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Novel hydrophilic-hydrophobic block copolymer based on cardo poly (arylene ether sulfone)s with *bis*-quaternary ammonium moieties for anion exchange membranes

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ABSTRACT

Two types of phenolphthalein-based copolymers, random and block cardo poly(aryl ether sulfone)s with pendant tertiary amine groups were synthesized via copolycondensation. Both of the copolymers were grafted with (3-bromopropyl) trimethylammonium bromide to prepare anion exchange membranes with *bis*-quaternary ammonium groups for hydroxide ion conductivity measurements. The block anion exchange membrane QBPES-60 with an ion exchange capacity (IEC) of 1.93 mmol g^{-1} exhibited higher ionic conductivity (40.5 mS cm^{-1}) in water at 60 °C than the random copolymer QRPES-60 (30.0 mS cm^{-1}) under the same conditions. Small-angle X-ray scattering and transmission electron microscopy suggested the membrane constructed from the block polymer exhibited a more obvious phase-separated structure and formed ion clusters which would be responsible for the high conductivity. Moreover, the block anion exchange membrane with *bis*-quaternary ammonium groups showed better alkaline stability than the random membrane where degradation could be recognized by ^{1}H NMR spectra as well as ion conductivities. In conclusion, integrating the block hydrophilic *bis*-quaternary ammonium ion groups along with the long aliphatic side chains, and the hydrophobic copolymer backbone, this synthetic strategy is promising to prepare AEMs with high conductivity and good alkaline stability.

1. Introduction

Alkaline membrane fuel cells (AMFCs) have recently received widespread attention among scientists because of their apparent property advantages. Compared with traditional proton-exchange membrane fuel cells (PEMFC), AMFCs, operated in alkaline conditions, own faster oxygen reduction kinetics and fuel oxidation kinetics in alkaline media, enabling the utilization of non-precious metal catalysts (e.g. cobalt, silver, nickel) and high cell efficiencies [1–4]. Anion exchange membranes (AEMs), the critical component of AMFCs to transport hydroxide ions from the cathode to the anode, have been rapidly developed over the past decade. To date, the design of AEMs materials in AMFCs has mainly focused on quaternary ammonium, quaternary phosphonium or guanidinium functionalized polymers, such as poly(arylene ether sulfone) [5–7], poly(arylene ether ketone) [8–10], poly(arylene ether)s [11,12], poly(phenylene oxide)s [13–15] and poly(phenylene)s [16,17]. The primary challenge to realize the commercialization of AEMs is to prepare membrane materials with adequate mechanical strength, superior ionic conductivity and necessary stability under alkaline fuel cells operating conditions. However, the application of AEMs is still limited due to its low hydroxide conductivity for OH^- in contrast with H^+ conductivity in proton exchange membranes (PEMs) [18–21].

So far, several strategies have been developed for the design and synthesis of polymers to prepare highly anion-conducting membrane materials. One of the most attractive methods is the preparation of multi-block copolymers composed of quaternary hydrophilic groups as well as hydrophobic groups [17,22–24]. The quaternary ion groups make up multiplets to aggregate into larger clusters which are embedded in hydrophobic domains and promote the formation of micro-phase separation. Through the phase-separation morphologies, this copolymer membrane structure leads to the formation of interconnected ionic channels and

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shows higher hydroxide ion conductivity than their corresponding random copolymers. Miyatake et al. synthesized anion conductive aromatic multiblock poly(arylene ether)s copolymers in which the formed hydrophobic/hydrophilic phase separation morphology and the interconnected ion transporting pathway effectively improved hydroxide ion conductivity up to 144 mS cm^{-1} at 80 °C [22]. Other methods to improve hydroxide ion conductivity include the adjustment of ion group density and distribution, as well as the incorporation of more flexible and longer aliphatic chains [20,25–28]. The multi-functionalized and flexible quaternary ammonium hydrophilic domains further promote a more apparent cluster-like segment and longer hydrophobic segment. For example, Xu et al. synthesized a series of polymers that were grafted with more flexible and multi-functionalized side chains containing multiple hydrophilic quaternary ammonium groups. They demonstrated that the designed flexible side chain polymer structure apparently facilitated the formation of hydrophilic-hydrophobic micro-phase separation, and correspondingly improved OH^- conductivity, dimensional stability and alkaline stability [27].

In regards to the fabrication and development of AEMs, high-performance membranes are also desirable. Previously, our group has synthesized phenolphthalein-based cardo poly(aryl ether sulfone)s with quaternary amine groups on aliphatic side chains as hydroxide ion conductive materials. The synthesis of the polymer avoided the chloromethylation process and extended a novel method to prepare anion membrane materials [29]. Moreover, phenolphthalein, one type of cardo group, was designed in the polymer because this bulky and fully aromatic structure provides certain thermal stability and mechanical properties to membranes. The prepared anion exchange membrane with an IEC value of 1.5 mequiv g^{-1} showed ionic conductivity of 30.0 mS cm^{-1} at 60 °C. On the basis of this polymer structure, we are motivated to further design a novel copolymer with block as well as flexible and multifunctional aliphatic side chains to improve membrane performance as it can be confirmed that the combination of block and *bis*-quaternary ammonium structure are effective manners to improve ionic conductivity and alkaline stability.

In this manuscript, two types of copolymers, random and block cardo poly(aryl ether sulfone)s with pendant tertiary amine groups were synthesized. Both of copolymers were grated with *bis*-quaternary ammonium groups in a certain length for aliphatic side chains to improve the density and flexibility of hydrophilic ionic segments. The corresponding anion exchange membranes based on these two copolymers were prepared and ion conductivity, mechanical properties, water uptake, swelling ratio, morphology as well as alkaline stability were investigated. In contrast to the membrane built by random copolymer, the membrane constructed from block copolymer with hydrophilic *bis*-quaternary ammonium ion groups and long aliphatic side chains is expected to exhibit high conductivity and good alkaline stability.

2. Experimental

2.1. Materials and reagents

Synthesis of 2-(3-(dimethylamino) propyl)-3, 3′- *bis* (4-hydroxyphenyl) isoindolin-1- one (PPH-DMPA) was prepared as we reported previously [29]. 4, 4′-Difluorodiphenylsulfone (DFDPS), (3-bromopropyl) trimethylammonium bromide and bisphenol A (BPA) were purchased from Sinopharm Group Chemical Reagent. Dimethylsulfoxide (DMSO) and dimethylacetamide (DMAc) were dried over CaH_2 and distilled under reduced pressure before use. All other reagents were obtained from commercial sources and used as received.

2.2. Synthesis of block poly(arylene ether sulfone)s with pendant tertiary amine groups BPES-60

The block copolymers were synthesized following the procedure in Scheme 1: A dried 250 mL three-necked flask equipped with a nitrogen inlet, a Dean-Stark trap with a condenser and a mechanical stirrer was charged with PPH-DMPA (12.07 g, 30 mmol), DFDPS (6.86 g, 27 mmol), anhydrous K_2CO_3 (7.46 g, 54 mmol), DMAc 90 mL and 25 mL toluene. The mixture was heated to reflux at 140 °C for 8 h. The toluene and water were removed from the mixture by azeotropic distillation. The reaction mixture was gradually raised to 180 °C and heated for 12 h. Another experiment using a dried 100 mL three-necked flask and same conditions was performed, using DFDPS (5.85 g, 23 mmol), BPA (4.56 g, 20 mmol), anhydrous K_2CO_3 (5.53 g, 40 mmol), 50 mL DMAc as well as 15 mL toluene. Then obtained two oligomers were mixed after being cooled to room temperature. The mixture was reacted at 180 °C for 12 h to obtain a viscous polymer solution. After cooling to room temperature, the mixture was diluted with 20 mL DMAc and poured into 70 °C water to obtain the pure polymer. The polymer was dried under vacuum at 120 °C for 20 h. The block poly(arylene ether sulfone)s with pendant tertiary amine groups was named BPES-60.

2.3. Synthesis of random poly(arylene ether sulfone)s with pendant tertiary amine groups RPES-60

The random copolymers, named as RPES-60, with same molar ratio of PPH-DMPA to BPA were synthesized under the same experimental equipments as above. A dried 250 mL three-necked flask equipped with a nitrogen inlet, a Dean-Stark trap with a condenser and a mechanical stirrer was charged with PPH-DMPA (12.07 g, 30 mmol), BPA (4.56 g, 20 mmol), DFDPS (12.71 g, 50 mmol), anhydrous K_2CO_3 (11.06 g, 80 mmol), 140 mL DMAc, and 50 mL toluene. The mixture was heated to reflux at 140 °C for 8 h, after which toluene and water were removed from the mixture by azeotropic distillation. The mixture was heated to 180 °C for 12 h to obtain a viscous polymer solution. After the solution was cooled to room temperature, the mixture was diluted with 20 mL DMAc, filtered and poured into 70 °C water to obtain the pure polymer. The obtained copolymer was dried under vacuum at 120 °C for 20 h.

2.4. Synthesis of bis-quaternary ammonium cardo poly(aryl ether sulfone)s QBPES-60 and QRPES-60

Synthesis of block and random cardo poly(aryl ether sulfone)s containing alkyl ammonium groups are described as follows: copolymer BPES-60 or RPES-60 (2.16 g, 40 mmol) and 15 mL DMSO were added to a reaction flask. Once the mixture formed a homogeneous solution, (3-bromopropyl) trimethylammonium bromide (36 g, 60 mmol) was added and the mixture was stirred at 80 °C for 48 h. The mixture was poured into ethanol and washed several times. The polymer was then dried in a vacuum oven for 12 h at 100 °C. The *bis*-quaternary ammonium block and random cardo poly(aryl ether sulfone)s were named QBPES-60 and QRPES-60, respectively.

2.5. Membrane preparation

The *bis*-quaternary ammonium copolymer (0.70 g, 1 mmol) was dissolved in 18 mL DMSO. The solution was filtered using a 0.45 mm Teflon syringe and cast onto a clean and flat glass plate. The membrane was dried in an oven at 80 °C for 12 h, and at 120 °C under vacuum for 24 h to remove the casting solvent. After the membrane was peeled off from the glass plate, the membrane