

Robust Hydroxide Ion Conducting Poly(biphenyl alkylene)s for Alkaline Fuel Cell Membranes

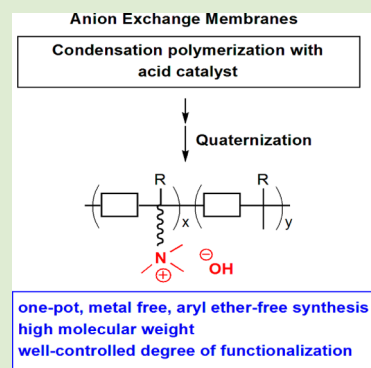
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Supporting Information

ABSTRACT: High molecular weight, quaternary ammonium-tethered poly(biphenyl alkylene)s without alkaline labile C–O bonds were synthesized via acid-catalyzed polycondensation reactions for the first time. Ion-exchange capacity was conveniently controlled by adjusting the feed ratio of two ketone monomers in the polymerization. The resultant anion exchange membranes showed high hydroxide ion conductivity up to 120 mS/cm and excellent alkaline stability at 80 °C. This study provides a new synthetic strategy for the preparation of anion exchange membranes with robust fuel cell performance and excellent stability.



The synthesis of robust, highly anion-conductive polymers has been a subject of intense research because of the great potential of anion exchange membranes (AEMs) for applications in fuel cells, electrolysis, water treatment, and other electrochemical energy conversion and storage technologies.^{1,2} Compared with acidic proton exchange membrane fuel cells, alkaline fuel cells offer the significant advantages of faster kinetics for the oxygen reduction reaction and the option to use earth-abundant transition metals (e.g., nickel) as electrocatalysts.^{3,4} Thus, AEM fuel cells, which use an AEM as the solid electrolyte, are significantly less costly than Nafion-based proton exchange membrane fuel cells. Unfortunately, most current AEMs lack sufficient ion conductivity. Furthermore, their poor chemical and mechanical stabilities under alkaline conditions, particularly above 80 °C, have been major barriers to the adoption of AEM fuel cells as reliable clean energy conversion technology.

In recent years, a variety of AEMs with main polymer chain structures ranging from polysulfones,^{5,6} poly(phenylene oxide)s,⁷ poly(phenylene)s,⁸ poly(benzimidazolium)s,⁹ poly(arylene ether ketone)s,^{10,11} and poly(arylene ether sulfone)s¹² have been investigated. These hydroxide ion conducting polymers are generally prepared by attaching pendant quaternary ammonium (QA) groups to premade polymer backbone chains. Aromatic polymer backbones, which typically contain aryl ether bonds, are postfunctionalized via chloromethylation or benzylic bromination followed by quaternization with trimethylamine (Figure 1a). Although the synthetic process is simple, the chloromethylation reaction often requires toxic reagents, long reaction times, and extensive optimization to reach a desired degree of functionalization. Side reactions (e.g., gelation) frequently occur over prolonged reaction times,

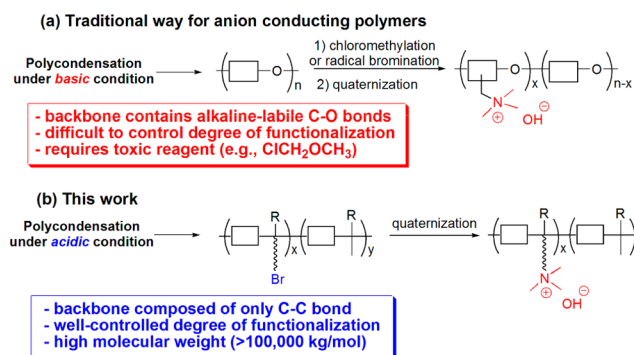


Figure 1. Graphical illustrations for synthesis of (a) typical AEM membranes and (b) our new hydroxide-conducting QA-aromatic polymers.

making it difficult to achieve an ion-exchange capacity (IEC) above 2.5 mequiv/g.¹³ Furthermore, these postfunctionalization approaches allow the installation of only benzyltrimethylammonium as a QA in AEMs. After screening a variety of model QAs, we recently reported that compared with benzyltrimethylammonium a long alkyl-tethered QA (e.g., hexyltrimethylammonium) has comparable or better thermochemical stability under alkaline conditions.¹⁴

The primary role of the polymer backbone in AEMs is to provide mechanical stability via entanglements of polymer chains. Because most base polymers for AEM applications are

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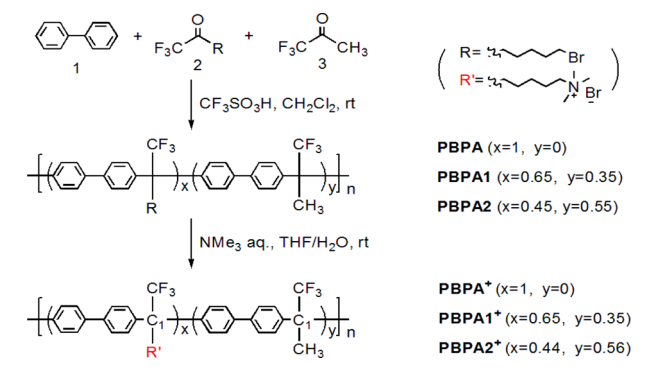
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prepared via nucleophilic aromatic substitution of aromatic diol and dihalide monomers, they unavoidably contain C–O linkages along the backbone. Although the aryl ether linkages allow more freedom of rotation along the polymer backbones and improve the solubility of the resulting polymers, the presence of such ether linkages also makes the AEMs potentially labile under high-pH conditions. The strongly nucleophilic hydroxide ions attack the C–O bonds adjacent to the benzyltrimethylammonium group and cause polymer backbone degradation.^{15,16} Thus, for enhanced chemical stability of AEMs, alternative polymer backbones free of aryl ether bonds should be developed.

To maintain robust mechanical stability (i.e., low swelling in water and high strength), the polymer backbone should be made of rigid repeating units with molecular weights high enough to create sufficient chain entanglements. Although AEMs prepared from conjugated aromatic polymers can achieve good alkaline stability due to the absence of aryl ether bonds and a low degree of swelling in water, if polymer backbones are too rigid, the resulting AEMs are rather brittle.¹⁷ The use of expensive palladium catalysts for the polymerization reaction also limits the scaling-up of materials.

Herein, we introduce a new synthetic design for AEM polymers that solves the problems of traditional AEM synthesis by reporting solvent-processable AEMs made of high-molecular-weight, bromoalkyl-tethered poly(biphenyl alkylene)s (Figure 1b; **PBPA**, **PBPA1**, and **PBPA2** of Scheme 1). A detailed synthetic route is shown in Scheme S1

Scheme 1. Synthetic Route for Quaternary Ammonium Polymers



(Supporting Information). The aromatic main-chain polymers, made solely of C–C bonds, were prepared by one-pot, acid-catalyzed Friedel–Crafts polycondensations^{18,19} of biphenyl (1) and trifluoromethyl alkyl ketones (7-bromo-1,1,1-trifluoroheptan-2-one and methyl trifluoromethyl ketone; compounds 2 and 3, respectively, of Scheme 1). Traditional AEM polymer synthesis via nucleophilic aromatic substitution requires a basic medium for polymerization; thus, it prevents monomers from having a potential leaving group such as alkyl halide. However, the use of acidic conditions in the reaction described in this report allows for the condensation polymerization of a monomer containing bromoalkyl side chains without affecting the QA precursor group. Although the repeating units of the condensation polymers are composed of a rigid biphenyl and a methine (C₁ in Scheme 1), they were all obtained in high molecular weights ($M_w > 100$ kg/mol measured by size exclusion chromatography; Table 1) while remaining soluble in common organic solvents (e.g., CHCl₃ and THF).

Table 1. Molecular Weight Properties of Precursor Polymers

polymer	M_n^a	M_w^a	PDI ^b	viscosity ^c (dL/g)
PBPA	70.8	110.1	1.6	2.18
PBPA1	72.1	138.8	1.9	1.16
PBPA2	59.6	106.3	1.8	1.54

^aIn kg/mol. ^bPolydispersity index (M_w/M_n). ^c0.5 g/dL in NMP at 30 °C.

The bromopentyl group on the side chain of the precursor polymers was subsequently converted to trimethylpentylammonium bromide via substitution reaction with trimethylamine, affording **PBPA**⁺, **PBPA1**⁺, and **PBPA2**⁺ (Scheme 1). These QA polymers were insoluble in water, THF, CHCl₃, and CH₂Cl₂ but were soluble in *N,N*-dimethylformamide, dimethyl sulfoxide, and methanol at room temperature. The chemical structures of the ionic polymers were analyzed with ¹H and ¹⁹F NMR spectroscopies (Figure S2, Supporting Information). Comparison of the integral ratio of the trimethylammonium protons at 3.02 ppm and the aromatic proton peaks at 7.30–7.80 ppm indicated that the quaternization reaction gave quantitative conversion. Two CF₃ groups in the polymer chain (labeled as F1 and F2; see Figure S2, Supporting Information) also displayed slightly different ¹⁹F NMR chemical shifts, which allowed convenient estimation of the ratio of repeating units in the polymers.

The NMR spectroscopic analysis confirmed that the ratio of the two different repeating units of the polymers (x and y in Scheme 1) matched well with the monomer feed ratio we added during polymerization. Thus, the IECs of the membranes can be easily controlled by adjusting the feed ratio of the two ketone monomers in the polymerization (Table 2). The

Table 2. Ion-Exchange Capacity (IEC), Water Uptake (WU), and Swelling Degree (ΔI) of Quaternary Ammonium Polymers

sample	IEC (mequiv/g)			WU (%) ^b	ΔI (%) ^b
	theo. ^a	NMR	titration		
PBPA ⁺	2.61	2.61	2.70	145	40
PBPA1 ⁺	2.00	1.91	1.94	110	10
PBPA2 ⁺	1.50	1.45	1.46	76	5

^aTheoretical values calculated from the monomer ratio. ^bAfter immersion in water at 80 °C for 24 h; an average of two measurements.

calculated IECs from the monomer feed ratio were 2.61, 2.00, and 1.50 mequiv/g for **PBPA**⁺, **PBPA1**⁺, and **PBPA2**⁺, respectively, which were in good agreement with the IECs determined with ¹H and ¹⁹F NMR (2.61, 1.91, and 1.45 mequiv/g) and titration (2.70, 1.94, and 1.46 mequiv/g; see Table 2).

Transparent and flexible membranes were prepared by dissolving the ionic polymers in dimethyl sulfoxide and casting them on a flat Teflon sheet (Figure S3, Supporting Information). The solvent processability of ionic polymers may enable their use not only as solid electrolytes in alkaline AEMs but also as ionomer electrode materials. The thermal stability of the synthesized bromoalkyl-tethered precursor and QA polymers was studied with thermogravimetric analysis (Figure S4, Supporting Information). The precursor polymers (**PBPA**, **PBPA1**, and **PBPA2**) were thermally stable without decomposition up to 350 °C. The QA polymers (**PBPA**⁺,

PBPA1⁺, and PBPA2⁺) exhibited a slight weight loss between 50 and 120 °C due to the evaporation of absorbed water. The decomposition of the QA groups occurred at 270 °C. The thermal stability of QA polymers produced in this study was better than that of reported QA poly(arylene ether sulfone)s.⁵

Water uptake and hydroxide ion conductivity are particularly critical for AEM fuel cell applications. An ideal material for AEMs should have good ion conductivity with manageable water uptake. The water uptake of the QA polymers in hydroxide ion form was measured after immersing the membranes in water at 80 °C (see Table 2). The polymer with the highest IEC, PBPA⁺, had a water uptake value (145%) higher than that of the polymers with lower IECs, PBPA1⁺ and PBPA2⁺ (110% and 76%, respectively). The water uptakes of the membranes also increased with increasing temperature (see Figure 2a and Table S1, Supporting Information). Surprisingly,

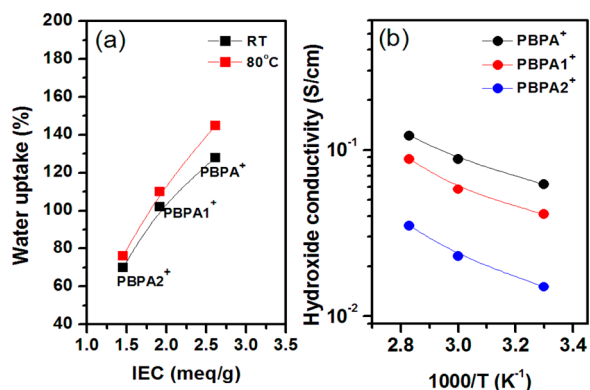


Figure 2. (a) Water uptake and (b) hydroxide ion conductivity of quaternary ammonium polymers.

all three QA polymers showed low swelling ratios despite their high water uptakes, probably due to the presence of the rigid aromatic backbone (Table 2).

Anion conductivity of the AEMs was measured with a four-point probe method. Hydroxide ion conductivities of the PBPA⁺, PBPA1⁺, and PBPA2⁺ membranes showed an approximate Arrhenius-type temperature dependence, as shown in Figure 2b and Table S1 (Supporting Information). As expected, conductivity increased as IEC increased for all AEMs. For example, PBPA⁺ (with the highest IEC of 2.61 mequiv/g) had the highest conductivity (62 mS/cm), a value almost four times that of PBPA2⁺ (15 mS/cm; IEC = 1.45 mequiv/g) at 30 °C. We noticed that PBPA1⁺ (IEC = 1.9 mequiv/g) afforded significantly higher hydroxide ion conductivity than those of other reported aromatic AEMs with similar IECs [e.g., quaternized poly(phenylene oxide)s,⁷ poly(arylene ether ketone)s,²⁰ and poly(arylene ether sulfone)s¹²]. This result is likely attributable to the relatively higher water uptake of PBPA1⁺, which helps the hydrated membrane diffuse hydroxide ions more effectively. Although additional study is needed, we believe that the incorporation of a QA at the end of the long alkyl chains of aromatic polymers might improve the mobility of the QA group, creating more space for better ion diffusion. When the morphologies of these ionic membranes were examined with small-angle X-ray scattering (SAXS), however, no obvious scattering peak was observed for PBPA⁺, PBPA1⁺, and PBPA2⁺ membranes (Figure S6, Supporting Information).

Increasing the temperature also enhanced the hydroxide ion conductivity of the polymer samples. For example, PBPA⁺, PBPA1⁺, and PBPA2⁺ had hydroxide ion conductivities of 62, 41, and 15 mS/cm, respectively, at 30 °C, whereas at 80 °C, these values increased to 122, 88, and 35 mS/cm, respectively. This is mainly due to faster migration of ions and higher diffusivity with increasing temperature.

Alkaline stability of the QA polymers was quantitatively evaluated by immersing the membranes into 1 M NaOH solution at 80 °C and measuring the change in IEC after alkaline treatments. The ¹H NMR spectra of PBPA⁺ in OH⁻ form before and after the alkaline test for 30 days are shown in Figure 3. No change in chemical shift was observed even after

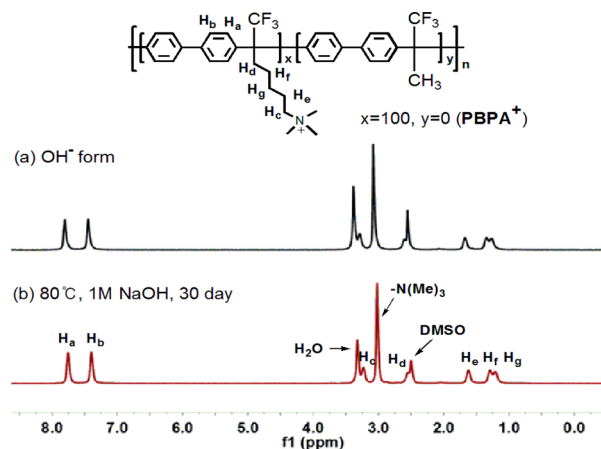


Figure 3. ¹H NMR spectra of PBPA⁺ (a) before and (b) after stability test.

30 days in 1 M NaOH at 80 °C for all QA polymers (Figure S5, Supporting Information). The ¹H NMR spectral data also suggest that the PBPA⁺, PBPA1⁺, and PBPA2⁺ membranes maintained their IECs even after an alkaline test in 1 M NaOH solution at 80 °C for 30 days; the NMR-based IEC values were 2.60, 1.93, and 1.46 mequiv/g, which were close to the initial values (2.61, 1.91, and 1.45 mequiv/g, respectively; Figure S5 and Table S2, Supporting Information). Hydroxide ion conductivity was also only negligibly different after the alkaline test, indicating that these membranes had good long-term thermochemical stability (Table S1, Supporting Information). Increasing alkaline test temperature further to 100 °C did not cause any sign of degradation either (Figure S8, Supporting Information). These results confirm that our AEM design concept of rigid polymer backbone structure without aryl ether bonds and QA on flexible alkyl tethered chains can afford remarkable chemical stability under alkaline conditions even at high temperatures.

The mechanical properties of AEMs are critical for practical applications in fuel cells. The mechanical properties of the ionic polymer membranes were measured under different humidity conditions (0%, 50%, and 90%) at 50 °C (Figure 4a and Figure S7, Supporting Information). At 50 °C and 50% relative humidity, the tensile strength and elongation at the break of the membranes were 20–35 MPa and 40–140%, respectively, which meet the requirements for building membrane electrode assemblies (MEAs) in AEM fuel cells. As shown in Figure 4a, the mechanical strength of the lowest IEC PBPA2⁺ membrane (35 MPa) was greater than that of the higher IEC PBPA⁺ membrane (22 MPa). Compared with Diels–Alder poly-

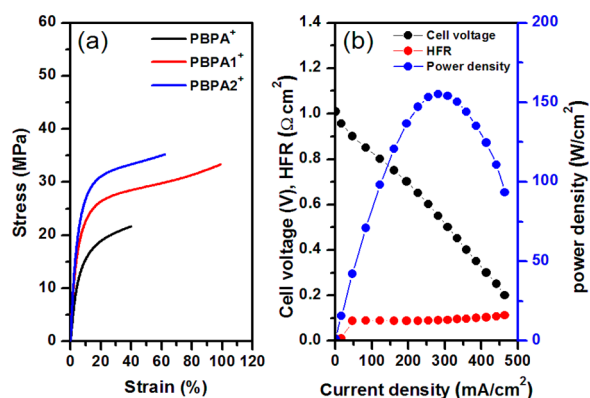


Figure 4. (a) Stress versus strain curves of QA polymer membranes at 50 °C and 50% relative humidity. (b) H₂/O₂ polarization, HFR, and power density of the single cell using PBPA1⁺ (film thickness = 18 μm) at 80 °C.

(phenylene) AEMs (IEC = 1.7 mequiv/g, 32 MPa maximum strength, and 40% maximum strain),¹⁵ the PBPA1⁺ membrane (IEC = 1.9 mequiv/g, 33 MPa maximum strength, and 100% maximum strain) showed similar tensile strength but significantly better elongation at break probably due to its more flexible backbone structure with the presence of a quaternary sp³ carbon. The excellent mechanical strength data indicated that the high-molecular-weight QA polymers in this study were tough and ductile enough for use as AEM materials in fuel cells.

Figure 4b shows the polarization curves of PBPA1⁺-containing AEM fuel cells at 80 °C. The open-circuit voltage (OCV) was 1.01 V, which is typical in hydrogen-supplied fuel cells. The maximum power density of 155 mW cm⁻² was obtained at 80 °C. The high-frequency resistance (HFR) of the cell is <0.1 Ω cm². While the membrane conductivity obtained from the HFR is 19.9 S/cm, lower than the value from the ex-situ measurement due to the nonmembrane resistance contributions of the MEA, the HFR value reported here was much smaller than typical values found in literature reports of AEM fuel cells. These results of QA poly(biphenyl alkylene)s clearly demonstrate superior chemical stability and fuel cell performance compared to other AEM materials. We are now optimizing MEA fabrication to improve fuel cell performance further.

In summary, a new class of robust aromatic AEMs was prepared via one-pot, metal-free, acid-catalyzed condensation polymerizations and subsequent conversion of tethered bromoalkyl groups to trimethylalkylammonium groups. These AEMs are flexible and chemically and mechanically stable enough for use as fuel cell membrane materials. Compared with the synthesis of other QA-functionalized polymer AEMs, the synthetic strategy reported herein affords the major advantage of being a simple procedure that avoids complicated post-modifications. In addition, the synthesized QA-functionalized polymer membranes showed excellent long-term alkaline stability at 80 °C and mechanical property, which fulfills a critical requirement for alkaline fuel cell applications. The solvent processability of these ionic polymers makes them useful as both AEMs and ionomer electrode materials.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details of the synthetic procedures and characterization and properties of polymers. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00375.

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Notes

The authors declare no competing financial interest.

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