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Synthesis of Soluble Poly(arylene ether sulfone) Ionomers with Pendant Quaternary Ammonium Groups for Anion Exchange Membranes

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ABSTRACT: A new bisphenol monomer, 2,2′-dimethylaminemethylene-4,4′-biphenol (DABP), was easily prepared by Mannich reaction of dimethylamine and formaldehyde with 4,4′-biphenol. Novel partially fluorinated poly(arylene ether sulfone)s with pendant quaternary ammonium groups were prepared by copolymerization of DABP, 4,4′-biphenol, and 3,3′,4,4′-tetrafluorodiphenylsulfone, followed by reaction with iodomethane. The resulting copolymers PSQNI-*x* (where *x* represents the molar fraction of DABP in the feed) with high molecular weight exhibited outstanding solubility in polar aprotic solvents; thus, the flexible and tough membranes of PSQNI-*x* with varying ionic content could be prepared by casting from the DMAc solution. Novel anion exchange membranes, PSQNOH-*x*, were obtained by an anion exchange of PSQNI-*x* with 1 N NaOH. All PSQNOH-*x* membranes showed conductivities above 10^{-2} S cm^{-1} at room temperature, for example, the hydroxide conductivity of PSQNOH-90 achieved to 8.4×10^{-2} S cm^{-1}, which was thus comparable to the proton conductivity of Nafion 117 (i.e., 9.0×10^{-2} S cm^{-1}).

Introduction

Historically, polymeric anion exchange membranes (AEMs) have been investigated intensively because of their current and potential applications as ion-exchangers,[1,2] biomaterials,[3] coatings,[4] and membranes in electrodialysis devices.[5−8] In recent years, however, interest has grown in their application toward more demanding uses such as alkaline fuel cells and electrolyzers due to the low overpotentials associated with many electrochemical reactions at high pH and the potential to forego noble metal catalysis.[9−12] Unlike cation exchange membranes where highly chemically stable perfluorinated membranes such as Nafion (DuPont) and Flemion (Asahi Glass) dominate the market, commercially available AEMs are typically based on cross-linked polystyrene and are not very stable in alkaline or electrochemical environments. In addition, the aminated cross-linked polystyrene is blended with other polymers and fabric supports that limit ionic conductivity and may decrease the chemical stability of the membrane.[13] To date, many polymers, such as polybenzimidazole,[14] poly(2,6-dimethyl-1,4-phenylene oxide),[15] poly(ether ketone),[16] polysulfone, and radiation-grafted PVDF, ETFT, and FEP[17] have been used to produce anion exchange membranes for application in alkaline fuel cells.

Polysulfone is one of the materials which has been most widely used in the manufacture of synthetic polymer membranes due to its excellent mechanical, thermal, and chemical stability.[18] AEMs based on the polysulfone, Udel 1700 (Amoco), were initially reported by Zschocke and Quellmalz, who described the material's alkaline stability and demonstrated its use in electrodialysis.[19] These AEMs were prepared by chloromethylation of the parent polysulfone and followed by exposure to trimethylamine to form benzyltrimethylammonium groups. In this way, various AEMs based on different polysulfones and amines were developed.[20−25]

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Although it is convenient, some specific limitations exist for AEMs prepared by the chloromethylation method. First, in the chloromethylation reaction, the amount of chloromethyl groups and their location along the polymer backbone could not be controlled precisely.[26] In addition, the chloromethylation regent, chloromethyl methyl ether used in most cases, is a carcinogen and is potentially harmful to human health.[27] Second, most of AEMs are not soluble in common organic solvent, which leads to difficulty for direct preparing various functional membranes.[28] Therefore, AEMs are generally fabricated by the preparation of nonionic chloromethylated polysulfone membrane and subsequent aminated reaction in the membrane state. As a result, it is hard to form microphase separational ion channels for hydroxide anion transport since there is no driving for ionic aggregation or phase separation during the casting process for the preparation of nonionic chloromethylated polysulfone membrane.[25]

The present paper describes the synthesis of a novel bisphenol monomer containing two tertiary amine groups, 2,2′-dimethylaminemethylene-4,4′-biphenol. With this monomer, partially fluorinated aromatic poly(arylene ether sulfone)s with pendant tertiary amine groups were prepared. Alkaline anion exchange membranes were made by the reaction of the tertiary amine groups with iodomethane to form quaternary ammonium groups which acted as the counterion for hydroxide anion. An advantage of this method is avoiding the use of toxic chloromethylation reagents. Furthermore, the amount of quaternary ammonium groups and their location along the polymer backbone could be controlled precisely by adjusting the composition of comonomers. Their properties, such as the solubility, thermal stability, mechanical strength, water uptake behavior, and hydroxide conductivity, have been investigated in detail.

Experimental Section

Materials. 4,4′-Biphenol, 1,2-difluorobenzene, and chlorosulfonic acid were purchased from Aldrich. Formaldehyde solution

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(37%) and dimethylamine solution (33%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. *N*,*N*-Dimethylacetamide (DMAc) was stirred over CaH_2 for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. All other reagents were obtained from commercial sources and used as received.

Synthesis of Monomer. *2,2′-Bimethylaminemethylene-4,4′-biphenol* (*DABP*). To a 250 mL round-bottomed flask, 4,4′-biphenol (11.0 g, 0.10 mol) was dissolved in ethanol, and aqueous solutions of dimethylamine (3.0 equiv, 33%) and formaldehyde (4.0 equiv, 37%) were added. The solution was stirred at 20 °C for 24 h. The precipitated solid was collected by filtration and washed with water several times. Recrystallizations from ethanol gave the product (19.5 g, 65%) as white crystals; mp 168 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 7.26−7.30 (4H, d), 6.73−6.76 (2H, d), 3.59 (4H, s), and 2.22 (12H, s). ^{13}C NMR (DMSO-d_6): δ 156.0, 130.9, 126.5, 125.7, 122.9, 115.6, 60.6, 44.2. Anal. Calcd for $C_{18}H_{24}N_2O_2$ (300.4): C, 71.97%; H, 8.05%; N, 9.33%. Found: C, 71.81%; H, 8.02%; N, 9.25%.

3,3′,4,4′-Tetrafluorodiphenylsulfone (*TFDPS*). 1,2-Difluorobenzene (10.3 g, 0.09 mol) was added into chlorosulfonic acid (33.7 g, 0.250 mol) slowly at 0 °C. The resulting solution was stirred at 80 °C for 1 h and was poured into crushed ice. The product was extracted with dichloromethane (2 × 30 mL). The organic extracts were combined, washed with distilled water, dried over anhydrous magnesium sulfate, and filtered, and the solvent was removed. Purification by distillation in vacuum gave 3,4-difluorobenzene-1-sulfonyl chloride (18.0 g, 94%) as a pale yellow liquid.

To a 250 mL round-bottomed flask, 3,4-difluorobenzene-1-sulfonyl chloride (10.6 g, 0.05 mol) and 1,2-difluorobenzene (22.8 g, 0.2 mol) were added. Then, about 1 equiv of $AlCl_3$ was introduced into the well-stirred mixture at 80 °C. Immediately, hydrogen chloride begins to evolve rapidly. The solution was heated to 100 °C and maintained at this temperature for 8 h until no more gas release was observed. The reaction solution was then cooled to room temperature and poured into crushed ice with stirring. The pink precipitate was collected by filtration and washed with a lot of water until the filtrate was neutral. The dried crude product was then recrystallized from ethanol twice to afford 3,3′,4,4′-tetrafluorodiphenylsulfone (10.9 g, 75%) as white crystals; mp 119 °C. ^{1}H NMR (DMSO-d_6, ppm): δ 8.20−8.27 (2H, m), 7.91−7.97 (2H, m), and 7.70−7.79 (2H, m). ^{13}C NMR (DMSO-d_6): δ 154.3, 151.8, 150.9, 148.4, 137.4, 125.8, 119.4, 117.9. Anal. Calcd for $C_{12}H_6F_4O_2S$ (290.23): C, 49.66%; H, 2.08%; F, 26.18%; S, 11.05%. Found: C, 49.73%; H, 2.06%; N, 26.21%.

Synthesis of Polysulfone Containing Pendant Tertiary Groups (PSTN-*x*). The DF values of the copolymers, where DF represented the degree of functionalization (the number of tertiary amine groups/repeat unit), were controlled by adjusting the molar ratio of DABP to biphenol monomer. A typical synthesis procedure of PSTN-60, where 60 refers to the feed percent of DABP, was as follows. A flame-dried 100 mL three-necked flask equipped with a nitrogen inlet and overhead stirrer was charged with DABP (1.8024 g, 6 mmol), BP (0.7448 g, 4 mmol), TFDPS (2.9023 g, 10 mmol), K_2CO_3 (2.90 g, 21 mmol), and dry DMAc (50 mL; 10% solids). The mixture was kept at room temperature for a few minutes and then slowly heated at 90 °C for 16 h. After cooling to room temperature, an additional 30 mL of DMAc was added so as to dilute the highly viscous solution, after which the solution was filtered and dropped into stirred deionized water. The fiberlike precipitate was filtered off and washed with hot water three times prior to being dried under vacuum to produce the final product. Yield: 98%.

Synthesis of Polysulfone Containing Pendant Quaternary Ammonium Iodide (PSQNI-*x*). The following represents a typical procedure for the synthesis of quaternary ammonium of PSTNI-*x*. PSTN-60 (1.0 g, 2.4 mmol) was dissolved in 20 mL of dimethylacetamide (DMAc), and then iodomethane (0.7 g, 4.8 mmol) was added. The reaction mixture was stirred at 30 °C for 12 h in the dark and then poured into distilled water. The precipitate was filtered off, washed with ethanol and distilled water thoroughly, and dried in vacuum oven for 24 h at 100 °C to give product with 97% of yield. NMR was used to confirm the synthesis of PSQNI-*x*, and the degree of conversion of tertiary amine group was close to 100%.

Membrane Casting and Preparation of Polysulfone Containing Pendant Quaternary Ammonium Hydroxide (PSQNOH-*x*). PSQNI-*x* membranes were cast from DMAc solutions (5 wt %) in a custom-built flat glass dish. The membranes were first dried at 40 °C for 4 h and at 80 °C for 12 h and then vacuum-dried at 100 °C for 24 h. PSQNOH-*x* membranes were obtained by treating PSQNI-*x* in 1 N NaOH at room temperature for 48 h; they were washed thoroughly and immersed in deionized water for 48 h to remove residual NaOH. Conversion of the PSQNI to the PSQNOH was confirmed with X-ray photoelectron spectroscopy.

Measurements. ^{1}H and ^{13}C NMR spectra were measured at 300 MHz on an AV300 spectrometer. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Elemental analyses were performed on an Elemental Analyses MOD-1106. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL^{-1} concentrations of polymer in $CHCl_3$ or DMAc. Thermogravimetric analysis (TGA) was performed in a nitrogen or air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. Molecular weights were also determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector operating at a wavelength of 260 nm. DMF was used as eluent. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min^{-1}.

Ion Exchange Capacity (IEC). The membranes in the OH^{-1} form were immersed in 100 mL of 0.1 M HCl standard for 48 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator.

Water Uptake and Swelling Ratio Measurements. The membranes were vacuum-dried at 100 °C for 10 h until constant weight to obtain the dry material. They were then immersed in deionized water at room temperature for 4 h. After this time, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of membranes was calculated according to

$$\text{water uptake } (\%) = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100\% \quad (1)$$

where W_{dry} and W_{wet} are the weight of the dry and the corresponding water-swollen membranes, respectively.

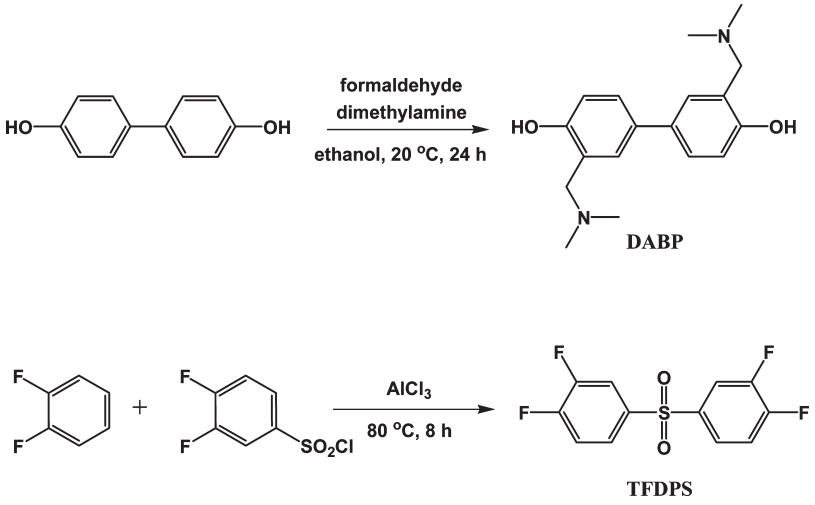
The water swelling ratio of the membranes was investigated by immersing the round-shaped samples into water at room temperature for a given time, and the swelling ratio was calculated from

$$\text{swelling ratio } (\%) = [(l_{\text{wet}} - l_{\text{dry}})/l_{\text{dry}}] \times 100\% \quad (2)$$

Here, l_{dry} and l_{wet} are the length of the dry and wet samples, respectively.

Hydroxide Conductivity. The hydroxide conductivities (σ, S/cm) of the copolymer membranes (size: 1 cm × 4 cm) were obtained using $\sigma = d/L_sW_sR$ (d is the distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The

Scheme 1. Synthetic Route for 2,2′-Bimethylaminemethylene-4,4′-biphenol (DABP) and 3,3′,4,4′-Tetrafluorodiphenylsulfone (TFDPS)



membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h prior to measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10 min interval until no more change in conductivity was observed.

Results and Discussion

The synthetic route of two novel monomers is outlined in Scheme 1. The biphenol monomer with two pendant tertiary amine groups, 2,2′-dimethylaminemethylene-4,4′-biphenol (DABP) was prepared from 4,4′-biphenol, formaldehyde, and dimethylamine at room temperature via a Mannich reaction in yield of 65%. 3,3′,4,4′-Tetrafluorodiphenylsulfone (TFDPS) was synthesized by an anhydrous aluminum chloride-catalyzed Friedel−Crafts acylation of 1,2-difluorobenzene with 3,4-difluorobenzene-1-sulfonyl chloride in yield of 75%. Elemental analysis and NMR spectroscopic techniques were used to identify the structures of the target monomers. As an example, the ^{1}H NMR and ^{13}C NMR spectra of DABP monomer are illustrated in Figure 1.

Scheme 2 shows a general synthetic procedure for the synthesis of the quaternized partially fluorinated poly(arylene ether sulfone) ionomers from the DABP, BP, and TFDPS. First, the functional polymers with pendant tertiary amine groups (PSTN-*x*, where *x* refers to the feed percent of DABP) were prepared by potassium carbonate-mediated direct aromatic nucleophilic substitution polycondensation of DABP, BP, and TFDPS. The tertiary amine content of the copolymers was readily controlled through the monomer feed ratio of DABP to BP. The preparation of polysulfone from DABP and difluorodiphenylsulfone failed due to the degradation of DABP during high-temperature polycondensation and the low activity of difluorodiphenylsulfone at low temperature. Therefore, the activated 3,3′,4,4′-tetrafluorodiphenylsulfone (TFDPS) was prepared and used as a monomer for the polymerization. TFDPS was much more reactive for the SNAr reaction than the corresponding dichloride or difluoride due to the extra activating effect of the additional C−F bonds on the phenyl rings in this monomer. As a consequence, the reaction of TFDPS with BP or DABP could be completed in a few hours (16 h) at 90 °C in the presence of 2.1 equiv of K_2CO_3. By the use of such mild reaction conditions,

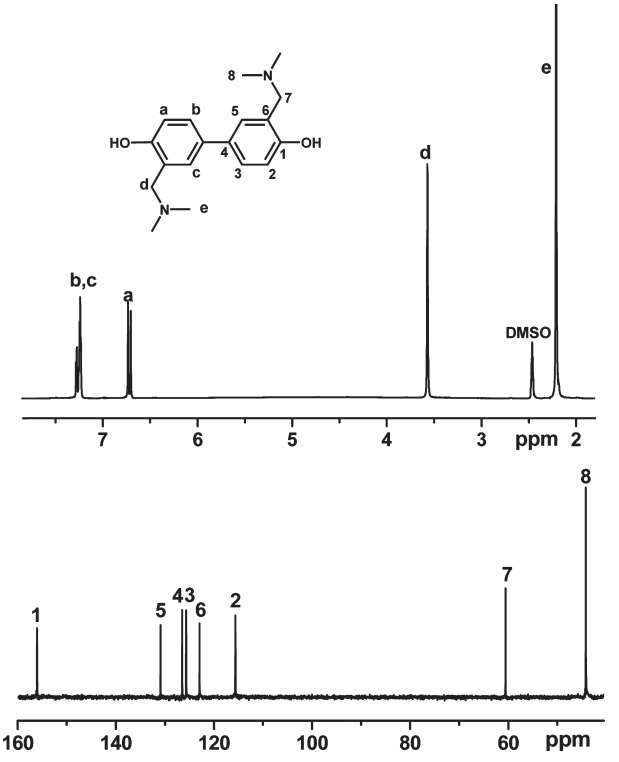


Figure 1. ^{1}H NMR and ^{13}C NMR spectra of DABP monomer in DMSO-d_6.

high-molecular-weight polymers were readily obtained, as shown by inherent viscosities and GPC in Table 1. Typical number-average molecular weights and polydispersities ranged from 81 000 to 124 000 and 2.1 to 2.3, respectively.

The chemical structure and compositions of the synthesized copolymers were characterized by ^{1}H NMR spectroscopy with $CDCl_3$ as the solvent. Figure 2 shows four spectra of the protons for the PSTN-40, -60, -80, and -100. The peaks at δ 3.4 and 2.2 could be assigned to the chemical shifts of protons on methylene and methyl groups, respectively. The intensity ratio of H ($-CH_2-$) to H ($-CH_3$) is close to 1:3, as expected for the composition of the tertiary amine groups on PSTN. The peaks at δ 7.2 and 7.6 were attributed to the hydrogen atom of the BP monomer. The DF values (number of the tertiary amine groups/repeat unit) of the copolymers were readily controlled through

Scheme 2. Synthetic Route of PSTN-*x*, PSQNI-*x*, and PSQNOH-*x*

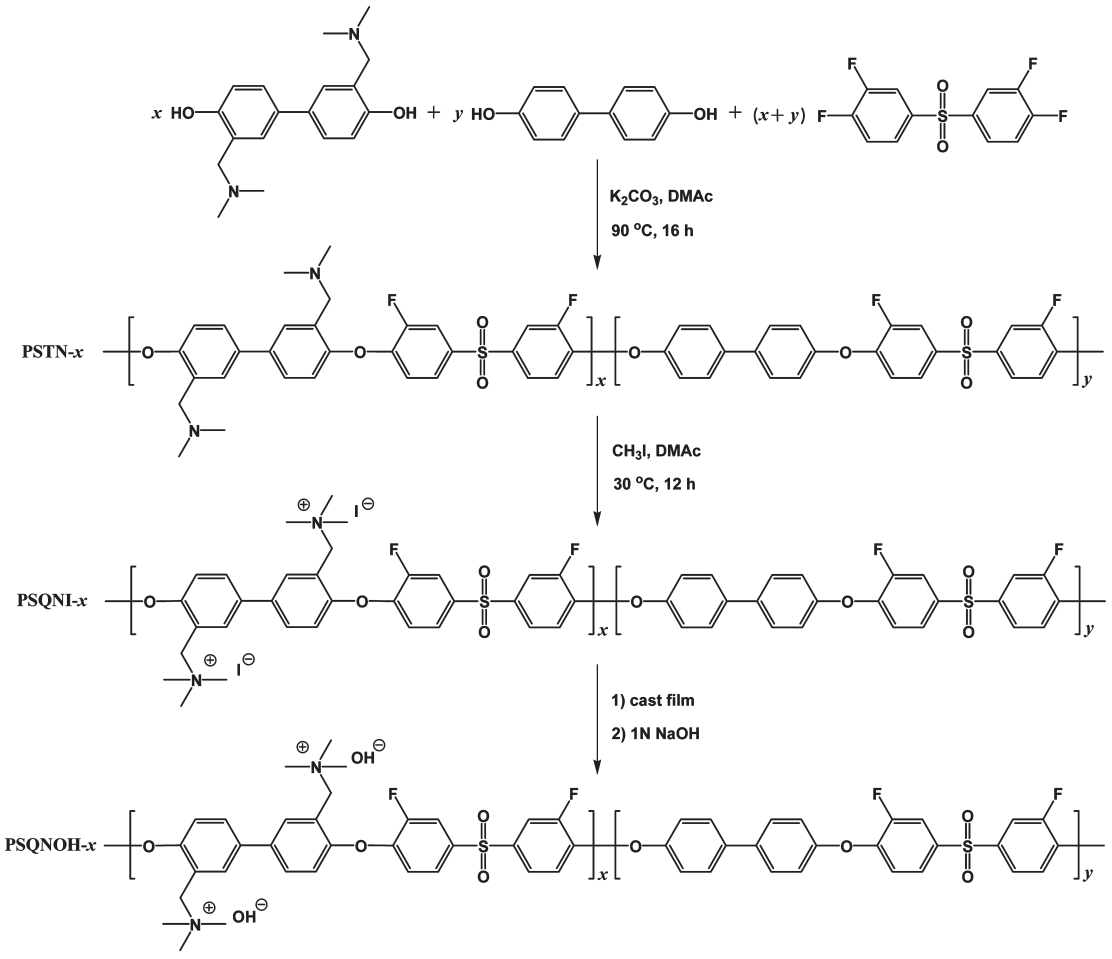


Table 1. Inherent Viscosity, Molecular Weight, and DF Values of PSTNs

sample	η_{inh}[a] (dL g^{-1})	DF[b]	$M_n \times 10^4$ (g mol^{-1})	$M_w \times 10^4$ (g mol^{-1})	PD[c]
PSTN-40	0.61	0.78	8.1	18.6	2.3
PSTN-60	0.65	1.21	9.2	21.2	2.3
PSTN-80	0.68	1.61	10.5	22.1	2.1
PSTN-90	0.70	1.79	11.2	24.6	2.2
PSTN-100	0.72	1.97	12.4	26.0	2.1

[a] Inherent viscosity measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 °C. [b] Degree of functionalizaton = (number of the tertiary amine groups/repeat unit). [c] Polydispersity.

the monomer feed ratios and were revised by ^{1}H NMR spectroscopy. As an example, the intensity ratio of the H_e to H_g signal for PSTN-60 was 4.6, resulting in 0.605 DABP units, while the DF value was 1.21. This result confirmed that the tertiary amine biphenol units were introduced successfully into polymers and were stable to the polymerization conditions employed.

The PSTN-*x* was converted to the quaternized poly(arylene ether sulfone)s (PSQNI-*x*) by reaction with iodomethane. The mole ratio of iodomethane to tertiary amine groups was set to be 2:1 to ensure complete conversion of the tertiary amine units into the quaternary ammonium moieties. The reaction was followed by ^{1}H NMR in DMSO-d_6, and as an example, the ^{1}H NMR spectra and peak assignments of both PSTN-100 and PSQNI-100 are given in Figure 3a,b. Two typical peaks of tertiary amine group were observed at δ 3.40 ($-CH_2-$) and 2.15 ($-CH_3$). After quaternization, proton signals of methylene and methyl was

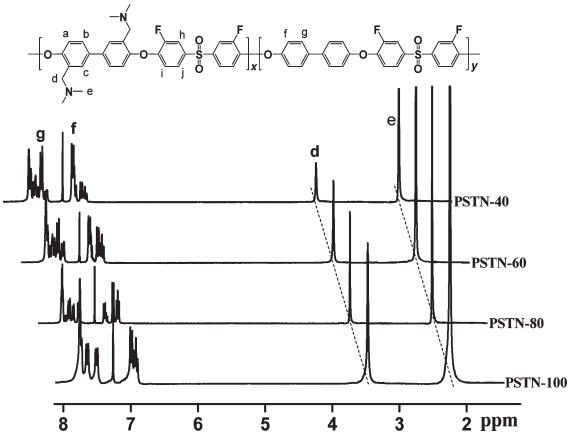


Figure 2. ^{1}H NMR spectra of PSTN-40, PSTN-60, PSTN-80, and PSTN-100 in $CDCl_3$.

shifted to higher frequencies due to deshielding from the quaternary nitrogen atom. The integration ratio of the H_g to H_h also changed from 1:3 to 2:9, as expected for the composition of quaternary ammonium group. The ^{13}C NMR spectrum of the PSQNI-100 exhibited 13 peaks in the range of 117−154 ppm for aromatic carbon atoms, as shown in Figure 3c. C9 showed clear double absorptions at δ 152−154 ppm, probably because of the J_{C-F} couplings of the carbon and fluorine atoms in the molecule. The peaks at δ 62 ($-CH_2-$) and 52 ($-CH_3$) were assigned to the chemical shifts of carbons on the quaternary ammonium groups,

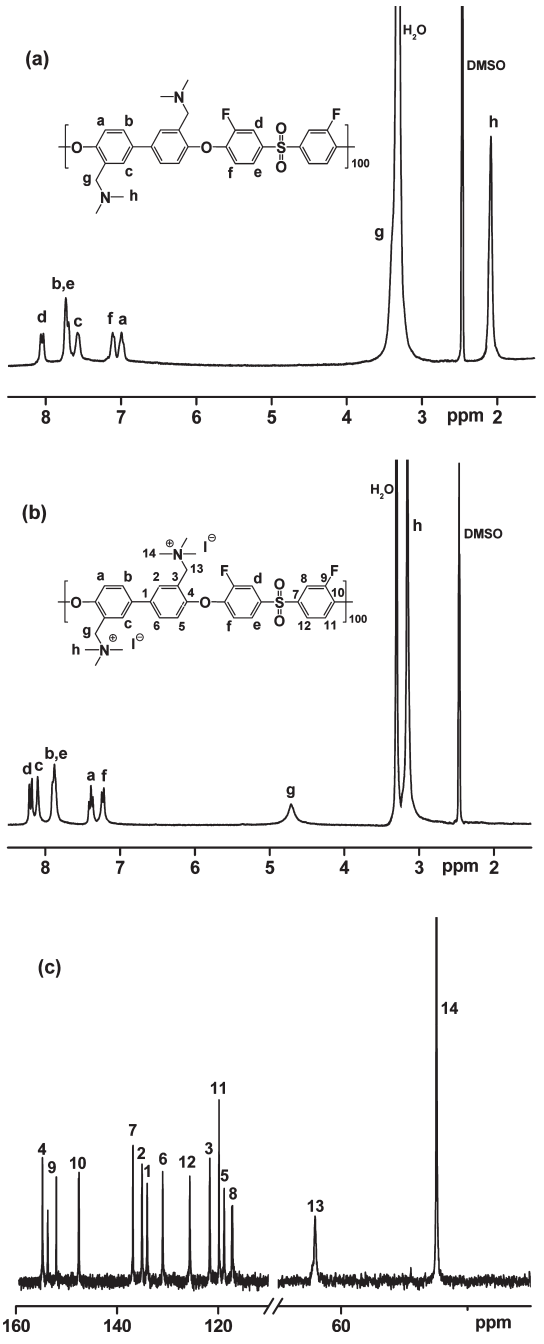


Figure 3. ^{1}H NMR spectra of PSTN-100 (a), PSQNI-100 (b), and ^{13}C NMR spectra of PSQNI-100 (c) in DMSO-d_6.

and the intensity ratio of C13 to C14 was close to 1:3. In addition, as listed in Table 2, the viscosity of PSQNI-*x* was even greater than the parent polymer in accordance with the reaction. This was due to the positive charges (the quaternary ammonium groups) located along the polymeric chains that repulsed each other in solution, inducing the chain extension. The higher the charge density and degree of ionization, the more marked the phenomenon. All these changes proved successful and quantitative incorporation of quaternary ammonium moiety into polysulfone.

The PSQNI ionomers exhibited outstanding solubility in polar aprotic solvents such as NMP, DMF, DMAc, and DMSO, as shown in Table 2. Then, PSQNI membranes (in the iodide form) could be cast from DMAc solutions in a flat glass dish. The drying procedure was optimized to produce flat, transparent membranes while quantitatively removing the casting solvent. PSQNOH membranes (in the hydroxide form) were obtained by treating PSQNIs in 1 N NaOH at room temperature for 48 h. PSQNOH-*x* were soluble in NMP, DMAc, and DMSO similarly to PSQNI-*x*; meanwhile, PSQNOH-90 and PSQNOH-100 were soluble in *n*-propanol. In the preparation of hydroxide exchange membrane fuel cells (HEMFCs), a required property for AEMs was their solubility in low boiling point solvent such as ethanol and *n*- or 2-propanol since a soluble ionomer could be used in the catalyst layer to build an efficient three-phase boundary and thus drastically improve the utilization of the catalyst particles and reduce the internal resistance.[25] Most of the AEMs prepared by traditional ways had poor solubility in the aforementioned simple solvents. Herein, PSQNOH-100 and PSQNOH-90 were soluble in *n*-propanol, whereas they were insoluble in pure water, even at 80 °C, suggesting that it could be used in the preparation of catalyst layer.

The thermal stability of the synthesized PSQN ionomers as well as pure polysulfone was studied under the same drying and heating conditions. Typical TGA curves are shown in Figure 4. Because of strong hydrophilicity of the quaternary ammonium group that attracts water from the atmosphere, a slight weight loss between 50 and 120 °C corresponding to the evaporation of absorbed water was observed. This behavior has been commonly found in other polymeric ion exchange membranes. To investigate the effect of the quaternary ammonium group on the thermal stability of the PSQNs, we also prepared pure polysulfone using a polyscondensation reaction of BP and TFDPS. The nonquaternized polymer was a thermally stable polymer and exhibited the starting decomposition temperature around 400 °C (Figure 4a). The introduction of the quaternary ammonium groups into the main chain of polymer lowered the thermal stability of the polymer. The first weight loss observed for PSQNI at 205 °C (Figure 4b) was related to the degradation of quaternary ammonium groups, whereas the value of corresponding PSQNOH

Table 2. Inherent Viscosity and Solubility[a] of PSQNs

		solubility[c]						
sample	η_{inh}[b] (dL g^{-1})	H_2O	$CHCl_3$	NPA	DMF	DMAc	NMP	DMSO
PSQNI-40	1.43	−	−	−	++	++	++	++
PSQNI-60	1.45	−	−	−	++	++	++	++
PSQNI-80	1.56	−	−	−	++	++	++	++
PSQNI-100	1.68	−	−	−	++	++	++	++
PSQNOH-40	1.43	−	−	−	++	++	++	++
PSQNOH-60	1.56	−	−	−	++	++	++	++
PSQNOH-70	1.62	−	−	−	++	++	++	++
PSQNOH-80	1.67	−	−	±	++	++	++	++
PSQNOH-90	1.68	−	−	+	++	++	++	++
PSQNOH-100	1.71	−	−	+	++	++	++	++

[a] ++, excellently soluble; +, soluble; ±, partially soluble; −, insoluble. [b] Inherent viscosity measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 °C. [c] NPA is *n*-propanol; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide.

(Figure 4c) was around 170 °C. The result indicated that $-(CH_2)NMe_3^+OH^-$ is less stable than $-(CH_2)NMe_3^+I^-$.

The mechanical properties of the PSQN membranes are summarized in Table 3. The samples in the iodide form (PSQNI-*x*) had tensile stress at maximum load of 52.3−66.5 MPa, Young's moduli of 1.43−1.72 GPa, and elongation at break of 16.8−23.6%. PSQNOH-*x* (in the hydroxide form), the tensile stress, and Young's moduli of the samples decreased. For example, the tensile stress and Young's moduli of PSQNOH-80 membrane decreased to 17.9 MPa and 0.35 GPa. However, their elongations at break increased to 65.5%, which indicated the samples become more flexible in hydroxide form. These results indicate that the PSQN membranes were tough and ductile enough for potential use as AEM materials.

The water uptake of sulfonated polymers is known to have a profound effect on PEMs conductivity and mechanical properties. It is the same to AEMs. Water molecules dissociate the alkali functionality and facilitate hydroxide transport. However, excessively high levels of water uptake can result in membrane fragility and dimensional change, which lead to the loss of mechanical properties. Basically, the amount of water uptake in the quaternary ammonium polymers will be strongly dependent upon the amount of quaternary ammonium salt groups and will also be related to IEC values. The water uptake was measured from the ratio of the weight of water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. These data are showed in Table 4 along with the swelling ratios. It could be seen that PSQNOHs exhibited a higher water uptake and swelling ratio than the PSQNIs because of hydrogen bond interactions between water molecules and the quaternary ammonium hydroxide groups. As expected, the water uptake and swelling ratio increased with IEC value. The water uptake of PSQNOH membranes with IEC from 1.47 to 2.88 was in the range 13−179%. An increase in water uptake with increase in temperature was also observed. For example, at 60 °C, PSQNOH-80 showed 253% water uptake and 123% swelling ratio in plane direction, much higher than that at 20 °C (86% water uptake and 33% swelling ratio). In general, the PSQNOH films showed lower water uptake and swelling ratio than other reported AEMs in the similar IEC.[22] Such a low water uptake and swelling ratio of PSQNOHs might be attributed to the introduction of hydrophobic fluorine groups in the polymer main chain, which would further increase the hydrophobic property of the polymer main chains.

The hydroxide conductivity of the PSQNOH membranes was measured at 100% RH (in water) and compared with that of Nafion 117. The values of the ionic conductivity reported in Table 4 have been expressed in Figure 5 as a function of the IEC. In general, a conductivity above 10^{-2} S cm^{-1} is required for hydroxide exchange membrane materials used in fuel cells. All the obtained membranes showed conductivities above 10^{-2} S cm^{-1} at room temperature; for example, PSQNOH-90 achieved higher hydroxide conductivity (8.4×10^{-2} S cm^{-1}), which was thus comparable to the proton conductivity of Nafion 117 (i.e., 9.0×10^{-2} S cm^{-1}). Some general trends were observed for all membranes. For example, their conductivities showed a trend that was similar to that for water uptake. At low IEC values, the

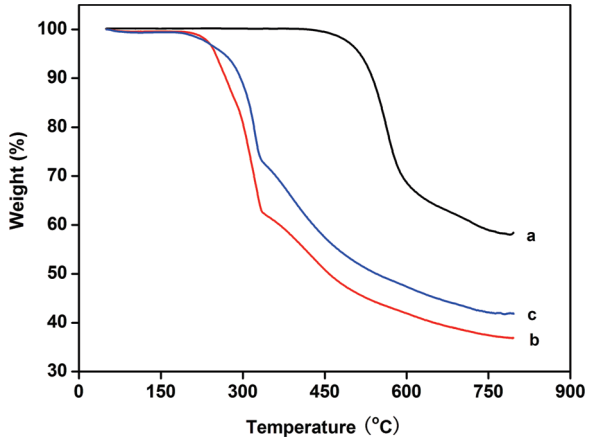


Figure 4. TGA curves for PS (a), PSQNI-100 (b), and PSQNOH-100 (c) in N_2.

Table 3. Mechanical Properties of PSQNs[a]

sample	tensile strength (MPa)	tensile modulus (GPa)	elongation at break (%)
PSQNI-40	66.5	1.72	16.8
PSQNI-60	64.3	1.67	17.2
PSQNI-80	60.6	1.65	18.6
PSQNI-90	56.1	1.54	19.4
PSQNI-100	52.3	1.43	23.6
PSQNOH-40	55.9	1.63	22.7
PSQNOH-50	51.2	1.52	28.4
PSQNOH-60	44.7	1.14	35.6
PSQNOH-70	38.8	0.87	37.2
PSQNOH-80	17.9	0.35	65.5

[a] Measured at 30 °C, 50% RH.

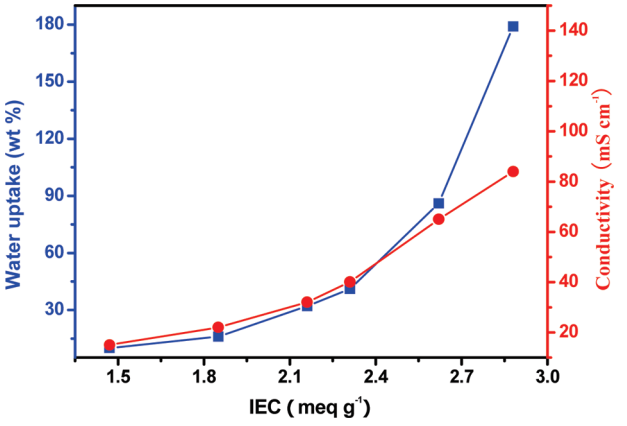


Figure 5. Water uptake and hydroxide anion conductivity versus ion exchange capacity: (■) water uptake; (●) conductivity.

Table 4. Ion Exchange Capacity, Water Uptake, Swelling Rate, and Hydroxide Conductivity of PSQNOH Membranes

	IEC (mequiv g^{-1})		water uptake (%)		swelling ratio (%)		conductivity (S cm^{-1})	
sample	theoretical[a]	experimental	20 °C	60 °C	20 °C	60 °C	20 °C	60 °C
PSQNOH-40	1.58	1.47	13	16	8	8	0.015	0.018
PSQNOH-50	1.90	1.85	15	19	11	12	0.022	0.032
PSQNOH-60	2.21	2.16	32	39	14	16	0.032	0.046
PSQNOH-70	2.49	2.31	41	52	17	21	0.040	0.061
PSQNOH-80	2.76	2.62	86	253	33	123	0.065	0.087
PSQNOH-90	3.02	2.88	179	–[b]	123	–	0.084	–

[a] Calculated from ^{1}H NMR. [b] Swelled to gel-like, could not be measured.

conductivity of the membranes was rather low and increased in a gradual fashion. In this regime, conductivity was thought to be limited by the connection between ionic domains, and as the IEC value increased, the conductivity increased rapidly as the volume fraction of water and concentration of ionic groups in the membrane increased. Additionally, the conductivity values also increased with the temperature. The ionic conductivity of PSQNOH-80 increased from 6.5×10^{-2} to 8.7×10^{-2} S cm^{-1}, corresponding to the temperature from 20 to 60 °C.

Conclusions

In conclusion, a facile and unconventional approach to prepare partially fluorinated copoly(arylene ether sulfone) ionomers containing pendant quaternary ammonium groups based on a novel biphenol monomer was developed. We demonstrated that using functionalized monomer it is possible to directly obtain different quaternized poly(arylene ether sulfone)s for anion exchange membranes. Compared with the traditional approach, this process could precisely control the amount of quaternary ammonium groups and their location along the polymer backbone. Additionally, this new route avoided the use of chloromethyl methyl ether, thus it was more environmentally friendly. The obtained quaternized ionomers exhibited excellent solubility and formed flexible and tough membranes of varying ionic content by casting from DMAc solution. The introduction of hydrophobic fluorine groups in the polymer main chain resulted in the low water uptake and the excellent dimensional stability of the PSQNOH membranes despite the high IEC value. They showed high hydroxide conductivity up to 8.4×10^{-2} S cm^{-1} in water at room temperature comparable to that of Nafion 117 (9.0×10^{-2} S cm^{-1}). These preliminary properties have demonstrated the potential availability as an electrolyte for hydroxide exchange membrane fuel cells. These results will aid in designing better membranes, such as the block copolymers for improved membrane performance.

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