Densely quaternized poly(arylene ether)s with distinct phase separation for highly anion-conductive membranes

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HIGHLIGHTS

- An octa-benzylmethyl-containing monomer was design as clustered reaction sites.
- Selective bromination and quaternization yielded flexible anion exchange membranes.
- Enhanced anion conductivity was related to distinct phase separation.
- Better flow battery performance than Nafion N212 was demonstrated.

GRAPHICAL ABSTRACT
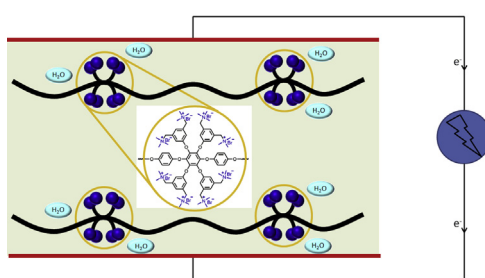
ARTICLE INFO

ABSTRACT

To develop high performance anion exchange membranes (AEMs), a novel bisphenol monomer bearing eight benzylmethyl groups at the outer edge of the molecule was synthesized, which after condensation polymerization with various amounts of 4,4′-dihydroxydiphenylsulfone and 4,4′-difluorobenzophenone yielded novel poly(arylene ether)s with densely located benzylmethyl groups. These benzylmethyl groups were then converted to quaternary ammonium groups by radical-initiated bromination and quaternization in tandem, leading to the emergence of densely quaternized poly(arylene ether sulfone)s (QA-PAEs) with controlled ion exchange capacities (IECs) ranging from 1.61 to 2.32 mmol g^{-1}. Both small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) studies revealed distinct phase separation in the QA-PAEs. The QA-PAE-40 with an IEC of 2.32 mmol g^{-1} exhibited a Br$^-$ conductivity of 9.2 mS cm^{-1} and a SO$_4^{2-}$ conductivity of 14.0 mS cm^{-1} at room temperature, much higher than those of a control membrane with a similar IEC but without obvious phase separation. Therefore, phase separation of AEMs was validated to be advantageous for the efficient conducting of anions. The experimental results also showed that the QA-PAEs were promising AEM materials, especially for non-alkaline applications.

1. Introduction

Anion exchange membranes (AEMs) have attracted more and more attention for applications in electrochemical devices such as polymer electrolyte membrane fuel cells [1,2], redox flow batteries [3,4], and electrodialysis plants [5,6]. The key function of AEMs in these devices is to conduct anions as efficiently as possible while separate the two electrodes from direct contact. Comparing to proton exchange membranes (PEMs) which have been extensively investigated over the past decade [7–9], the study of AEMs regarding their chemical structures,

morphology structures, water affinities, anion conductivities, and chemical stabilities have been less reported [10–14]. There is still a strong need to develop new AEMs with different chemical structures in order to better understand the structure-morphology- performance relationship of the membranes.

The synthesis of AEMs generally involves the halomethylation of a polymer precursor, followed by the Menshukin reaction with a tertiary amine or tertiary phosphine to form benzylammonio [15–17] or benzylphosphonio [18–20] groups, respectively. For the halomethylation, chloromethylation at phenyl rings of polymer precursors using chloromethyl methyl ether (CMME) is often reported due to the high reactivity of CMME. For example, Tanaka et al. reported the chloromethylation of a series of fluorene-containing poly(arylene ether)s using CMME, and found that the functionalization degree could be easily tuned by the reaction temperature and the molar ratio of CMME [21]. Nevertheless, CMME is a known human carcinogen. To avoid direct handling of this highly toxic reagent, *in situ* generation of CMME in the reaction mixture was proposed [22]. Hibbs et al. reported the chloromethylation of a polysulfone precursor using a mixture of $SOCl_2$ and dimethoxymethane as chloromethylating agent, and $ZnCl_2$ as catalyst [23]. The highest functionalization degree of ~68.5% was achieved at the optimized reaction conditions—1 equiv. of $ZnCl_2$, 63 equiv. of chloromethylating reagent, 60 °C of reaction temperature, and 6 days of reaction time. While chloromethylation can be realized by many ways, the produced chloromethyl groups may react with the remaining phenyl rings of polymer precursors following a Friedel–Crafts alkylation mechanism to result in crosslinked products.

Bromination at benzylmethyl sites of polymer precursors using *N*-bromosuccinimide (NBS) is another important halomethylation route for the synthesis of AEMs. This route relies on the synthesis of benzylmethyl-containing polymer precursors with desirable structures or the employment of commercially available ones such as poly(2,6-dimethyl-1,4-phenylene oxide) [24–26]. For example, Zhang et al. reported the synthesis of benzylmethyl-containing multi-block poly(arylene ether sulfone) polymer precursors and its subsequent bromination using NBS for high performance AEMs [27]. The functionalization degree was obtained in the range of 70–80% after reacting at 80 °C for 8 h using azobisisobutyronitrile as initiator. After quaternization, the cationic groups were unequivocally introduced to the brominated benzylmethyl sites, enabling the control of cationic group distribution along the polymer backbone by tuning the distribution of benzylmethyl groups in the polymer precursors. Compared to the chloromethylation route, the bromination route is much easier to be carried out because of the short reaction time, high conversion degree, and absence of risk of crosslinking.

Phase separation is critically important for enhancing the anion conductivity of AEMs, a phenomenon similar to what has been observed for enhancing the proton conductivity of PEMs. To promote phase separation in AEMs, several strategies have been proposed, including the attachment of multi-cationic side chains [28] or the design of multi-cationic segments from densely chloromethylated polymer precursors [29]. In order to develop high performance AEMs with high anion conductivity from a more controllable and safer synthetic route, we report herein (1) the design and synthesis of a novel bisphenol monomer containing eight benzylmethyl groups at the outer edge of the molecule, (2) the condensation polymerization of the monomer to yield octa-benzylmethyl-containing poly(arylene ether) precursors, (3) the selective bromination of the benzylmethyl groups by NBS, and (4) the quantitative quaternization of brominated benzylmethyl groups using trimethylamine. As such, the quaternary ammonium groups are densely tethered to the predesigned monomer units for the formation of distinct ionic phase. The physicochemical and electrochemical properties of the resulting AEMs, in terms of water uptake, anion conductivity, morphology, mechanical strength, thermal and oxidative stabilities, are characterized in detail.

2. Experimental

2.1. Materials

Hexafluorobenzene, 4-methoxyphenol, 3,5-dimethylphenol, boron tribromide, *N*-bromosuccinimide (NBS), benzoyl peroxide (BPO), calcium hydride, potassium carbonate, 1,3-dimethyl-2-imidazolidinone (DMI), *N,N*-dimethylformamide (DMF), chloroform, cyclohexane, ethanol, methanol, 1,2-dichloroethane, dichloromethane, toluene, trimethylamine aqueous solution (30 wt.%), *N,N*-dimethylacetamide (DMAc), 4,4′-dihydroxydiphenylsulfone, and 4,4′-difluorobenzophenone were purchased from Aladdin Co., Ltd. (Shanghai, China). 4,4′-Difluorobenzophenone was purified by recrystallization form ethanol and dried under vacuum at 60 °C overnight. Dichloromethane was distilled from calcium hydride. The other chemicals were used as received.

2.2. Synthesis of 4,4'-((perfluoro-1,4-phenylene)bis(oxy))bis (methoxybenzene) (compound 1)

Compound **1** was synthesized by the nucleophilic substitution of hexafluorobenzene with 4-methoxyphenol, as depicted in Scheme 1. Hexafluorobenzene (1.86 g, 10.0 mmol), 4-methoxyphenol (2.98 g, 24.0 mmol) and potassium carbonate (6.62 g, 48.0 mmol) were introduced to a 50 mL three-necked round-bottom flask equipped with a magnetic stirrer, a condenser, and an argon inlet and outlet. Then 20 mL of DMF were added as solvent and the reaction mixture was stirred at 90 °C for 8 h. After cooling to room temperature, the mixture was poured into 500 mL of deionized water. The precipitate was collected by filtration and recrystallized from ethanol/chloroform twice to produce 3.63 g of compound **1** (yield: 92%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.99 (d, J = 8.8 Hz, 4H), 6.89 (d, J = 9.2 Hz, 4H), 3.82 (s, 6H). ^{19}F NMR (400 MHz, CDCl$_3$, ppm): δ −154.89 (s, 4F).

2.3. Synthesis of 5,5′,5″,5‴-((3,6-bis(4-methoxyphenoxy)benzene-1,2,4,5-tetrayl)tetrakis(oxy))tetrakis (1,3-dimethylbenzene) (compound 2)

To a 25 mL three-necked round-bottom flask equipped with a Dean-Stark trap and an argon inlet and outlet, a condenser, a magnetic stirrer, compound **1** (0.39 g, 1 mmol), 3,5-dimethylphenol (0.73 g, 6 mmol) and potassium carbonate (0.89 g, 6 mmol) were charged. Then, DMI (5 mL), and toluene (3 mL) were added as solvent and azeotropic agent, respectively. The mixture was stirred at 145–150 °C for 2 h. After removal of toluene, the reaction mixture was stirred at 160–165 °C for 24 h and then at 220 °C for another 24 h. After cooling to room temperature, the mixture was poured to 1 wt.% of NaOH aqueous solution. The precipitate was collected by filtration and purified by column chromatography on silica gel (dichloromethane: hexane = 1:1) to produce 0.74 g of compound **2** (yield: 70%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ 6.67 (s, 8H), 6.54 (s, 4H), 6.32 (s, 8H), 3.72 (s, 6H), 2.17 (s, 24H).
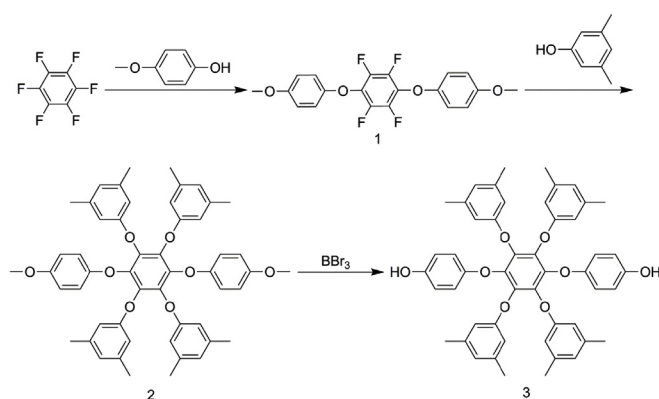
Scheme 1. Synthesis of compounds **1**, **2**, and **3**.