Anion exchange membranes based on terminally crosslinked methyl morpholinium-functionalized poly(arylene ether sulfone)s

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HIGHLIGHTS

- Terminally crosslinked polymers are developed as anion exchange membranes.
- Bulky morpholinium is introduced as a OH^- conducting group.
- High conductivity and physicochemical stabilities are provided to membranes.

GRAPHICAL ABSTRACT
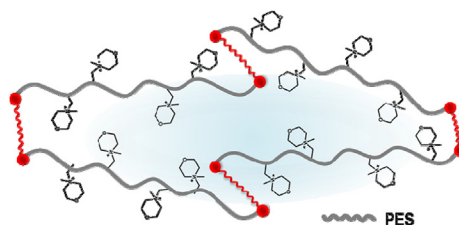
Terminally-crosslinked system (xMM-PESs)

ABSTRACT

Azide-assisted terminal crosslinking of methyl morpholinium-functionalized poly(arylene ether sulfone) block copolymers yields products (xMM-PESs) suitable for use as anion exchange membranes. By combining the advantages of bulky morpholinium conductors and our unique polymer network crosslinked only at the termini of the polymer chains, we can produce AEMs that after the crosslinking show minimal loss in conductivity, yet with dramatically reduced water uptake. Terminal crosslinking also significantly increases the thermal, mechanical and chemical stability levels of the membranes. A high ion conductivity of 73.4 mS cm^{-1} and low water uptake of 26.1% at 80 °C are obtained for the crosslinked membrane with higher amount of hydrophilic composition, denoted as xMM-PES-1.5-1. In addition, the conductivity of the crosslinked xMM-PES-1.5-1 membrane exceeds that of its non-crosslinked counterpart (denoted as MM-PES-1.5-1) above 60 °C at 95% relative humidity because of its enhanced water retention capacity caused by the terminally-crosslinked structure.

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1. Introduction

Anion exchange membranes (AEMs) have garnered considerable attention over the past few years, and much work has been done to apply them in electrochemical energy conversion and storage devices such as fuel cells, electrodialysis setups, and redox flow batteries [1—4]. Utilizing AEMs for these devices potentially reduces the costs because operations in alkaline conditions allow nonprecious metals to be used for the electrocatalysts. However, AEMs are relatively unstable at their high-pH (i.e., highly alkaline) operating conditions, especially at high temperatures (>80 °C), and have hence not found extensive successful use in such devices. Thus, significant efforts in recent years have focused on improving the chemical stability of the polymer backbones and anion (OH^-)-conducting groups in AEMs.

Various types of polymer backbones, including poly(arylene

ether sulfone)s [4—6], poly(phenylene oxide)s [7—9], poly(olefin)s [10,11], poly(styrene)s [12,13] and poly(phenylene)s [14,15] have been widely investigated as AEMs, but there is no agreement on which one works best. While crosslinking polymer backbones of AEMs has been shown to be an efficient way to increase the alkaline stability of these backbones and hence long-term durability of the membranes [16—19], such crosslinking has generally been found to reduce the ion conductivity of these systems, primarily due to the decreased amount of water absorbed by the formed rigid 3D networks. But specialized crosslinking approaches, including blending [20,21] or ion conductor-mediated crosslinking [22,23], have been developed to minimize the conductivity loss caused by the cross-linked network.

Various systematic studies have been carried out to improve the alkaline stability levels of the conducting groups of AEMs, and, in addition to the most commonly used quaternary ammonium (QA) group [24—29], other cations, including imidazolium [30—34], guanidinium [35,36], phosphonium [37], sulfonium [38], and metal-based hybrid cations [39], have been incorporated into these membranes. Of these cations, the aliphatic heterocyclic QA head groups, including piperidinium [40,41] and morpholinium [41,42] groups, have been recently regarded to confer the greatest degree of stability due to their bulky structures hindering the approach of OH⁻ to these anion-conducting groups. Another advantage of these conductors is the enhanced ion conductivity due to their high levels of ion dissociation caused by their bulky structures [41]. The polymers functionalized with N-methyl piperidinium and N-methyl morpholinium groups have hence displayed excellent levels of alkaline stability as well as high OH⁻ conductivity levels.

Recently, we reported the azide-assisted terminal crosslinking of sulfonated ionomers (ion-conducting polymers) to yield a product used to form novel proton-exchange membranes (PEMs) [43—45]. Only the ends of these polymer chains were crosslinked, in contrast to most crosslinked polymer systems. Membranes prepared from these terminally crosslinked sulfonated poly(-arylene ether sulfone)s (sPESs) showed little loss of conductivity as a result of the crosslinking, since there was minimal formation of a 3-D crosslinked network, yet they showed the same high structural integrity as the crosslinked polymers described above. Moreover, exceptionally high proton conductivity levels, especially at elevated temperatures and/or partially hydrated (or relative humidity (RH)) conditions, were obtained for these terminally crosslinked membranes. These high conductivity levels were attributed to the unique properties of our terminally cross-linked system, specifically to the relatively high amounts of water in its 3-D network at high temperatures as a result of its polymer backbone being induced by the high temperatures to undergo a structural reorganization that increased its volume and trapped water [44,45].

In the current work, we combined the advantages of bulky morpholinium conductors and our unique terminally cross-linked polymer network to prepare terminally crosslinked methyl morpholinium-functionalized poly(arylene ether sulfone)s (xMM-PESs) as novel AEMs. The crosslinked membranes obtained from xMM-PESs showed excellent thermal, mechanical and chemical stability levels, together with high ion conductivity levels, especially at elevated temperatures as well as partially hydrated RH conditions. The effects of crosslinking on the morphologies and physical properties of the polymers, as well as on the ion conductivity and alkaline stability levels of the corresponding polymer membranes were thoroughly investigated.

2. Experimental

2.1. Synthesis of the methyl morpholinium-functionalized poly(arylene ether sulfone) multiblock copolymer with terminal allyl groups (allyl-MM-PES, **5**)

2.1.1. Synthesis of the 2,5-bis(morpholinomethyl)benzene-1,4-diol (M-OH)

This was prepared following our previous literature procedure [42]. To a stirred solution of paraformaldehyde (4.09 g, 136.23 mmol) and morpholine (11.87 g, 136.23 mmol) in IPA (30 cm³), hydroquinone (5 g, 45.41 mmol) solution in IPA (20 cm³) was slowly added under nitrogen at 60 °C. The solution was stirred under reflux at 60 °C for 12 h. After this time, the reaction mixture was cooled to room temperature and the solvent was evaporated. The resultant solid was collected by filtration and washed with methanol several times to give the product (M-OH) as a white solid (6.86 g, 49.0%); δ_H(400 MHz, CDCl₃) 10.07 (2H, s, 2 × ArOH), 6.47 (2H, s, 2 × ArH), 3.8—3.7 (8H, br signal, 4 × OCH_2), 3.61 (4H, s, 2 × NCH_2Ar), 2.7—2.3 (8H, br signal, 4 × NCH_2CH₂O).

2.1.2. Synthesis of the OH-terminated oligomers **1**

A typical procedure to prepare oligomer **1** with different molecular weights (or chain lengths) is described as follows:

OH-terminated oligomer with DP (degree of polymerization) of 21: 2,5-Bis(morpholinomethyl)benzene-1,4-diol (M-OH, 2.00 g, 6.49 mmol), bis(4-fluorophenyl)sulfone (1.57 g, 6.18 mmol) and potassium carbonate (1.80 g, 13.04 mmol) were added to a mixture of DMAc (18 cm³) and toluene (15 cm³) in a 200 cm³ round bottom flask equipped with a Dean—Stark apparatus and a nitrogen inlet. The reaction mixture was heated at 150 °C for 4 h. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled away. The temperature of the reaction mixture was then raised to 170 °C, and the mixture was stirred at this temperature for another 16 h under a nitrogen atmosphere. At the end of the reaction, a small amount of 2,5-bis(morpholinomethyl) benzene-1,4-diol (M-OH) was added to ensure end capping. After stirring the mixture at 170 °C for 2 h, the reaction mixture was cooled to room temperature and added to methanol (150 cm³). The product was collected by filtration and washed with deionized water several times before drying at 80 °C under vacuum for at least 24 h to give the hydroxy-terminated oligomer **1** as a brown powder (2.86 g, 80.0%); δ_H(400 MHz, CDCl₃) 7.85 (89H, d, J = 8.5, ArH_1), 7.13 (43H, s, ArH_3), 6.92 (88H, d, J = 8.5, ArH_2), 6.63 (2H, s,ArH_7), 6.54 (2H, s, ArH_8), 3.5—3.3(240H, br signal containing s, $H_{4,5}$), 2.30 (159H, br signal, H_6), 2.08 (8H, s, H_9).

OH-terminated oligomer with DP of 11: Yield 81.6%; δ_H(400 MHz, CDCl₃) 7.85 (49H, d, J = 8.5, ArH_1), 7.13 (22H, s, ArH_3), 6.92 (48H, d, J = 8.5, ArH_2), 6.63 (2H, s, ArH_7), 6.54 (2H, s, ArH_8), 3.5—3.3(137H, br signal containing s, $H_{4,5}$), 2.30 (90H, br signal, H_6), 2.08 (8H, s, H_9).

2.1.3. Synthesis of the F-terminated oligomer **2** with a D.P. of 13

Bis(4-fluorophenyl) sulfone (2.00 g, 7.87 mmol), 2,2-bis(4-hydroxyphenyl) hexafluoropropane (2.45 g, 7.28 mmol), and potassium carbonate (2.19 g, 15.81 mmol) were added to a mixture of DMAc (15 cm³) and toluene (15 cm³) in a 250 cm³ round bottom flask which was equipped with a Dean-Stark apparatus and a nitrogen inlet. The reaction mixture was heated at 150 °C for 4 h. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled out. The temperature of the reaction mixture was then raised to 170 °C and stirred at this temperature for another 20 h under a nitrogen atmosphere. At the