Supporting Information

Aromatic Polymers Incorporating Bis-*N*-spirocyclic Quaternary Ammonium Moieties for Anion-Exchange Membranes

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Experimental description

Materials

Tetramethylhydroquinone (4MHQ, 95%, TCI) and bisphenol A (BPA, 97%, Acros) were recrystallized from toluene. 4,4'-Dichlorodiphenylsulfone (DCDPS, 97%, Acros) was recrystallized from *N,N*-dimethylformamide. K_2CO_3 (99%, Acros), *N*-bromosuccinimide (NBS, 99%, Acros), azobisisobutyronitrile (AIBN, 98%, Acros), pyrrolidine (99%, Aldrich), piperidine

(≥ 99.5%, Aldrich), hexamethyleneimine (99%, Aldrich), *N*-ethyldiisopropylamine (DIPEA, ≥ 99.5%, Merck), toluene (reagent grade, Honeywell), *N,N*-dimethylacetamide (DMAc, ≥ 99%, Aldrich), 2-propanol (IPA, ACS Basic, Scharlau), 1,2-dichlorobenzene (99%, Fluka Analytical) and *N*-methyl-2-pyrrolidinone (NMP, reagent grade, Acros) were all used as received.

Polycondensation

A two-neck 100 ml round-bottom flask equipped with a Dean-Stark trap, a condenser, a $CaCl_2$ trap and a nitrogen inlet was charged with 4MHQ (0.6493 g, 3.906 mmol), BPA (0.8982 g, 3.934 mmol), DCDPS (2.2514 g, 7.840 mmol), DMAc (30 ml) and toluene (30 ml). The reaction mixture was first dehydrated by azeotropic distillation at 110 ºC during for 4 h under nitrogen flow. Next, all toluene was removed by distillation at 165 ºC and the reaction mixture was kept under nitrogen atmosphere at the same temperature for 20 h. The product was then precipitated in IPA. The precipitate was repeatedly washed with IPA and water to yield the pure grayish-white PAES.

Benzylic bromination

The dry unmodified PAES (1.0 g) was dissolved in 1,2-dichlorobenzene (20 ml) in a two-neck 50 ml round-bottom flask equipped with nitrogen inlet and condenser with a $CaCl_2$ trap. The solution was degassed by nitrogen bubbling during 1 h. AIBN (48 mg, 0.29 mmol) and NBS (3.5 g, 20 mmol) was then added to the solution and the reaction was heated to 110 ºC under nitrogen flow. After 2 h, extra NBS (3.5 g, 20 mmol) and AIBN (48 mg, 0.29 mmol) were added. After an additional 2 h, the product was precipitated in IPA to yield a light yellow precipitate. The precipitate was repeatedly washed with IPA and water and dried to give the brominated PAES derivative (PAES-Br).

Cyclo-quaternization

PAES-Br was reacted with pyrrolidine, piperidine or azepane via cyclo-quaternizations, resulting in three different polymers containing bis-*N*-spirocyclic QA groups. Here follows a typical procedure for synthesis of PAES-*spiro*-pyr. PAES-Br (0.525 g) was dissolved in NMP (50 ml) in a 100 ml round-bottom flask equipped with a condenser. A solution of DIPEA (0.172 ml, 1.01 mmol) and pyrrolidine (0.083 ml, 0.994 mmol) in NMP (1 ml) was added drop-wise to the polymer solution. The color of solution changed immediately from light yellow to light orange. After keeping the solution at 60 °C overnight, the solution turned red. PAES-*spiro*-pyr was isolated by precipitation in IPA and then purified by repeatedly washing with IPA and water, before drying under vacuum.

Membrane preparation

AEMs were cast from the different bis-*N*-spirocyclic QA functionalized polymers in Br^- form. Approximately 0.15 g polymer was dissolved in 3 g NMP. The solution was poured into a Petri dish and placed in a ventilated casting oven at 80 °C overnight. The resulting membrane was then washed thoroughly with deionized water and kept in the medium before analysis.

The AEMs in Br^- form were transformed into OH^- form by ion-exchange in 1 M aqueous NaOH solution under nitrogen atmosphere during at least 24 h. Next, the membranes were thoroughly washed with degassed deionized water and stored in degassed deionized water under nitrogen atmosphere.

Structural characterization

The chemical structures of all polymers were confirmed by ^{1}H-NMR spectroscopy. Spectra were recorded on a Bruker DRX400 spectrometer at 400.13 MHz using $CDCl_3$ ($\delta = 7.26$ ppm) or *d*6-DMSO ($\delta = 2.50$ ppm) as solvent.

The molecular weight and polydispersity index (PDI) of unmodified PAES were determined using size-exclusion chromatography (SEC). A 3 wt. % solution of PAES in chloroform was passed through a series of three Shodex columns (KF-805,-804, and -802.5) and a refractive index detector at room temperature. The elution rate was 1 ml chloroform min^{-1}. Four low-polydispersity polystyrene (PS) standard samples ($M_n = 650$ kg mol^{-1} from Water Associates, 96 kg mol^{-1} from Polymer Laboratories, 30 kg mol^{-1} from Polysiences, Inc. and 3.18 kg mol^{-1} from Agilent Technologies) were used for calibration.

Thermal analysis

The thermal degradation of the polymers was examined by thermogravimetrical analysis (TGA) using a TGA Q500 (TA Instruments). Prior to the analysis the samples were kept isothermally at 150 ºC for 10 min to remove solvent residues. The thermal degradation was evaluated under nitrogen flow, with heating ramp 10 ºC min^{-1} up to 600 ºC. The degradation temperature ($T_{d,95}$) was determined at 5% weight loss.

The glass transition temperature (T_g) of PAES was determined by differential scanning calorimetry (DSC) using a DSC Q2000 (TA Instruments). The sample was analyzed during the sequence 50 - 300 - 50 - 300 ºC at a heating/cooling rate of 10 ºC min^{-1}. The value of T_g was determined from the second heating cycle.

Ion exchange capacity determination

The ion exchange capacity (IEC) of the membranes in Br^- form was determined by Mohr's titration. The membranes were dried in vacuum oven at 50 ºC for 2 days, weighed and immersed in 25 mL 0.2 M aq. $NaNO_3$ solution during at least 48 h. The resulting solutions were titrated with 0.01 M aq. $AgNO_3$ solution to determine the concentration of Br^- ion (C_{Br}), using 0.1 M aq. K_2CrO_4 as color indicator. The IEC was calculated as:

$$IEC(meq \cdot g^{-1}) = \frac{C_{Br} \cdot 25}{m_{membrane}} \qquad \text{(Eq. 1).}$$

Water uptake measurement

The water uptake of the membranes was studied at 20, 40, 60 and 80 ºC. The membranes were immersed in water at each temperature until a constant water uptake. The membranes was then quickly wiped with tissue paper to remove the excess water on the surface and weighed to obtain the weight at hydrated state (W_{wet}). The weight in the dry state (W_{dry}) of the membranes in Br^- form was obtained after drying the membranes in vacuum oven at 50 ºC for at least 48 h. W_{dry} of membranes in OH^- form was recalculated from W_{dry} of the same membranes in Br^- form and their IECs as follows:

$$W_{OH} = W_{Br} - \frac{W_{Br} \cdot IEC \cdot 62.9}{1000} \qquad \text{(Eq. 2).}$$

The water uptake (WU) was determined as:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \cdot 100\% \qquad \text{(Eq. 3).}$$

Conductivity measurement

The conductivity of fully hydrated membranes was measured by electrochemical impedance spectroscopy (EIS) in the temperature range -20-80 °C. The measurements were performed using a sealed cell by a two-probe method using a Novocontrol high resolution dielectric analyzer V 1.01S in the frequency range 10^1-10^7 Hz at 50 mV.

Small-angle X-ray scattering

The phase separation by clustering of ions was studied by small-angle X-ray scattering (SAXS) measurements of the AEMs in Br^- form. Data in the *q*-range 0.14-7.5 nm^{-1} was collected using a SAXSLAB SAXS instrument, from JJ X-ray Systems Aps (Denmark) equipped with a Pilatus detector. The radiation was Cu K_α with wavelength (*l*) of 1.542 Å. The wave vector (*q*) was calculated as:

$$q = \frac{4\pi}{l\, sin2\theta} \qquad \text{(Eq. 4)}$$

, where 2θ is the scattering angle. The characteristic separation length (*d*) was calculated using the Bragg's law:

$$d = \frac{2\pi}{q} \qquad \text{(Eq. 5).}$$

Membrane degradation

The alkaline stability of the AEMs was evaluated by immersing the membranes in 1 M aq. NaOH solution at 20, 40 and 60 ºC during different time periods. After the immersion, the membranes were immediately washed with deionized water and immersed in an 1 M NaBr solution to exchange back to the Br^- form. After thorough washing and drying, the membranes were dissolved in *d*6-DMSO and analyzed by ^{1}H NMR spectroscopy as described above. The spectra were then compared with the corresponding spectra recorded before the degradation test.

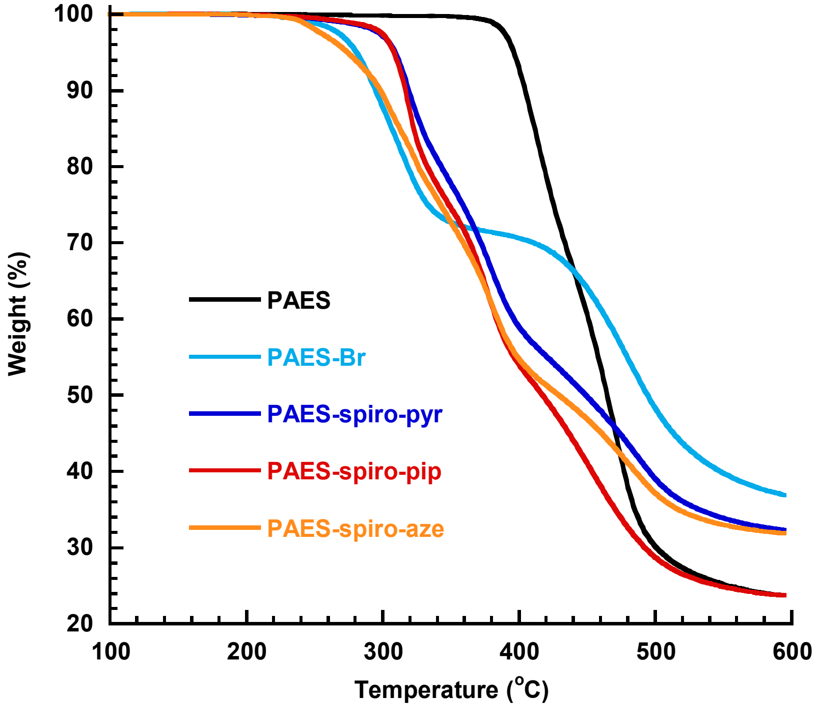

Figure S1. TGA traces of unmodified PAES, benzyl brominated PAES, and AEMs based on the three polymers incorporating the bis-*N*-spirocyclic moieties in Br^- form. The data was recorded under N_2 at 10 °C min^{-1}.

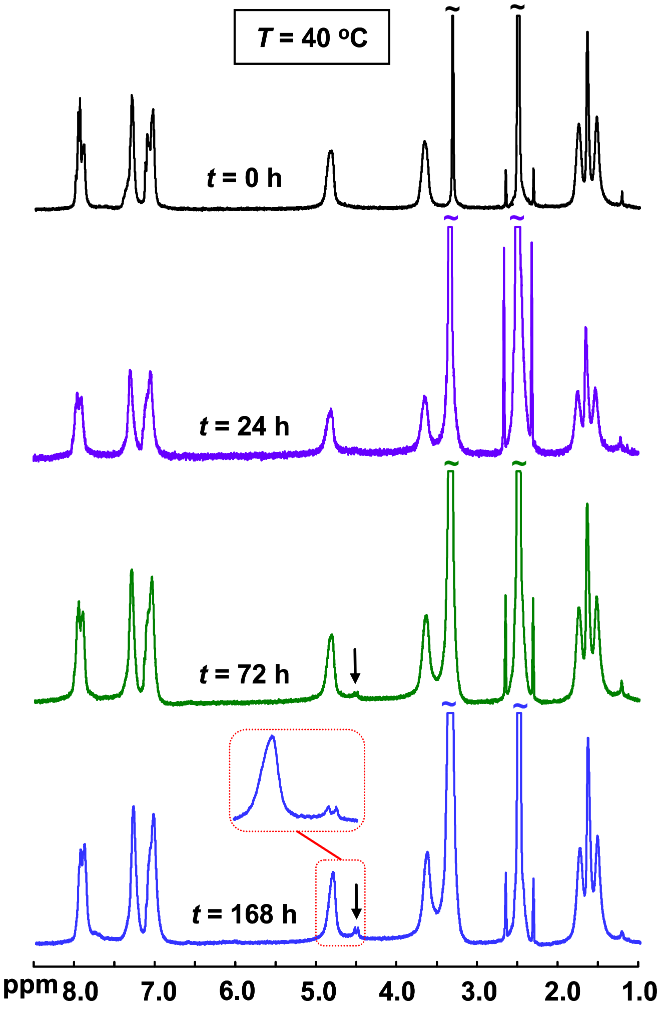

Figure S2. ^{1}H NMR spectrum of AEMs based from PAES-*spiro*-aze in Br$^-$ form before and after storage in 1 M aq. NaOH at 40 ºC during 24, 72 and 168 h. The new signals appearing at 4.5 ppm are indicated by arrows.

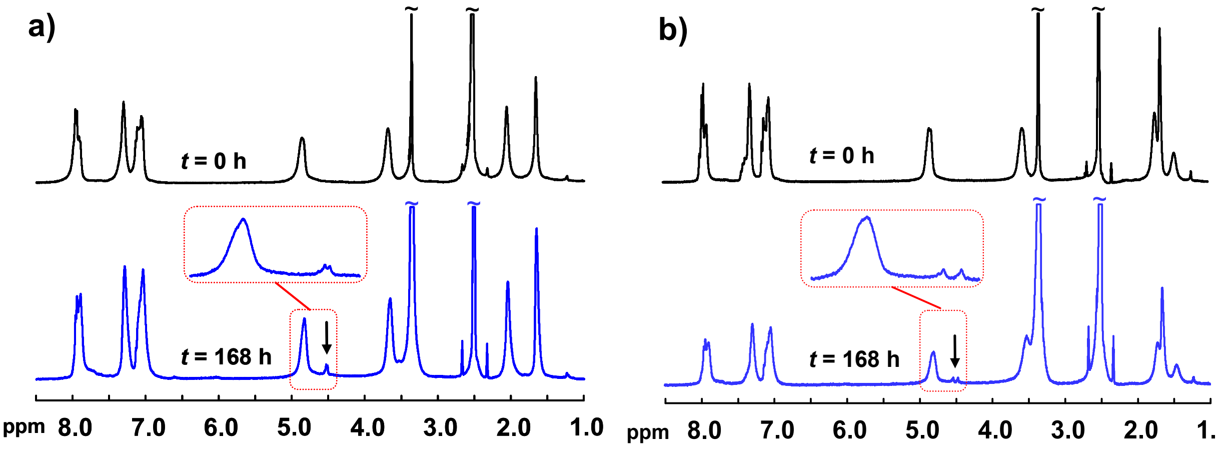

Figure S3. ^{1}H NMR spectra of AEMs based on a) PAES-*spiro*-pyr and b) PAES-*spiro*-pip in Br$^-$ form before and after storage in 1 M aq. NaOH solution at 40 ºC during 168 h. The new signals appearing at ~ 4.5 ppm are indicated by arrows.