# **Supporting information**

# Crosslinked Comb-shaped Anion Exchange Membranes with High Base Stability

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## Synthesis of N,N-dimethyl -10-undecen-1-amine

11-Bromo-1-undecene (10 mL) was dissolved in toluene (100 mL), and a 50 wt % N,Ndimethylamine THF solution (50 mL) was added. After stirring at 60 °C for 2 days, the resulting mixture was sequentially extracted with satd. NaHCO<sub>3</sub> soln. (3 × 30 mL) and distilled water (3×30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated by evaporation of the solvent under vacuum. The resulting colorless liquid with a yield of 85 % was dried *in vacuo* at room temperature for 12 h. The chemical structure was confirmed by <sup>1</sup>H NMR in CDCl<sub>3</sub>. As shown in Figure S1, a peak which corresponded to the methyl/methylene protons (H1 and H2) was observed while proton peaks of the alkene (H5 and H6) retained their integrity without any decreases in peak integral values. The disappearance of the bromomethyl peak at ~3.3 ppm along with the appearance of peaks for H1 and H2 at 2.3 ppm indicated that the target compound was synthesized successfully. The compound was used in the Menshutkin step, without further purification.



Figure S1. The <sup>1</sup>H NMR N,N-dimethyl 10-undecen-1-amine in CDCl<sub>3</sub>.

#### Synthesis of crosslinkable comb-shaped PPO in the bromide form

Br-PPO which was synthesized according to previous reports with a DS (x) of 0.6 (1.7 g, 10 mmol) was dissolved in 10 mL of NMP. Subsequently, N,N-dimethyl-10-undecen-1-amine (0.3 g, 1.5 mmol) was added. The mixture was stirred for 48 h at room temperature. Then, N,N-dimethylhexan-1-amine (0.58 g, 4.5 mmol) was added into the mixture and stirred at room temperature for another 24 h. The reaction mixture was poured into 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 at room temperature for 12 h to obtain the crosslinkable comb-shaped PPO (X60Y15, where the X is the degree of bromomethylation and Y refers to the ratio of crosslinkable groups to X) in the bromide form with a yield of 90 %.



Scheme 1. Synthesis of crosslinked comb-shaped AEMs, *XxYy*, using olefin metathesis with Grubbs II catalyst.

The above-mentioned procedures were followed for the synthesis of other XxYy polymers. The only exception was a different molar ratio of crosslinkable groups and Br-PPO with different bromomethylation (Table S1).



Fig. S2. <sup>1</sup>H NMR of crosslinkable comb-shaped X80Yy in the bromide form in DMSO- $d_6$ .

The crosslinkable PPO (X80Yy) ammonium bromide salts were isolated and characterized by <sup>1</sup>H

NMR spectroscopy (Figure S2). The disappearance of the bromo benzylic peak at 4.3 ppm along with the appearance of new peaks at 3.1 ppm which were ascribed to methyl or methylene groups on the quaternized ammonium groups indicated that the quaternary ammonium center was formed successfully. A broad peak from 4.42 ppm to 4.61 ppm was observed, which was assigned to the two benzylic protons H11 or H12, likely due to the deshielding effects of the quaternary ammonium salt. The functionalization of the alkene was demonstrated by the appearance of the characteristic alkene proton peak at 5.0 and 5.8 ppm in the <sup>1</sup>H NMR spectrum and their intensity increased with an increase in the amount of N,N-dimethyl-10-undecen-1-amine added, as shown in Figure S2. Meanwhile, the integrity of the methyl peak in the hexane alkyl chains at 0.8 ppm decreased gradually and disappeared finally with the addition of increased amounts of N,N-dimethyl 10-undecen-1-amine during the Menshutkin reaction. Thus, the ratio of crosslinkable alkene groups in **XxYy** could be determined by the comparison of the integration of the alkene proton at 5.0 ppm.

	DB <sup>a</sup> (%)	Target RC <sup>b</sup> (%)	RC <sup>c</sup> (%)	IEC <sup>d</sup> (meq./g)	IEC <sup>e</sup> (meq./g)	Gel fraction (%) <sup>f</sup>
X60Y15	61	25	27	2.71	2.76	81
X60Y30	61	50	48	2.65	2.63	88
X60Y60	61	100	100	2.39	2.42	97
X80Y20	82	25	24	3.25	3.20	80
X80Y40	82	50	53	3.10	3.04	84
X80Y80	82	100	100	2.71	2.75	98

**Table S1.** Properties of XxYy copolymers.

<sup>a</sup> degree of bromomethylation (calculated from <sup>1</sup>H NMR); <sup>b</sup> target ratio of crosslinkable alkene groups (RC); <sup>c</sup> RC calculated from <sup>1</sup>H NMR; <sup>d</sup> IEC value calculated from H NMR; <sup>e</sup> IEC measured by titration; <sup>f</sup> After crosslinking, the gel fraction was obtained from the ratio of the weight of the polymer after extraction from NMP at 80 °C for 1 day and the initial weight.

#### Membrane casting and ion exchange

The **XxYy** copolymers (1 g) in the bromide form were dissolved in n-propanol/toluene (3:2 vol) (20 mL) to form a 5 wt % solution. Subsequently, Grubbs II generation catalyst (35 mg) was added into the polymer solution. The solution was then cast onto a PTFE mold. Drying of the solution at room temperature for 24 h gave a thick, transparent, tough film. The film was dried further in a vacuum oven at 80 °C for 20 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 membranes were treated in 1 N NaOH at room temperature for 24 h to obtain the hydroxide form **XxYy** membranes. The samples were then washed thoroughly and immersed in deionized water that was degassed and blanketed with flowing Ar.

## Characterization and measurements

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 mass was obtained, giving the weight-based (IEC) water uptake. The membranes in the bromide form were immersed in 100 mL of 0.1 M NaNO<sub>3</sub> standard solution for 24 h. The solutions were then titrated with a standardized AgNO<sub>3</sub> solution using  $K_2CrO_3$  as an indicator to obtain the titrated gravimetric IEC values.

Conductivity ( $\sigma$ , Scm<sup>-1</sup>) of each membrane coupon (size: 1 cm × 4 cm) was calculated using  $\sigma = d/L_s W_s R$  (*d* is the distance between reference electrodes, and *L*s and *W*s are the thickness and width of the membrane, respectively). The resistance (*R*) was measured over the frequency range

from 100 mHz to 100 kHz by two-point probe alternating current (AC) impedance spectroscopy using an impedance/gain-phase analyzer (Solartron 1260A, Farnborough Hampshire, ONR, UK). 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 to exclude as much  $CO_2$  as possible.

Small-angle X-ray scattering curves of unstained dry bicarbonate form membranes were obtained using a Rigaku (formerly Molecular Metrology) instrument equipped with a pinhole camera with an Osmic microfocus Cu K $\alpha$  source and a parallel beam optic. Typical counting times for integration over a multiwire area detector were 1 h with typical membrane thicknesses on the order of 100  $\mu$ m. Measurements were conducted under vacuum at ambient temperature on dry samples. Scattering intensities were normalized for background scattering and beam transmission.



**Figure S3.** Bicarbonate conductivity of crosslinked and non-crosslinked comb-shaped AEMs and TMA-20 membranes based on trimethyl amine as a function of time during immersion in 1 M NaOH solution at 80 °C.



**Figure S4.** IEC values of crosslinked and non-crosslinked comb-shaped AEMs and TMA-20 membranes from trimethyl amine during immersion in 1 M NaOH solution at 80 °C.