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Poly(phenylene oxide) functionalized with quaternary ammonium groups via flexible alkyl spacers for high-performance anion exchange membranes[†]

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Detailed experimental description

Materials

Tetrahydrofuran (THF, HPLC grade, Honeywell) was dried over molecular sieves (Acros; 4Å, 8-12 mesh) before use, Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, Sigma-Aldrich), *n*-butyllithium (*n*-BuLi, 2.5M, solution in hexanes, Acros), 1,6-dibromohexane (98%, Acros), NBS (99%, Acros), azobisisobutyronitrile (AIBN, 98%, Acros), chlorobenzene (99+%, Fluka Analytical), *N*-methyl-2-pyrrolidone (NMP, reagent grade , Acros), trimethyl amine (TMA, 7.3 M aqueous solution, Acros), diethyl ether (99+%, Sigma-Aldrich), silver nitrate (99,995%, Sigma-Aldrich), methanol (MeOH, HPLC grade, Honeywell), 1,2-dichlorobenzene (99+%, Fluka Analytical) and 2-propanol (IPA, HPLC grade, Honeywell) were used as received.

Polymer synthesis

A series of five quaternized PPO-7Q polymer samples with various ion contents were synthesized by employing benzylic lithiation, bromoalkylation and quaternization using TMA in accordance with Scheme 1. In the first step, PPO was bromoalkylated by lithiation and reaction with 1,6-dibromohexane to form samples with different degrees of bromination (DB, percentage of bromoalkylated benzylic methyl groups of the PPO). The samples were designated as PPO-7Br-*DB*. As an example, sample PPO-7Q-11 was prepared as follows: a 4-neck 250 mL round bottomed flask equipped with thermometer, a rubber septum and an argon inlet-outlet was charged with PPO (1g, 8.32 mmol repeat units) and dry THF (100 mL). The heterogeneous mixture was first degassed by seven vacuum/ argon cycles and heated to 55 °C until the PPO fully dissolved. The clear homogeneous solution was cooled to room temperature and degassed again with seven cycles of vacuum/ argon.

Then, *n*-BuLi (2.2 mL, 5.5 mmol) was added drop-wise to the colorless solution using a gastight syringe. Initially, traces of impurities quickly consumed the *n*-BuLi before the lithiated PPO intermediate was formed. This was indicated by a color change from light yellow to reddish orange. The lithiated polymer solution was stirred for 3 h under argon flow, followed by cooling to -78 °C using a dry ice/IPA bath. Once the temperature was stable at -78 °C, 1,6-dibromohexane (1.7 mL, 11 mmol) was quickly added by syringe and the resulting solution was maintained at -78 °C for 4 h under stirring. Subsequently, the slightly yellow solution was filtered, poured drop-wise into 1000 mL of methanol and then stirred for at least 3 h. The polymer precipitate was collected by filtration, washed thrice with methanol, and dried at 50 °C for 48 h.

Two PPO-1Q-*IEC* reference materials with benzyltrimethyl ammonium groups were prepared. In the first step, controlled fractions of the benzylic positions of PPO were brominated by using NBS and AIBN as the radical source to produce two PPO-1Br-*DB* samples. The following describes the synthesis of sample PPO-1Br-22, precursor to sample PPO-1Q-1.5. PPO (10.0 g) was dissolved in 1,2-dichlorobenzene (200 ml) in around bottomed flask. The colourless solution was degassed followed by addition of NBS (4.47 g) and AIBN (0.265 g). The reaction then proceeded for 4 h at 110 °C after which the solution was poured into IPA to precipitate the product. The brominated polymer was finally washed in IPA and water and dried *in vacuo* at 50 °C for 24 h.

The brominated PPO-7Br and -1Br polymers were quaternized using TMA under homogeneous conditions. First, solutions containing 5 wt% polymer in NMP were prepared. A 1000% excess of TMA was subsequently added to form a homogenous mixture. The reaction solution was stirred in a sealed vessel for at least 4 days at room temperature to ensure complete displacement of the bromines. The quaternized polymer solution was then added drop-wise to 200 mL of diethylether whereby a white precipitate was formed. The solid was collected by filtration, washed twice with 500 mL of diethylether. The final quaternized polymer in Br⁻ form was obtained after drying under vacuum during 2 days at room temperature.

Membrane preparation

AEMs with different IEC values were prepared from the PPO-7Q and -1Q polymers. An amount of 0.15 g of the polymer was dissolved in NMP (3 g) and poured onto a glass Petri dish with a 5 cm diameter. The membrane was cast in an oven at 80 °C during 36 h, whereafter the resulting film was peeled from the dish and thoroughly washed with deionized water. The membranes were then stored in deionized water during at least 48 h at room temperature prior to analysis.

Structural characterisation

All polymers were characterized by ¹H-NMR spectroscopy with a Bruker DR X400 spectrometer at 400.13 MHz using CDCl₃ (δ = 7.26 ppm) or DMSO-*d*6 (δ = 2.50 ppm) solutions of the samples.

A size-exclusion chromatograph equipped with a series of three Shodex colums (KF-805,-804 and -802.5) and a refractive index detector was employed for the determination of M_n and M_w of the bromoalkylated polymers. Polystyrene standards ($M_n = 650$ kg mol⁻¹ from Water Associates, 96 and 30 kg mol⁻¹ from Polymer Laboratories, and 3.18 kg mol⁻¹ from Agilent Technologies) with low polydispersity were used to calibrate the SEC. All samples were dissolved in chloroform and filtered through a 0.45 µm pore size syringe filter. The analysis was performed at room temperature at an elution rate of 1 mL min⁻¹.

Thermal characterisation

The thermal degradation of the polymers was examined by thermogravimetrical analysis (TGA) using a Q500 analyzer (TA instruments). All samples were dried in a vacuum oven at 50 °C for 48 h, and in order to remove any solvent residues, the samples were preheated at 150 °C for 10 min. The TGA data were collected at scanning rate of 10 °C min⁻¹ in the temperature range 50 - 600 °C under nitrogen atmosphere. The degradation temperature ($T_{d,95}$) was determined at 5% weight loss. The glass transition temperature (T_g) of the polymer samples was analyzed by differential scanning calorimetry (DSC) using TA instruments Q2000 analyzer. DSC heating/cooling/heating data was recorded between 50 and 280 °C and T_g was determined from the second heating cycle.

Determination of IEC and water uptake

The ion exchange capacity (IEC) of the quaternized membranes in Br⁻ form was measured by Mohr titrations. First, membrane samples were dried in a vacuum oven at 50 °C at least 24 h and weighted before immersion in 0.2 M aq. NaNO₃ (25.00 mL) for at least 48 h under gentle stirring. The resulting solution was titrated with 0.01 M aq. AgNO₃ using potassium chromate as indicator.

All quaternized membranes in Br⁻ form were dried in a vacuum oven at 50 °C for at least 48 h and weighted to measure the dry weight (W_{Br}) The dry membranes were then immersed in 1M degassed aq. NaOH solution in a desiccator for 48 h under nitrogen flow. The membranes in OH⁻ were then quickly transferred to a beaker containing degassed deionized water and washed for a few seconds. This process was repeated until the pH of the immersing water reached a value of 7 and the membranes were then immersed in DI water at least 24 h at room temperature in a nitrogen atmosphere. After equilibrium with water, the membranes were wiped with tissue paper and the weight of the wet membranes in hydroxide form (W'_{OH}) was determined. The dry weight of quaternized membranes in OH⁻ form (W_{OH}) was precisely calculated using IEC titration results and W_{Br} . The water uptake (WU) was calculated as:

$$WU = \frac{W'_{OH} - W_{OH}}{W_{OH}} \times 100\%$$

Using the same procedure, water uptake measurements were carried out at temperatures of 40, 60, and 80 $^{\circ}$ C.

The hydration number (λ) was defined as the number of water molecules per quaternized group and was calculated as:

$$\lambda = \frac{1000 \times (W'_{OH} - W_{OH})}{IEC \times W_{OH} \times 18}$$

Conductivity measurement

The ionic conductivity of immersed AEMs was measured in a sealed cell between -20 and 80 °C using a Novocontrol in high resolution dielectric analyzer V 1.01S at 50 mV and the scanning frequency was from 10^{-1} – 10^{7} Hz. The membranes in Br⁻ form were first ion exchange to the OH⁻ form by immersion in 1 M NaOH for at least 48 h in a desiccator under an atmosphere of nitrogen. Then, the membranes were repeatedly washed with degassed distillated water until the washing solution became neutral (pH \approx 7.0) to confirm removal of excess of OH⁻ ions and were stored in degassed water under nitrogen prior to the measurements.

Small angle X-ray scattering

Small-angle X-ray scattering (SAXS) technique was employed to study the clustering of ions of AEMs in Br⁻ form. SAXS tests were carried out using a SAXSLAB SAXS instrument, from JJ X-ray Systems ApS (Denmark) combined with a Pilatus detector. The scattering vector (q) was calculated based on the following equation:

$$q = \frac{4\pi}{l \sin 2\theta}$$

, where *l* is the wavelength of the CuK(α) radiation (1.542 Å) and 2 θ is the scattering angle. The average distance between ionic clusters (*d*) in the prepared membranes was calculated as:

$$d = \frac{2\pi}{q}$$

Membrane degradation

The AEM degradation under alkaline conditions was studied by using ¹H NMR spectroscopy. Pieces of PPO-7Q-1.5 and PPO-1Q-1.5 membranes were kept in a sealed vessel containing 1 M aq. NaOH in a temperature-controlled silicone oil bath at 80 °C. After 4 and 8 days of immersion, membrane samples were taken out and washed with DI water, before immersed in 1 M aq. NaBr to exchange OH⁻ ions for Br⁻ ions. After at least 48 h in the NaBr solution, the samples were extensively washed by

immersion in deionized water for at least 24 h to remove excess NaBr. Finally, all the samples were dried at 50 °C for 24 h, dissolved in DMSO- d_6 under gentle heating, and analyzed by ¹H NMR spectroscopy.

Table S1. Molecular weight and thermal data of PPO and the bromoalkylated PPO-7Br materials.								
sample	$M_{\rm n}^{[a]}$	$M_{\rm w} M_{\rm n}^{-1} {}^{[{ m a}]}$	DB ^[b]	$T_{ m g}$	$T_{d,95}^{[c]}$			
	$[\text{kg mol}^{-1}]$		[%]	[°C]	[°C]			
PPO	20	2.3	0	216	419			
PPO-7Br-11	19	2.8	11	175	365			
PPO-7Br-17	28	2.8	17	173	364			
PPO-7Br-19	28	9.1	19	167	351			
PPO-7Br-24	26	4.0	24	158	345			
PPO-7Br-29	22	3.8	29	147	353			

^[a] Examined by SEC using polystyrene standards, ^[b] Degree of bromination, evaluated from ¹H NMR data, ^[c] Measured by TGA under N₂, 10 $^{\circ}$ C min⁻¹.

Table S2. Properties of the PPO-7Q and PPO-1Q AEMs.								
AEM	IEC _{NMR} ^[a]	IEC _{titr} ^[a]	$T_{d,95}^{[b]}$	water	λ ^[c]			
	$[meq. g^{-1}]$	$[meq. g^{-1}]$	[°C]	uptake ^[c]				
				[wt%]				
PPO-7Q-0.8	0.8 (0.8)	0.8 (0.8)	272	8	6			
PPO-7Q-1.2	1.2 (1.1)	1.3 (1.2)	267	17	8			
PPO-7Q-1.3	1.3 (1.2)	1.3 (1.2)	247	23	10			
PPO-7Q-1.5	1.5 (1.4)	1.5 (1.4)	241	30	11			
PPO-7Q-1.8	1.8 (1.6)	1.8 (1.6)	241	43	13			
PPO-1Q-0.8	0.8 (0.8)	1.0 (0.9)	249	9	6			
PPO-1Q-1.5	1.5 (1.4)	1.5 (1.4)	234	20	8			

^[a] In the OH⁻ form (values within parenthesis are in the Br⁻ form), ^[b] Measured by TGA in the Br⁻ form, ^[c] Immersed in OH⁻ form at 20 °C.



Fig. S1. DSC traces of PPO with different degrees of bromination (0-29%). Data was recorded at 10 $^{\circ}$ C min⁻¹.



Fig. S2 SAXS profiles of dry PPO-7Q and PPO-1Q AEMs in the Br⁻ form. The data have been shifted vertically for clarity.



Fig. S3 Hydration numbers (λ) of the fully hydrated AEMs as a function of temperature. The data are derived from the water uptake data in Fig. 3a.



Fig. S4 ¹H NMR spectra of PPO-7Q-1.5 and PPO-1Q-1.5 stored in 1 M aq. NaOH solution at 80 $^{\circ}$ C during 0, 96 and 192 h.



Fig. S5 Representative TGA traces of PPO before modification and after bromoalkylation and quaternization, respectively (10 $^{\circ}$ C min⁻¹, N₂).



Fig. S6 TGA traces all the PPO-7Q AEMs (10 °C min⁻¹, N₂).



Fig. S7 Summarizing bar diagrams of the water uptake and OH^{-} conductivity of the PPO-7Q and PPO-1Q AEMs at 20 and 60 °C.