

Analysis and characterization of an atropisomeric ionomer containing quaternary ammonium groups

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ABSTRACT

Polyethersulfone ionomers containing quaternary ammoniums were prepared for the applications on alkaline anion exchange membrane (AAEM) fuel cells. The ionomers were synthesized from 2,2'-dimethyl-4,4'-biphenyldiol and bis(4-chlorophenyl) sulfone via nucleophilic substitution followed by bromination, quaternization and anion exchange reaction. The biphenyl structure in polymer main chain exhibited atropisomerism after bromination, leading to the anisochronous signals of geminal protons on bromomethyl groups in ¹H NMR spectra. Model compounds were synthesized to confirm the atropisomerism by EI mass and ¹H NMR spectra. The resonance peaks from five possible repeating units of brominated polyethersulfones in the ¹H NMR spectra were identified and discussed in detail. The rotational barriers of biphenyl structures containing brominated methyl groups at 2 and 2' positions were calculated by density functional theory. The properties of these polyethersulfone anion exchange membranes (AEMs) were characterized. Their IECs ranged from 0.81 to 1.75 mequiv/g. The corresponding water uptakes and dimensional changes were in the ranges of 19–42% and 12–38%, respectively. The tensile strength of an AEM (1.75MQAPES-OH) with an IEC of 1.75 mequiv/g remained 17 MPa even though the water uptake was 42%. The hydroxide conductivity of 1.75MQAPES-OH could reach 51.4 mS/cm at 98%RH and 80 °C. After alkaline stability test for 168 h, the AEMs degraded slightly in terms of their IECs and hydroxide conductivity.

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1. Introduction

Anion exchange membranes (AEMs) have been considered as a candidate for anion-conducting components in various electrochemical energy devices including fuel cells, redox flow batteries, microbial energy system and reverse electrodialysis cells. [1–3] Especially for fuel cell applications, alkaline anion exchange membrane fuel cells (AAEMFCs) promise some benefits that proton exchange membrane fuel cells (PEMFCs) cannot achieve, such as facile oxygen reduction reaction, replacement of platinum with inexpensive metal and reduced carbonate precipitation and fuel crossover. [4] However, the ionic groups (e.g. quaternary ammonium) bound covalently to a polymer main chain are likely to decompose via S_N2 nucleophilic substitution, Hofmann elimination, E1 elimination or intermediate ylides formation followed by

Hauser and Stevens rearrangements. [2,4].

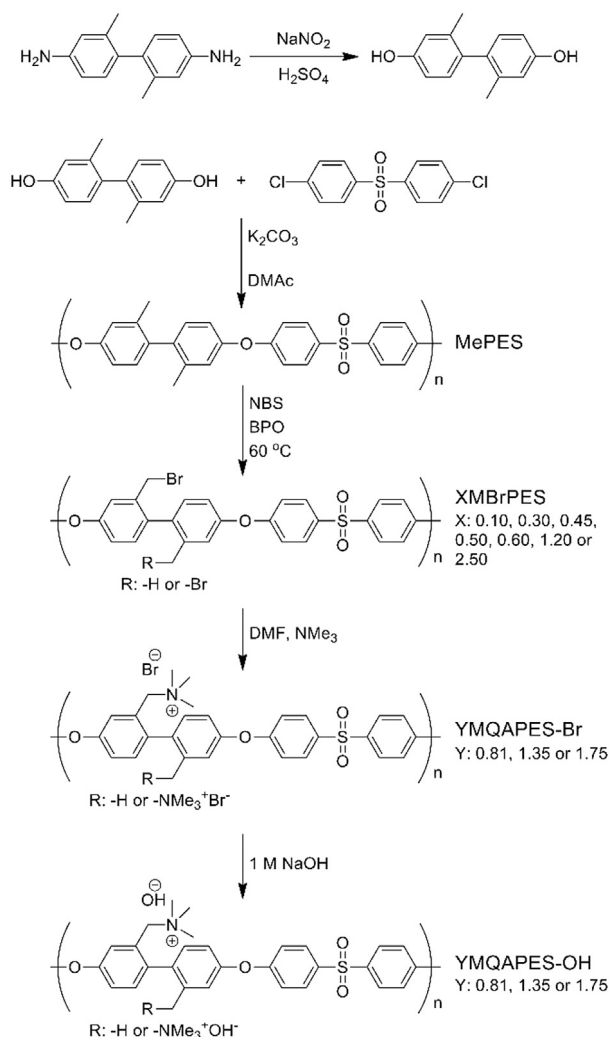
Up to the present, diverse structures were chosen as polymer backbones, such as poly (arylene ether)s [5–7], polybenzimidazoles [8,9], poly (biphenyl alkylene) [10], polystyrene and polyvinyl types [11–13]. Recently, polyethersulfone anion exchange membranes were recognized that the ether linkages would decompose under alkaline treatments. [14,15] Hickner et al. indicated that both electron-withdrawing force of sulfone and quaternary ammonium groups would trigger the cleavage of ether linkages. [16,17] After then, Li [18] and Wang [19] et al. reported that inserting a phenyl group between backbones and quaternary ammoniums could improve the alkaline stability efficiently. Recently, Miyanishi et al. reported a mechanism detailing the degradation of the ionic groups triggered by ether cleavage in polyethersulfone. [20] Moreover, Mohanty et al. mentioned that polymers with aryl ether bonds exhibited poor chemical stability than those without them and confirmed that electron-withdrawing group adjacent to aryl ether bonds was detrimental to chemical stability. [21] Therefore, we would like to know that the alkaline stability of polyethersulfone

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AEM could be enhanced if quaternary ammoniums are introduced at the meta positions to ether leakages.

In this report, a 4,4'-biphenyl diol with methyl groups at 2 and 2' positions was prepared as well as the derived polyethersulfone and brominated polyethersulfones as shown in Scheme 1. This biphenyl structure surprisingly leads to a unique atropisomeric phenomenon after bromination.

Since Christie and Kenner first discovered axially chiral enantiomers in 1922 [22], rotationally hindered biaryl compounds have played a critical role in governing the pharmacological properties of a bioactive compound and have been the fundamental basis for useful reagents and catalysts in asymmetric synthesis. [23] In addition, a chiral chromatography has been a tool to separate the enantiomers of peculiar chiral compounds. [24] However, most researches about atropisomers focused on small molecules such as the well-known vancomycin, knipholone and mastigophorene A. [23] Polymers with chiral centers, such as helical polymers, have also been investigated because of their chiroptical and stereospecific properties. [24] Usually, an atropisomeric polymer was prepared from optically active monomers or prochiral monomers by specially designed chain-growth polymerization. [24,25] Few scientists utilized step-growth polymerization to obtain helical polymers. [26–28] Besides, rare atropisomeric polymer was synthesized by the modification from a polymer without chiral centers.



Scheme 1. Synthetic route of monomer and polymers.

Therefore, in this work, we report a polyethersulfone ionomer containing quaternary ammoniums and demonstrate the atropisomeric phenomenon of the brominated polyethersulfones. The ^1H NMR spectra of brominated polyethersulfones and brominated model compounds were used to characterize the atropisomeric structures. Density functional theory was also used to calculate the rotational barrier of some compounds with similar structures to polyethersulfone prepared in this study. Furthermore, the properties of the ionomer, such as ion exchange capacity (IEC), water uptake, dimensional change, mechanical strength, thermal properties, hydroxide conductivity and alkaline stability, were evaluated.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and used as received unless specified otherwise. 2,2'-Dimethyl-4,4'-biphenyldiamine was prepared according to the previous literature. [29] N-Methyl-2-pyrrolidinone (NMP) and dimethylacetamide (DMAc) were dried over calcium hydride for 24 h, distilled under reduced pressure and stored under N_2 atmosphere in a sealed bottle.

2.2. Measurement

All melting points were determined on a Mel-Temp capillary melting point apparatus. ^1H and ^{13}C NMR measurements were performed on a Bruker Avance-600 spectrometer operating at 600 and 150 MHz, respectively. Mass spectrometry was conducted on a high resolution mass spectrometer (JEOL JMS-700). Elemental analyses were performed on a Heraeus Vario analyzer. Molecular weights were measured on a JASCO GPC system (PU-980) equipped with an RI detector (RI-930), a Shodex GPC KF-804 column, using dimethylacetamide (DMAc) as the eluent and calibrated with polystyrene standards. Thermal gravimetric analyses (TGA) were performed in nitrogen with TA TGA Q500 thermal gravimetric analyzer using a heating rate of $10^\circ\text{C}/\text{min}$. Mechanical properties were measured by Universal Testing Machine (Testometric M500-25AT) at a cross-head speed of 5 mm/min under ambient conditions. The initial dimensions of the rectangle-shaped membranes were 50 mm in length, 10 mm in width and 30–60 μm in thickness. Density functional theory (DFT) calculations were performed using the B3LYP functional and the 6–31 G (d,p) basis set as implemented in GAUSSIAN 09.

2.3. Preparation of monomer and polymers

2.3.1. Synthesis of monomer, 2,2'-dimethyl-4,4'-biphenyldiol

2,2'-Dimethyl-4,4'-biphenyldiamine (4.00 g, 14.02 mmol) and 40% sulfuric acid solution (50 mL) were stirred in a flask under N_2 atmosphere at room temperature until a homogeneous solution was obtained. A 2.0 M NaNO_2 aqueous solution (20 mL) was added dropwisely into the former solution after both solutions were cooled in an ice bath for 30 min. The mixed solution was then added slowly into a 50% sulfuric acid solution (200 mL) at 160°C . After the reaction mixture was heated at 160°C for 10 min, it was poured into ice. The aqueous solution was then extracted by ethyl acetate. The organic solution was washed with water, dried with anhydrous magnesium sulfate and concentrated by rotary evaporator. The crude product was purified by column chromatography using hexane/ethyl acetate (3/2, v/v) as the eluent, followed by sublimation at 115°C and recrystallization in CHCl_3 to afford 1.96 g of white crystal (yield: 49%). mp: $127\text{--}129^\circ\text{C}$. ^1H NMR (600 MHz,

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