form PPO-DMHDA-*x* membranes (in $CDCl_3$)is different from that of PPO-DMHDA-*x* in the bromine form (in DMSO-d_6) which results from probably the different solvent. Moreover, after exchanging to hydroxide form, the benzylic protons H6 shift to high chemical shifts due to the strong electro-withdrawing ability of hydroxide. However, all of these proton peaks retained their integrity without any decreases in integration, as shown in Table S2. This result suggests that there is no decomposition occurring during the hydroxide exchange.

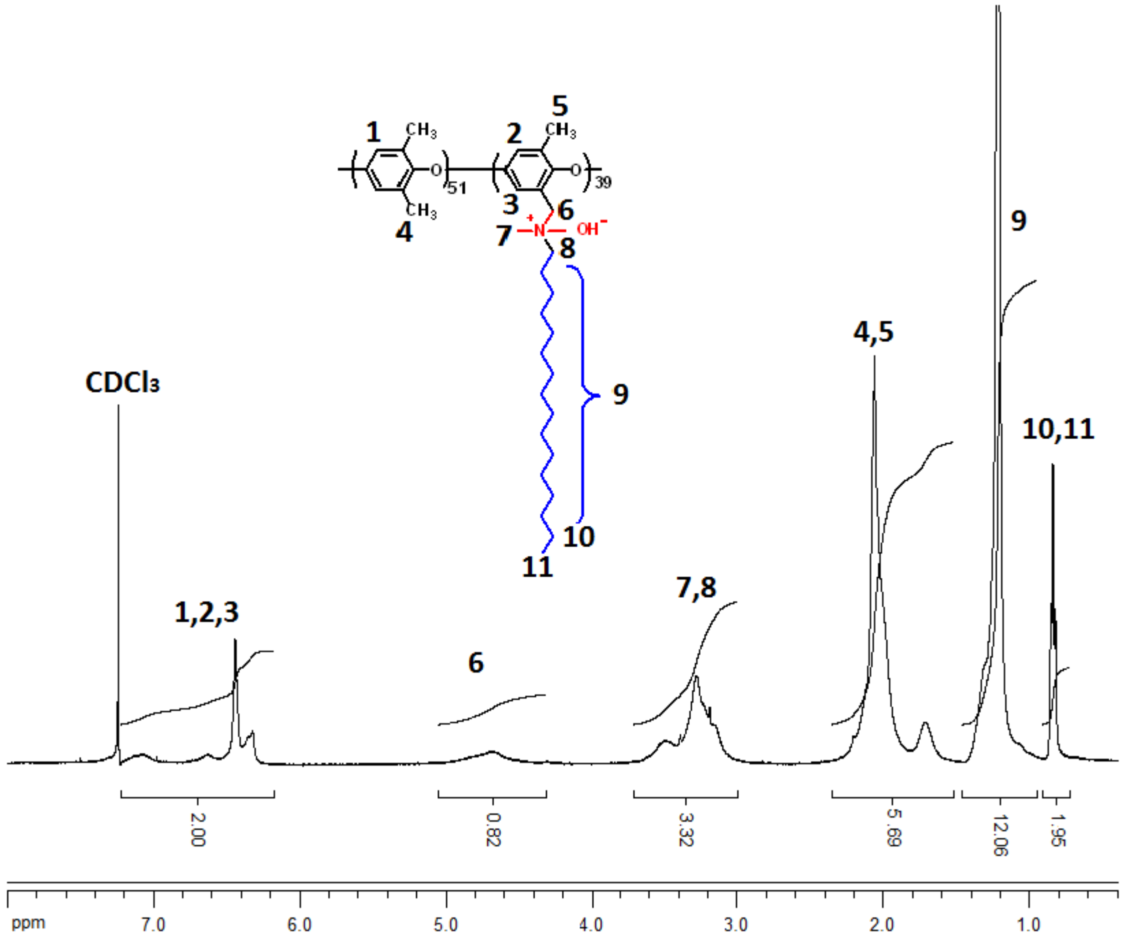


Fig. S3. ^{1}H NMR of comb-shaped PPO-DMHDA-40 in the hydroxide form in $CDCl_3$.

Table S2. Comparison of the ^{1}H NMR relative integration of PPO-DMHDA-40 in the bromine form in DMSO-d_6 and in the hydroxide form in $CDCl_3$.

	bromine form (DMSO-d_6)		hydroxide form ($CDCl_3$)		theoretical value
	chemical shift (ppm)	integration	chemical shift (ppm)	integration	
H1, H2, H3	6.48-6.90	2.00	6.35-7.03	2	N/A
H6	4.38	0.78	4.65	0.82	
H7, H8	2.97-3.3	3.12	3.12-3.62	3.32	
H4, H5	1.65-2.01	5.61	1.68-2.02	5.69	
H9	1.22	11.99	1.19-1.25	12.06	
H10, H11	0.81	1.99	0.82	1.95	
Ratio: H6/H1, H2, H3	0.39		0.41		0.39
Ratio: H7, H8/H6	4.00		4.05		4.00

Table S3. The solubility of PPO-DMHDA-*x* membranes in the hydroxide form.

	methanol	*n*-propoanol	chloroform	acetone	DMF	NMP	DMSO
PPO-DMHDA-20	+-	+-	+	+	+	+	-
PPO-DMHDA-30	+	+	+	+	+	+	-
PPO-DMHDA-40	+	+	+	+	+	+	-
PPO-DMHDA-55	+	+	+	+	+	+	-
PPO-TMA-20	+-	+-	-	-	+	+	+

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; +-, swelling; -, insoluble; the solid polymer did not dissolve in the solvent.

4. Characterization and measurements.

Thermo gravimetric analysis (TGA) was performed in a nitrogen atmosphere with a Perkin-Elmer TGA-2 thermo gravimetric analyzer at a heating rate of 10 ^{o}C min^{-1}. The membranes in the OH^{-} form were immersed in 100 mL of 0.01M HCl standard for 24 h under Ar protection. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator to get the titrated IEC values.

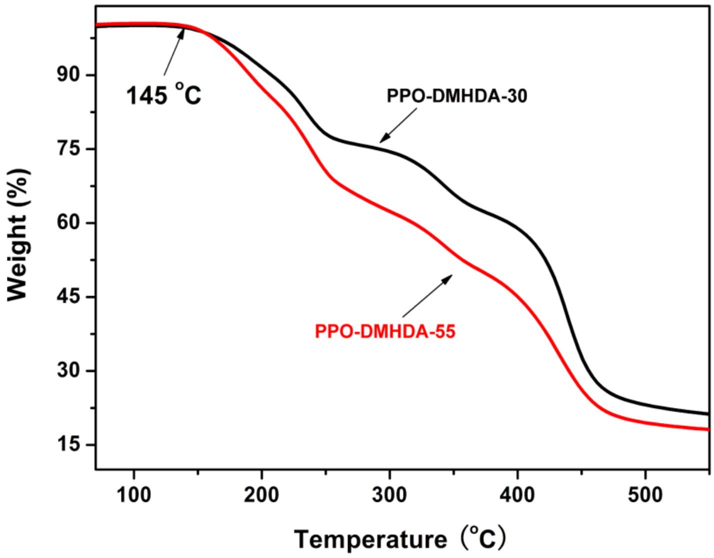


Fig. S4.TGA curves for the PPO-DMHDA-*x* membranes from measurements run at 10 ^{o}C/min in N_2.

Water uptake was measured after drying the membrane in hydroxide form at 60 °C under vacuum for 24 h. The dried membrane was immersed in water and periodically weighed on an analytical balance until a constant weight was obtained, giving the weight-based (IEC) water uptake.

Conductivity (σ, $\mathrm{Scm^{-1}}$) of each membrane coupon (size: 1 cm×4 cm) was obtained using $\sigma = d/L_sW_sR$ (d is the distance between reference electrodes, and Ls and Ws are the thickness and width of the membrane, respectively). The resistance value (R) was measured over the frequency range from 100 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The hydroxide conductivity measurements under fully hydrated conditions in the longitudinal direction were carried out with the cell immersed in water which was degassed and blanketed with flowing Ar.

Small angle X-ray scattering measurements were performed on a SAXS setup using a Rigaku generator of rotating anode type with Cu target, equipped with a focusing multilayer optics. The flight path is fully evacuated, a 2D-Siemens Hi-Star served as detector. All the measurements were performed at room temperature. Typical exposure time was in the range from 20min to 40min, depending on the thickness of the sample. The samples were pressed to films at a temperature of about 25°C and had a typical thickness about 0.1mm. The accessible range of scattering vectors $q = 4\pi\sin\theta/\lambda$ was about 0.6 $\mathrm{nm^{-1}}$ to 6.2 $\mathrm{nm^{-1}}$. Here λ_i and 2θ are the X-ray wavelength and Bragg scattering angle, respectively.

Atomic force microscopy AFM tapping-mode height profiles were acquired with a JPK Instruments AG multimode NanoWizard (Germany) for AFM micrographs. The instrument was equipped with a NanoWizard scanner. For tapping-mode AFM, a commercial Si cantilever. (TESP tip) of about 320 kHz resonant frequency from JPK was used.

Table S4. SAXS results of PPO-DMHDA-*x* membranes (position of scattering peak *q**, periodicity *d*=2π/*q**, peak width FWHM, correlation length l_c=2π/FWHM). For all samples the measured values for the peak width are considerably larger than the instrumental resolution σ≈0.15 nm^{-1}.

samples	*q**(nm^{-1})	*d*(nm)	*FWHM* (nm^{-1})	l_c (nm)
PPO-DMHDA-20	2.13	2.95	1.07	5.87
PPO-DMHDA-30	1.91	3.29	0.836	7.51
PPO-DMHDA-40	1.88	3.34	0.7	8.97
PPO-DMHDA-55	1.79	3.51	0.567	11.08
PPO-TMA-20	--	--	--	--

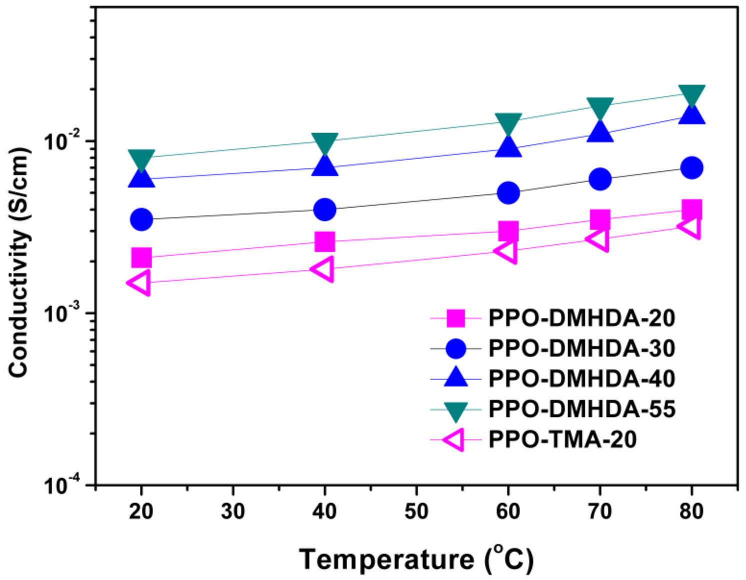


Fig. S5. The conductivities of PPO-DMHDA-*x* membranes in the form of bicarbonate under fully hydrated state (in water) as a function of temperature.