



# Poly(ether sulfone) copolymers containing densely quaternized oligo(2, 6-dimethyl-1, 4-phenylene oxide) moieties as anion exchange membranes



Wenhai Mei <sup>a</sup>, Zhen Wang <sup>b, \*\*</sup>, Jingling Yan <sup>a, \*</sup>

<sup>a</sup> Laboratory of Polymer Composites Engineering, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, China

<sup>b</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Science, Changchun, 130022, China

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## ABSTRACT

Anion exchange membranes (AEMs) with phase-separated morphologies were prepared by brominating poly(ether sulfone) copolymers with oligo(2, 6-dimethyl-1, 4-phenylene oxide) moieties, followed by quaternization and ion exchange. By this synthetic strategy, quaternary ammonium groups were densely and selectively introduced into oligo(phenylene oxide) moieties. Small angle X-ray scattering patterns of quaternized poly(ether sulfone) with oligo(2, 6-dimethyl-1, 4-phenylene oxide) segments (QPES-co-PPO) showed obvious ionic peaks, whereas no peak was observed for quaternized poly(phenylene oxide) (QPPO) homo-polymers. The properties of these AEMs were studied according to their water uptake, hydration numbers, conductivities, mechanical properties, alkaline stability. In comparison with QPPO-based AEMs with similar ion exchange capacities, AEMs based on QPES-co-PPO showed markedly higher conductivity. This could be ascribed to the existence of ionic clusters stemmed from their phase-separated morphologies.

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## 1. Introduction

Alkaline anion exchange membrane fuel cells (AEMFCs) have been receiving extensive interest in last decades because AEMFCs have the potential to provide several significant advantages over traditional proton exchange membrane fuel cells (PEMFCs) [1–5]. The basic operating conditions of alkaline fuel cells enables the use of non-noble metals (Fe, Co, Ni) as the electro-catalysts, and fast oxygen reduction reaction in the cathode. In addition, AEMFCs can offer increased fuel choices in basic environments and reduced cost of the devices [5]. AEM is a critical component for AEMFC, which determines fuel cells' performance and durability. Thus, considerable research efforts have been aimed at developing AEMs with high conductivity, and favorable chemical and mechanical stability [1–5]. Various polymers, such as polystyrenes [6–8], poly(ether sulfone)s [9–11], poly(ether ketone)s [12–14], polyphenylenes [15–17], poly(phenylene oxide)s [18–20], and polyolefin [21–23], were functionalized with quaternary ammonium

groups and then evaluated as AEM materials. Quaternary ammonium groups are typically incorporated into aromatic polymers by either the chloromethylation of activated aromatics or radical bromination of benzylmethyl functionalities, and then amination reactions with tertiary amines [9,10]. Chloromethylation is a powerful methodology for introducing quaternary ammonium functionalities into existing aromatic polymers. Nevertheless, excessive, carcinogenic reagents, such as chloromethyl methyl ether, are usually involved in chloromethylation. Compared with chloromethylation, bromination of benzylmethyl groups has several merits such as much faster reaction rates, and higher efficiency. Furthermore, bromomethyl and quaternary ammonium functionalities could be introduced into specific sites, which allows the preparation of AEMs with well-controlled morphologies [9,10,16].

Anion exchange membranes tend to show lower conductivity than PEMs, which can be rationalized according to their lower anion mobility and incomplete ionic dissociation stemmed from the much weaker basicity of quaternary ammonium [24,25]. The conductivity in AEMs could be enhanced by simply increasing ion exchange capacity (IEC). Nevertheless, high IEC often leads to excessive swelling and subsequently poor mechanical properties. So far, it is still a major challenge to develop highly conductive

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [wangzhen@ciac.ac.cn](mailto:wangzhen@ciac.ac.cn) (Z. Wang), [jyan@ciac.ac.cn](mailto:jyan@ciac.ac.cn) (J. Yan).

AEMs without compromising their mechanical properties [10]. One efficient approach is to develop AEMs with distinct hydrophilic-hydrophobic phase-separated morphologies. The hydrophilic ionic segments spontaneously segregate from hydrophobic matrix to form ionic clusters during membrane casting process. Ionic clusters with good connectivity induce the formation of hydrophilic channels and facilitate fast ion conduction and water diffusion. Consequently, AEMs with hydrophilic channels show markedly higher conductivity than AEMs without hydrophilic channels for a given IEC. AEMs with well-defined hydrophilic channels can be constructed by concentrating ionic groups to specific blocks, grafts, and other small segments [24,26–29]. Chen and Hickner reported a series of AEMs based on a bisphenol with six benzylmethyl groups that were subsequently converted into quaternary ammonium functionalities. The highly concentrated ionic groups gave rise to the formation of ionic clusters and consequently enhanced  $\text{Br}^-$  conductivity [30]. Miyatake et al. developed segmented poly(arylene ether)s containing highly quaternized oligophenylene moieties, which exhibited higher hydroxide conductivity and improved durability in aqueous KOH [31]. Jannasch and coworkers investigated AEMs based on poly(sulfone)s with 2–4 quaternary ammonium functionalities per benzene ring. Highly localized ionic groups promoted the formation of ionic clustering, which resulted in high conductivity at low water uptake compared with randomly functionalized polymers [32]. Bai et al. prepared ABA triblock copolymers containing poly(sulfone)s as hydrophobic blocks and quaternized poly(phenylene oxide)s as hydrophilic blocks. AEMs based on triblock copolymers simultaneously possessed high conductivity at low water uptake and good mechanical properties because of their distinct phase-separated morphologies [33]. Comb-shaped copolymers were also constructed by the introduction of short alkyl chain, which showed phase-separated morphologies and thus enhanced conductivities [20].

In this paper, we report the synthesis and characterization of AEMs based on poly(sulfone) copolymers with densely quaternized oligo(2,6-dimethyl-1,4-phenylene oxide) as hydrophilic segments. Phenolic hydroxyl-terminated oligo(2, 6-dimethyl-1, 4-phenylene oxide) (PPO-2OH) possesses two terminal phenolic hydroxyl groups for polycondensation, and an average of around 30 benzylmethyl groups for bromination and further amination [34]. Its unique structure allows the concentration of ionic groups in the PPO segments through an accessible procedure, affording AEMs with phase-separated morphologies and continuous hydrophilic ionic channels. The compositions of these AEMs were tuned by adjusting the PPO-2OH contents and the amounts of brominating reagent. The properties of QPES-co-PPO-based AEMs were comprehensively studied through various analytic techniques, and their structure-property relationship was elaborated.

## 2. Experimental section

### 2.1. Materials

PPO-2OH (PPO SA-90, hydroxyl equivalent weight =  $800 \text{ g mol}^{-1}$ ,  $M_n = 1800 \text{ g mol}^{-1}$ , PDI = 1.5) and high-molecular-weight PPO (PPO 640,  $M_w = 56,200 \text{ g mol}^{-1}$ , PDI = 2.8) were purchased from SABIC Innovative Plastics (Shanghai, China). All the other chemicals were obtained from J&K Chemicals (Beijing, China). All reagents were of analytical grade, and used as received except that 4-fluorophenyl sulfone was purified by recrystallization from ethanol. For comparison, quaternary ammonium-functionalized PPO (QPPO) homo-polymers were synthesized according to a literature procedure (Scheme 1b) [20].

### 2.2. Synthesis of poly(ether sulfone) copolymers with oligo(2, 6-dimethyl-1, 4-phenylene oxide) segments (PES-co-PPO)

PES-co-PPO copolymers were prepared via a weak base route according to a literature procedure [35], using PPO-2OH, bisphenol A (BPA), and 4-fluorophenyl sulfone as the monomers (Scheme 1a). The molar ratios of PPO-2OH in the total of bisphenols were 10%, 20% and 30%. Thus, the copolymers were named by these ratios, e.g. PES-co-PPO-10 was made from a mixture of PPO-2OH (10%) and BPA (90%). A typical process for copolymer synthesis follows. PPO-2OH (1.120 g, 0.700 mmol), 4-fluorophenyl sulfone (1.781 g, 7.000 mmol), BPA (1.438 g, 6.300 mmol), anhydrous potassium carbonate (1.119 g, 8.100 mmol), toluene (20 mL), and *N*-methyl-2-pyrrolidinone (NMP) (12 mL) were placed into a 50 mL, three-necked flask with an overhead stirrer and a Dean–Stark trap. The reaction was held at  $150^\circ\text{C}$  for 6 h in argon. Toluene and water in the system were depleted as an azeotrope. The reaction mixture was heated at  $175^\circ\text{C}$  until the viscosity of the solution was constant. After cooling to ambient temperature, the polymer solution was slowly added into DI water (200 mL). The fibrous polymer was purified by Soxhlet extraction with DI water for one day, and dried at  $120^\circ\text{C}$  in vacuum for one day to yield PES-co-PPO-10 as a white solid (3.589 g, 96%).

### 2.3. Bromination of PES-co-PPO

PES-co-PPO was brominated with *N*-bromosuccinimide (NBS) in chlorobenzene in the presence of benzoyl peroxide (BPO). A representative process for bromination follows: PES-co-PPO-10 (1.00 g) and chlorobenzene (25 mL) were charged to a 50 mL, two-necked flask with a condenser and a magnetic stir bar. The reaction was heated at  $85^\circ\text{C}$  in argon until PES-co-PPO-10 was completely dissolved. Then NBS (0.534 g, 3 mmol), and BPO (0.0363 g, 0.15 mmol) were added. The mixture was then heated at  $85^\circ\text{C}$  for 3 h. After cooling to ambient temperature, the polymer solution was added into ethanol (100 mL). The brominated polymer was filtered, Soxhlet extracted with acetone for one day, and dried in vacuum at  $90^\circ\text{C}$  for one day to afford brominated PES-co-PPO-3 as a white powder (1.13 g, 91%). Brominated (BPES-co-PPO) was designated after its copolymer precursor and the millimoles of NBS per gram of polymer, e.g. BPES-co-PPO-10-4 was the product of brominating PES-co-PPO-10 with 4 mmol of NBS per gram of polymer.

### 2.4. Membrane formation

AEMs were prepared via homogeneous amination of BPES-co-PPO. To the NMP solution of BPES-co-PPO (7 wt%) was added 45% trimethylamine aqueous solution (300% excess). The solution was kept at ambient temperature for two days to afford quaternized PES-co-PPO (QPES-co-PPO). The QPES-co-PPO solution was then filtrated to onto a glass substrate. The membrane was then dried  $50^\circ\text{C}$  in a conventional oven for one day, and then at  $70^\circ\text{C}$  in vacuum for one day to deplete NMP. The membrane was immersed in 2 M KOH for two days, and washed thoroughly with DI water. AEMs in this study were transformed into bicarbonate form through exposure to  $\text{CO}_2$  in air for 50 h, and stored in DI water before characterizations.

### 2.5. Characterizations

$^1\text{H}$  NMR spectra were obtained on a Bruker spectrometer at 400 MHz. The solvents for neutral and polymers bearing quaternary ammonium groups were  $\text{CDCl}_3$ , and  $\text{DMSO}-d_6$ , respectively. The degree of functionalization (DF) of BPES-co-PPO was calculated

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