**Novel quaternary ammonium microblock poly
(*p*-phenylene-*co*-aryl ether ketone)s as anion exchange membranes
for alkaline fuel cells**

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ABSTRACT

Using cation compounds as raw materials, three quaternized microblock poly(*p*-phenylene-*co*-aryl ether ketone)s (s-, m-, and l-QPP-*co*-PAEK) were synthesized using a nickel (0)-catalyzed coupling reaction. Hydrophilic and hydrophobic moieties were affixed using cationic quaternary ammonium (QA) groups attached to poly(*p*-phenylene) by a three-carbon interstitial spacer and nonionic dichloride monomers of various lengths, respectively. The morphology, water uptake, swelling ratio, mechanical properties, thermal stability, hydroxide conductivity and alkaline stability of these new membranes were investigated. Experimental results

indicated that the membrane with the longest hydrophobic microblock exhibited high hydroxide conductivity (37.6 mS cm^{-1} at 80°C) resulting from the aggregation of ionic clusters observed using TEM. The copolymers with longer hydrophobic nonionic segments exhibited improved alkaline stability, suggesting that the hydrophobic chain shields the QA groups and that the polymer chains pack in a manner that restricts rotation. Controlling the distribution of QA groups in poly(*p*-phenylene) moieties and tuning the block length of nonionic segments are demonstrated to be effective methods for improving the hydroxide conductivity and alkaline stability of anion exchange membranes.

1. Introduction

Fuel cells have attracted considerable attention as promising environmentally friendly power generators due to their efficient energy conversion from chemical energy to electricity [1, 2]. Among the fuel cells, proton exchange membrane fuel cells (PEMFCs) have been extensively developed for practical applications in the fields of portable devices, cogeneration systems, residential power supplies, and electric vehicles [3]. Due to the acidic nature of proton exchange membranes (PEMs), noble metal electrocatalysts (such as Pt and Pd) are typically required for the preparation of PEMs, which leads to high cost requirements for commercial application of PEMFCs [4-6]. Recently, alkaline anion exchange membrane fuel cells (AEMFCs) have been explored as attractive alternatives to PEMFCs [7]. In AEMFCs, the transport direction of hydroxide ion opposes that of proton conduction, which can mitigate or

possibly eliminate adverse effects of fuel permeation in PEMFCs and direct methanol fuel cells (DMFCs). Most importantly, oxygen reductive reaction kinetics can be increased, and the use of non-precious metal electrocatalysts can be achieved. [8, 9] Therefore, significant attention has been directed towards developing highly conductive anion exchange membranes (AEMs).

In recent years, polymers with various backbone and cation structures have been investigated for the preparation of high performance AEMs, such as quaternary ammonium (QA)-functionalized poly (arylene ether ketone)s (PAEKs), [10, 11] guanidinium- or phosphonium-functionalized PAEKs or poly (arylene ether sulfone)s [12-14], dialkylation- functionalized poly (benzimidazolium)s [15], imidazolium-functionalized poly (phenylene oxide)s [16], QA-functionalized poly(phenylene)s [17] and poly(ethylene)s [18]. Despite exhibiting high hydroxide ion conductivity, the attack of hydroxide ions on vulnerable cations and main chains in basic environments is a major challenge in the development of AEMs.

Among the various cationic structures, QA groups are simple and easily introduced into the backbone of the polymer. However, QA groups are prone to degradation via nucleophilic substitution (S_N2) to form alcohol or amine and E2 Hofmann elimination reactions when the hydrogen is located in the beta position. In addition, QA groups, especially those located in benzylic positions and attached to a polysulfone backbone through methylene linkages, can bring about the scission of the polymer backbone due to the strong

electron-withdrawing sulfone linkage activating the breakage of adjacent ether links [19, 20]. Several strategies have been developed to overcome these degradation pathways. For example, Jannasch et al. prepared a PPO polymer with QA groups attached either to the backbone via flexible alkyl spacer units or directly to the benzylic positions. Their study suggested that polymers with flexible alkyl spacer units exhibit better stability than polymers with QA groups directly attached to the benzylic positions [21]. Their calculations indicated that QA head-groups attached to long and flexible alkyl side chains (≥ 4 carbon atoms) pendant to the aromatic polymer backbone facilitate alkaline stability in AEMs. Moreover, introducing high electron density or steric shielding around the β -hydrogen to the alkyl chain has been shown to suppress Hofmann elimination reactions [22]. More recently, Hicker et al. found that if the linkage between the QA head-groups and the aromatic ring is a three-carbon interstitial spacer, Hofmann elimination is not observed in 0.6 M NaOD in a CD₃OD/D₂O mixture or in D₂O at 120 °C [23]. Due to the ability to produce low-cost phenylpropantrimethyl ammonium-derived monomers, the scope and feasibility of polymerization based on a three-carbon interstitial spacer for preparing AEMs can be greatly expanded.

Compared with investigations of cation degradation pathways, examination of the alkaline stability of the polymer backbone is less common but has attracted more attention in recent years [24]. Yamaguchi et al. synthesized six model compounds, including different anion exchange groups with diphenyl

sulfone as a scaffold, to investigate their stabilities in alkaline media [25]. The study found that the instability of these compounds mainly results from the cleavage of aryl ether bonds rather than the decomposition of ionic groups. More recently, Bae and coworkers systematically investigated the alkaline stability of nine AEM model compounds [20]. The authors found that unsubstituted, small molecule PPO analogues were stable in alkaline conditions due to the absence of adjacent electron-withdrawing groups.

Poly (phenylene)s (PPs) were once considered to consist of polymer backbone structures made entirely of carbon with linear, rigid-rod architectures and multiple phenyl rings that provided selective functional sites. Aromatic main chains with coplanar molecular packing have been shown to exhibit a long π -conjugation length in the solid state, leading to the high C-C bond dissociation energy (BDE) of phenyl-phenyl groups [26]. This provides functionalized-PP AEMs with excellent chemical stability and mechanical strength. Hibbs et al. reported the synthesis of AEMs based on a poly(phenylene) backbone by a Diels-Alder reaction [17]. The prepared AEMs exhibited hydroxide ion conductivities as high as 50 mS cm⁻¹ in water and were stable under highly basic conditions (4 M NaOH) at elevated temperatures (60 °C). However, brittleness is an undesirable feature of PPs that can be attributed to their inherent rigid backbones and steric encumber. More recently, Miyatake and coworkers reported a series of aromatic PP copolymers containing ammonium-functionalized groups prepared via Yamamoto coupling,

chloromethylation and quaternization [3]. Using the partially fluorinated oligo(arylene ether) chains as hydrophobic blocks and the chemically robust oligophenylenes as hydrophilic components, the brittleness of the polymer was improved. Moreover, their study also showed membranes containing oligophenylene moieties as scaffolding for high-density QA functionality that exhibited high hydroxide ion conductivity (138 mS cm^{-1} at 80°C). It was noted that the synthetic process of these copolymers may have drawbacks such as the use of chloromethylation reagents (chloromethyl methyl ether or CMME), relatively high catalyst loadings (1.25 equivalents of catalyst relative to aryl), high catalyst cost (bis(1,5-cyclooctadiene)nickel(0)), and difficulty in controlling the number and location of QA groups [27]. These factors encourage the investigation of new synthetic pathways to optimize QA-functionalized poly (*p*-phenylene) preparation through an environmentally friendly and low-cost synthetic route.

In this paper, a new hydrophilic monomer (2, 5-dichlorophenyl) [4-[3-(trimethylamino)propyl]-phenyl]-methanone (DTPPM) with QA groups was designed. The linkage between QA head-groups and aromatic rings is a three-carbon interstitial spacer, which may provide high hydroxide ion conductivity and alkaline stability. Based on DTPPM, a series of novel microblock poly (*p*-phenylene-*co*-aryl ether ketone) (*s*-, *m*-, and *l*-QPP-*co*-PAEK) AEMs were synthesized by nickel (0)-catalyzed coupling copolymerization. For the preparation of these copolymers, the commonly used chloromethylation reagent (CMME) was avoided, and the expensive

Ni(COD)₂ compound was replaced with the an *in situ* generated Ni⁰ species as the coupling reagent. To the best of our knowledge, although they are widely used to prepare PEMs, using cationic compounds as raw materials to directly synthesize AEMs via nickel (0)-catalyzed coupling reactions are rarely reported. The effects of hydrophobic nonionic segments with various microblock lengths on the dimensional stability, morphology, hydroxide ion conductivity, and alkaline stability of the membrane are reported.

2. Experimental

2.1 Materials and reagents

[4-(3-bromopropyl) phenyl-2, 5-dichlorophenyl]methanone (BPDPM) was prepared as reported in the literature [28]. 2, 6-bis[4-(4-chlorobenzoyl)-phenoxy]benzonitrile (CPBN), 2, 6-bis[3-[4-(4-chlorobenzoyl)phenoxy]phenoxy]benzonitrile (CPPBN), and 6, 6'-[1, 3-phenylene-bis(oxy))bis[2-[3-[4-(4-chlorobenzoyl)phenoxy]phenoxy]benzonitrile] (PCPPBN) were synthesized following our previously published procedure [29]. Anhydrous NiBr₂ was dried at 200 °C under vacuum. Triphenylphosphine (PPh₃), *N*-methyl-2-pyrrolidone (NMP), trimethylamine (33 wt% in water) and zinc dust were purchased from Sinopharm Group Chemical Reagent. Dimethylacetamide (DMAc) was dried over CaH₂ and distilled under reduced pressure before use. Sodium deuterioxide (40 wt% in D₂O) was purchased from Aldrich.

2.2 Synthesis of the (2, 5-dichloro phenyl) [4-[3- (trimethylamino) propyl] -phenyl]-

methanone (DTPPM) monomer

First, 20 g of BPDPM and 40 ml of 1, 4- dioxane were added to the reaction flask and stirred at 40 °C. When the mixture was homogeneous, 20 ml of a 33% trimethylaminesolution was added and stirred at room temperature for 24 h. Then, the reaction mixture was poured into 200 ml of diethylether. The target product was obtained using extraction and purification in diethylether solvent (98% yield).

2.3 Synthesis of QPP-*co*-PAEK copolymers

The copolymer m-QPP-*co*-PAEK was synthesized as shown in Scheme 1. NiBr₂ (0.22 g, 1 mmol), PPh₃ (1.84 g, 7 mmol) and Zn (3.66 g, 56 mmol) were added to a three-necked round bottom flask that was dried and degassed by nitrogen. Then, anhydrous DMAc (20 ml) was added via syringe, and the mixture was stirred at 80 °C. When the mixture color became red brown, the reaction monomers DTPPM (2.89 g, 67 mmol) and CPPBN (2.47 g, 33 mmol) were added, and the mixture was reacted at 80 °C for 12 h. After cooling to room temperature, the viscous mixture was filtered using a Savary-Gilliard funnel, and the obtained mixture was poured into ethanol solution. The white fiber-like polymer was collected and washed with water and ethanol, and dried under vacuum at 100 °C for 24 h. The synthesis of the s-QPP-*co*-PAEK and l-QPP-*co*-PAEK copolymers using the CPPBN and PCPPBN monomers, respectively, followed the procedure given above. The ion-exchange capacity (IEC) of all QPP-*co*-PAEK copolymers was controlled at 1.6 meq g⁻¹. All the polymerizations produced yields above 98%.

2.4. Membrane preparation

The copolymer was dissolved in NMP at an 8 wt% concentration. After filtration, the mixture was cast onto a clean glass plate. The solvent was evaporated in an oven at 70 °C for 12 h and in a vacuum oven at 120 °C for 24 h. The obtained membrane was immersed in deionized water. When the membrane could be peeled from the plate, it was immersed in a 1 mol L⁻¹ NaOH solution at room temperature for 48 h to exchange Br⁻ ions in the membrane for OH⁻ ions. Finally, the membrane was washed with deionized water to remove residual NaOH inside of the membrane.

2.5. Characterization and measurements

¹H NMR and ¹³C NMR were performed on a Bruker AV400 spectrometer at room temperature. Fourier-transform infrared spectroscopy (FT-IR) was conducted using a Bio-Rad Digilab Division FTS-80 FT-IR spectrometer with the 20 μm thickness membrane samples. Atomic force microscopy (AFM) images were obtained using a SPI 3800/SPA 300HV (Seiko Instruments Inc., Japan) instrument in tapping mode. All of the samples were affixed to a 1 cm² specimen holder and scanned using a SiN₄ cantilever with a spring constant of 2 N m⁻¹. Transmission electron microscopy (TEM) images were obtained using following method. A drop of 5 mg ml⁻¹ QPP-*co*-PAEK copolymer solution was dropped on a copper grid using a syringe and dried at 80 °C for 12 h. The copper grid with the thin copolymer membrane was immersed into a H₂PtCl₆ aqueous solution for a set time to exchange the Br⁻ ions into PtCl₆²⁻ ions.

Finally, the copper grid was immersed in deionized water for 1 h to remove residual salt ions and then dried at room temperature for TEM measurements. The TEM images were obtained on an ultra high-resolution transmission electron microscope (JEOLJEM-2010FEF) using an accelerating voltage of 200 kV.

The thermal stability of the membranes was examined by thermo gravimetric analysis (TGA) (Perkin Elmer TGA-2) under nitrogen at a heating rate of 10 °C min⁻¹. Thermal transition temperatures (*T_g*) of the copolymers were measured on dynamic mechanical thermal analyzer (01db-Metravib DMA+450). The film samples (length: 10 mm) were operated on in a tensile mode (strain: 0.1%; initial static force: 0.2 N; static force 10% greater than dynamic force; minimum static force: 0.01 N; maximum auto tension displacement: 3.0 mm) at a heating rate of 3 °C min⁻¹ and a frequency of 1 Hz. Mass spectra were measured using electrospray mass spectrometry (ESMS). The intrinsic viscosities of the copolymer solutions were determined in a 0.5 g dL⁻¹ DMAc solution using an Ubbelohde capillary viscometer at 30 ± 1 °C. Mechanical properties were determined using an Instron-1211 mechanical tester at a speed of 5 mm min⁻¹ at room temperature.

The IEC values of the membranes were obtained via titration. The membranes containing OH⁻ ions were immersed in 100 ml of 0.1 mol L⁻¹ HCl standard for 48 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator.

The water uptake of the membranes in the hydroxide form was measured at different temperatures. The anion exchange membranes were dried under vacuum in an oven and were then immersed in deionized water for 4 h. The membrane was removed from solution and immediately wiped with tissue paper prior to measuring its mass. Water uptake was calculated from Eq. (1)

$$\text{Water uptake(\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

where W_w and W_d represent the weights of the wet and dry membrane, respectively.

The swelling ratio representing the dimensional change of the dry and wet membranes was obtained from Eq. (2)

$$\text{Swelling ratio(\%)} = \frac{L_w - L_d}{L_d} \times 100 \quad (2)$$

where L_d and L_w are the length of the dry and wet membrane, respectively.

The hydroxide conductivities (σ , mS cm^{-1}) of all of the anion exchange membranes ($1 \text{ cm} \times 4 \text{ cm}$) were obtained using the equation $\sigma = d/L_s W_s R$ (where d represents the distance between reference electrodes, and L_s and W_s represent the thickness and width of the membrane, respectively). The conductivity measurements were conducted under previously published conditions [6]. Ohmic resistance (R) was measured using four-point probe alternating current (ac) impedance spectroscopy with an electrode system connected with an impedance/gain-phase analyzer (Solartron 1260) and an electrochemical interface (Solartron 1287, Farnborough Hampshire, ONR, UK). Before measurement, the membranes were sandwiched between two pairs of

gold-plate electrodes. The electrodes and the membranes 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 a given temperature with 10 min intervals until no change in conductivity was observed.

The chemical stability of the membranes was assessed by detecting changes in both the ionic conductivity and ^1H NMR spectra. All of the membrane samples were immersed in 1 mol L^{-1} NaOH solutions at 60°C for a defined period of time.

Performance tests for a single cell were conducted according to the literature [30]. In this procedure, 3 mg cm^{-2} PtRu/C (with 40 wt% Pt and Ru atomic ratio of Pt to Ru $^{1/41:1}$), 1.8 mg cm^{-2} Nafion (5 wt% Nafion solution) were dispersed in an aqueous solution of isopropyl alcohol using ultrasonic treatment. After the suspension was uniformly dispersed, we sprayed it onto carbon paper to form the anode. The cathode was formed by spraying 3.0 mg cm^{-2} Pt/C (with 40 wt% Pt and 1.8 mg cm^{-2} Nafion as a binding agent) onto carbon paper. The effective electrode area of the single cell was 9 cm^2 . The performance of the single cell was measured at 40°C with a Fuel Cell Test System (Arbin Co.). The measurement used 2.0 M CH_3OH solution and 2.0 M

NaOH solutions at a flow rate of 5 ml min⁻¹ and oxygen at a flow rate of 100 ml min⁻¹ at 0.05 MPa. Each single cell was measured three times.

Here, in the preparation and measurement of AEMs, the effect of ambient carbon dioxide on membrane performance is still inevitable. To reduce the membrane contact with carbon dioxide from the air, the wet membranes were kept in the de-ionized water, and the dry membranes obtained by drying in a vacuum oven were stored in a glove box before property measurement.

3. Results and Discussion

3.1 Design and synthesis of DTPPM monomer

Due to the possible attack by nucleophilic OH⁻ on the QA groups and polymer backbone, the long-term operational stability of AEMs under highly alkaline conditions is a major concern. Specifically, the instability of QA groups caused by direct nucleophilic substitution or β -hydrogen elimination needs to be overcome. For tethered QA cation structures, several reports have found that QA groups attached to the polymer backbone via long alkyl chains enhance the ionic conductivity and alkaline stability of the membrane [22]. For example, Hibbs reported that if the linkage between the QA head-groups and the aromatic ring is a hexamethylene interstitial spacer, the membrane stability is obviously improved compared with the membrane containing methylene groups locating between trimethylammonium cations and the aromatic ring [31].

To obtain AEMs with excellent performances, the new monomer DTPPM was firstly synthesized as shown in Scheme 1. This synthesis process avoids the

use of traditional dangerous chloromethylation reagents. The structure of the monomer was identified by ^1H NMR (Fig. 1 (1)), ^{13}C NMR (Fig. 1 (2)) and ESMS spectra (Fig. S1). As shown in Fig. 1, the peaks at 2.04 ppm, 2.71 ppm and 3.34 ppm were assigned to the methylene protons in alkyl chains, and the peak at 3.07 ppm was assigned to the methyl protons in the quaternary ammonium groups. Except for the peak for methylene protons adjacent to the QA groups which completely overlapped with the peak for H_2O , the ratio of methylene and methyl peaks was 2: 2: 9, well-assigned to the expected structure of DTPPM.

Scheme 1. The synthesis process of copolymers s-, m-, l-QPP-co-PAEKs

Fig. 1. ^1H NMR (1) and ^{13}C NMR (2) spectra of monomer DTPPM

3.2 Alkaline stability of DTPPM

The degradation pathways for QA groups are well known to include direct nucleophilic substitution, β -hydrogen Hofmann elimination, and nitrogen ylide formation. Herein, DTPPM was selected as a small molecular model compound to assess the alkaline stability of covalently tethered QA groups. DTPPM was dissolved in a 1.4: 1 solution of CD₃OD /D₂O with 1 mol L⁻¹ NaOD and stored at 60 °C for further measurement. The degradation of DTPPM was quantified using ¹H NMR spectra. Fig. 2 (1) shows the ¹H NMR spectra of DTPPM after exposure to NaOD for 5, 17 and 30 days. After 5 days, the peak at 2.79 ppm disappeared, which can be attributed to the exchange between deuterium and the hydrogen close to the phenyl group (Fig. 2 (2)). After the compound was exposed to NaOD for 17 days, new peaks at 2.09 ppm, 2.22 ppm and 3.13 ppm appeared in the ¹H NMR spectra, indicating approximately 4.8 % degradation. After 30 days of exposure, the intensity of these new peaks increased, indicating approximately 9.4% degradation. Additionally, no new peaks could be found in the aromatic proton area (7.0 - 8.5 ppm) of ¹H NMR spectra (Fig. 2 (1)). This indicates that there was no degradation of carbonyl groups in DTPPM during the alkaline treatment. The mainly reason can be due to the long alkyl space in DTPPM could increase the copolymer's electron density and hydrophobicity, inhibiting the attack from OH⁻. The major degradation route was assigned to aliphatic methylene substitution to form alcohol and trimethylamine, as shown in Fig. 2 (1). The long-chain interstitial spacer is expected to limit the extent of DTPPM degradation in alkaline media. Hofmann elimination was not observed for DTPPM under these testing conditions, which may be attributed to the high electron density

around the β -hydrogens in the alkyl chains.

Fig. 2. The degradation pathways for the model compound DTPPH as well as the stacked overlay of ^1H NMR spectra of DTPPM after immersion in a 1.4: 1 solution of $\text{CD}_3\text{OD} / \text{D}_2\text{O}$ with 1 mol L⁻¹ NaOD at 60 °C for 30 days (1), and the exchange

mechanism between deuterium and hydrogen in DTPPM at room temperature for 60 h (2).

3.3 Synthesis and characterization of QPP-*co*-PAEK copolymers

Using the new hydrophilic monomer DTPPM, s-, m-, and l-QPP-*co*-PAEK copolymers were synthesized by nickel(0)-catalyzed coupling copolymerization of DTPPM and three nonionic dichloride monomers with different hydrophobic block lengths, as shown in Scheme 1. The polymerization yields were all above 98%, and the polymeric structures were confirmed by ^1H NMR spectra and FT-IR spectra. Fig. 3 (1) shows the ^1H NMR spectra of QPP-*co*-PAEK copolymers. The peaks at 1.98 ppm, 2.65 ppm and 3.35 ppm were assigned to the methylene protons in the alkyl chains, despite the overlapping D_2O peak at 3.34 ppm. The peak at 3.06 ppm was assigned to the methyl protons in the quaternary ammonium groups. The integration ratio for methylene and methyl peaks was 2: 2: 9, consistent with the anticipated copolymer structure. The structure of the QPP-*co*-PAEK copolymers in the [hydroxide](#) form was further analyzed by FT-IR spectra (Fig. 3 (2), Fig. S2 and Table (S1)). The band at 2230 cm^{-1} was assigned to the symmetric stretching vibration of nitrile groups in the hydrophobic nonionic segment. The characteristic peaks from 2800 to 3000 cm^{-1} were assigned to the symmetric and asymmetric C-H stretching vibration in methylene and methyl from the hydrophilic segment. FT-IR spectra summarized the characteristic peaks in both the hydrophilic and hydrophobic

segments. The inherent viscosities of the copolymers varied from 1.02 to 1.39 dL g⁻¹, indicating that copolymerization was successful (Table 1).

Fig. 3. ¹H NMR (1) and FT-IR (2) spectra of QPP-co-PAEKs (a) s-QPP-co-PAEK (b) m-QPP-co-PAEK (c) l-QPP-co-PAEK.

Table 1. Mechanical properties and glass transition temperature for QPP-co-PAEK membranes.

Sample	η_{inh}^a (dL g ⁻¹)	TS ^b (MPa)	TM ^b (GPa)	EB ^b (%)	T _{d5%} ^c (°C)	T _g ^d (°C)
s-QPP-co-PAEK	1.02	26.4	0.912	5.0	228.2	202.8
m-QPP-co-PAEK	1.16	40.0	0.900	11.0	240.3	181.8
l-QPP-co-PAEK	1.39	43.1	1.260	8.9	239.4	161.0

^a Measured in DMAc with 0.5 g dL⁻¹ at 25 °C.

^b TS: Tensile strength; TM: Tensile modulus; EB: Elongation at break.

^c T_{d5%}: The T_{d5%} mean the 5% weight loss temperatures.

^d T_g: Glass transition temperature.

3.4 Thermal stability and mechanical properties

The TGA curves of QPP-co-PAEK membranes in the hydroxide form were recorded from 50 to 700 °C under nitrogen atmosphere. As shown in Fig. S3, the stage from 200 to 500 °C is assigned to the degradation of the quaternary

ammonium side chain. The second degradation stage occurred above 500 °C is attributed to the decomposition of the copolymer main chain. The temperatures where 5% weight loss occurred are higher than 228 °C for these copolymers. This is higher than that of QA- or imidazolium- functionalized PAEKs [32] or poly (arylene ether sulfone)s [33] in which QA groups are attached to the backbone in benzylic positions. Therefore, the QPP-*co*-PAEK membranes show good thermal stability, which is important for their application in fuel cells.

Dynamic mechanical properties of the QPP-*co*-PAEK membranes are depicted in Fig. S4, and T_g values are listed in Table 1. The *s*-QPP-*co*-PAEK membrane had the shortest hydrophobic segment and demonstrated the highest rigidity, with a glass transition temperature exceeding 200 °C. The *l*-QPP-*co*-PAEK membrane had the longest hydrophobic segment and exhibited the highest flexibility, where softening began at temperatures above 160 °C. The increase in length of the hydrophobic nonionic segments effectively reduced the T_g values and improved membrane flexibility.

Good mechanical properties are crucial for the preparation of AEMs and the operational durability of AEMFCs. Generally, PPs composed of phenyl-phenyl groups tend to be brittle, even at high temperature or high molecular weight (MW). Furthermore, membranes with low elongation capabilities are not beneficial to electrode assembly. Here, the PP copolymers include a PAEK moiety, and the mechanical strength properties are listed in Table 1. The three membranes showed tensile strengths at ambient humidity ranging from 26.4 to 43.1 MPa, elongation at

break from 5.0 to 11.0%, and Young's modulus ranging from 0.90 to 1.26 GPa. The membrane with longer reinforced PAEK chains showed better tensile strengths. This is possibly from the higher viscosities or molecular weight (MW), and the introduction of polar nitrile groups that enhance the intra/intermolecular interactions in the AEMs, leading to the higher tensile strength of the polymer network structure.

3.5 Morphology of membranes

The morphology of AEMs affects the comprehensive performance of the membrane, including the dimensional stability, hydroxide ion conductivity, alkaline stability, and mechanical properties. The morphologies of AEMs can be controlled by modifying the structure of the copolymer backbone, altering the distribution of ionic groups, and adjusting the membrane forming process. The hydrophilic/hydrophobic structure of the AEMs was investigated using TEM, as shown in Fig. 4 a, b and c. The dark areas represent the hydrophilic ionic clusters containing QA ion groups formed by PtCl_6^{2-} staining, while the bright regions represent hydrophobic moieties composed of copolymer main chains. As shown in the TEM images, 1-QPP-*co*-PAEK membrane exhibits a larger quantity of the ionic clusters, and some ionic clusters are connected slightly. Thus, the increase of the length of the hydrophobic segment from a short hydrophobic chain (Fig. 4 g) to a long hydrophobic chain (Fig. 4 i) can produce more ionic clusters in the TEM images and contribute the connectivity between clusters. In the preparation of QPP-*co*-PAEK copolymers, dichloromonomer 3 (Scheme 1, monomer 3) was used for the construction of the microblock structure, and the formation of continuous ion-conducting channels was attributed to the long

hydrophobic block length. Therefore, the experimental results above demonstrate that altering the block length of the hydrophobic segment can effectively control membrane morphology.

To reveal the relationship between the architecture and morphology of AEMs, atomic force microscopy (AFM) was used to study the morphologies of QPP-*co*-PAEK membranes with hydrophobic nonionic segments of various block lengths. The AFM surface images were obtained on a $1.0 \times 1.0 \mu\text{m}$ area in tapping mode, as shown in Fig. 4 d, e and f. The dark domain in the phase image is the soft, hydrophilic domain, and the bright domain is assigned to the hard, hydrophobic backbones. Hydrophilic/hydrophobic nanophase separation was clearly observed in all membranes. The s-QPP-*co*-PAEK membrane (Fig. 4 d) showed a different connectivity of the ionic domains, wherein the dark regions were dispersed arbitrarily throughout the hydrophobic copolymer matrix and were separated from each other. Notably, by increasing the length of the hydrophobic segment, the ionic domains of AEMs tended to be more interconnected, affording a more distinct phase-separated morphology.

Fig. 4. AFM and TEM micrographs, and hydrophobic segments for membranes (a) (d) (g) s-QPP-co-PAEK, (b) (e) (h) m-QPP-co-PAEK, and (c) (f) (i) l-QPP-co-PAEK.

3.6 Water uptake (WU) and swelling ratio (SR)

IEC values, water uptake and swelling ratios are listed in Table 2. The values of IEC are always lower than the theoretical values, which is possibly the existence of counteranion (chloride, bicarbonate, etc.) in addition to the hydroxide form due to the effect of ambient carbon dioxide on membranes. Water molecules within the membrane facilitate ionic dissociation of the alkali functionalities and promote hydroxide ion transport. Optimizing the water uptake and swelling of AEMs is critical to increase the ionic conductivity and mechanical strength. The water uptake and

swelling ratios for the QPP-*co*-PAEK membranes in the OH⁻ form at different temperatures are listed in Table 2. Due to the hydrophilic unit bearing rigid-rod poly(phenylene) moieties and hydrophobic nonionic segment of the membrane possessing multiple hydrogen bond interactions, water uptake and swelling ratios measured at 60 °C are not remarkably different from those measured at room temperature. In the comparison of the three QPP-*co*-PAEKs, the membrane with a longer hydrophobic chain exhibited higher water uptake and lower swelling ratio. For example, l-QPP-*co*-PAEK exhibited 23.5% water uptake and a 5.6% swelling ratio at 30 °C; the water uptake and the swelling ratio of s-QPP-*co*-PAEK are 18.4% and 8.8%, respectively. As confirmed by AFM and TEM, the membranes with longer hydrophobic segments contained more abundant ion clusters and a more distinct microphase-separated structure. This microphase-separated structure allows more water molecules to be held in the hydrophilic ionic domains, leading to increased water uptake. Inevitably, the strong interaction of the longer hydrophobic segments can hinder rotation of the polymer chains and constrain membrane swelling. Moreover, compared with other types of aromatic AEMs (quaternized PAEKs) reported in the literature, the QPP-*co*-PAEK membranes with similar IECs and hydroxide conductivities showed lower swelling ratios and lower water uptake. QPP-*co*-PAEK membranes with rigid-rod poly(phenylene) moieties as well as the introduction of polar nitrile groups in the hydrophobic nonionic segments reinforces copolymer intra/intermolecular interactions and constrains membrane swelling.

Table 2. IEC, conductivity, water uptake and swelling ratios for QPP-*co*-PAEKs.

Samples	IEC (mequiv g ⁻¹)		Conductivity (mS cm ⁻¹)		Water uptake (%)		Swelling Ratios (%)	
	T ^a	E ^b	60 °C	80 °C	30 °C	60 °C	30 °C	60 °C
s-QPP- <i>co</i> -PAEK	1.60	1.56	14.3	21.7	18.4	22.5	7.8	8.3
m-QPP- <i>co</i> -PAEK	1.60	1.58	19.6	32.1	20.7	24.9	7.1	7.8
l-QPP- <i>co</i> -PAEK	1.60	1.54	21.7	37.6	23.5	27.5	5.6	7.3
QMPAEK-70 [34]	1.54	1.22	16.0	24.1	50.0	62.5	9.0	11.3
PAEK-QTPM-30 [32]	1.58	1.58	-	47.0	91.5	100.0	15.0	29.0
PSf-ImmOH-50 [30]	1.66	1.61	15.0	-	20.0	30.0	15.0	21.0

^a IEC in theoretical values, ^b IEC from titration.

3.7 Ionic conductivity

From Fig. 5, m-QPP-*co*-PAEK and l-QPP-*co*-PAEK AEMs show conductivities above 10 mS cm⁻¹ over the experimental temperature range. As expected, all membrane conductivities increase with temperatures, over a range of 30 °C to 80 °C, due to enhanced water mobility at elevated temperature. Compared with the s-QPP-*co*-PAEK membrane, the m-QPP-*co*-PAEK and l-QPP-*co*-PAEK membranes exhibited higher hydroxide ion conductivities. For example, the l-QPP-*co*-PAEK membrane showed the highest conductivity of 37.6 mS cm⁻¹ at 80 °C, while s-QPP-*co*-PAEK showed the lowest conductivity of 21.7 mS cm⁻¹ under the same conditions (Table 2). The presence of longer hydrophobic segments in the l-QPP-*co*-PAEK backbone facilitated the formation of a more-developed hydrophilic/hydrophobic phase-separation structure, confirmed by AFM and TEM, thereby resulting in more effective hydrophilic channels for hydroxide transport and hydration. Furthermore,

compared with AEMs with polymer main chains composed of poly (arylene ether ketone)s [32, 34] or poly (arylene ether sulfone)s [30], the m-QPP-*co*-PAEK and l-QPP-*co*-PAEK membranes with similar IECs displayed higher ionic conductivity (Table 2). The higher conductivity suggests that QPP-*co*-PAEK with microblock structures contains more ion conduction.

Fig. 5. The temperature dependence of the hydroxide conductivities for QPP-*co*-PAEK membranes.

3.8 Alkaline stability

After the membranes was immersed in 1 M NaOH at 60 °C for certain time, their alkaline stabilities were further analyzed by Fourier-transform infrared spectrum (FT-IR), conductivity, and ^1H NMR spectroscopy. Fig. 6 shows the ^1H NMR spectra of s-, m-, and l-QPP-*co*-PAEK AEMs after exposure to 1 M NaOH at 60 °C for 9, 17 and 30 days. As shown in Fig. 6, new peaks appear at 1.88 ppm, 2.68 ppm and 2.76 ppm, which can be attributed to the degradation of the ionic groups via substitutional displacement. These results are consistent with the degradation mechanism of the monomer. Moreover, Hofmann elimination was not observed over all time ranges.

The m-QPP-*co*-PAEK and l-QPP-*co*-PAEK membranes exhibited greater resistance to alkaline degradation, based on the ratio of *H1*: *H5* in the pendant groups (Fig. 6, 2-4). The degradation resistance of the membranes can also be attributed to their longer hydrophobic chains. As shown in the TEM and AFM analyses (Fig. 4), the m-QPP-*co*-PAEK and l-QPP-*co*-PAEK membranes have more favorable hydrophilic-hydrophobic phase-separation morphologies. The longer nonionic segments around hydrophilic ionic segments inhibit attack from hydroxide groups, leading to decreased membrane degradation compared with s-QPP-*co*-PAEK. With the increase in the block length of the nonionic segments, the concentration of aromatic rings in the hydrophobic phase increases, which further improves the stability of the membrane. On the other hand, l-QPP-*co*-PAEK membrane exhibits higher water uptake and denser ionic clusters, which contribute to increasing the solvation shell of hydroxide ion and correspondingly increase the activation barrier and the free energy ΔG of the transition state for the degradation of cation groups. The retaining of water effectively shields the hydroxide ion and mitigates the attack on the tethered ionic groups [35]. Fig. S5 shows the FT-IR spectra after the membrane samples were immersed in NaOH for 9, 17 and 30 days. The FT-IR spectra of the membranes after 30 days show a slight decrease in the 2232 cm^{-1} nitrile group peak intensity, which may result from hydrolysis of the nitrile groups. Although the polar nitrile groups may be not stable over long periods of time, their existence in the hydrophobic segments may enhance the intra/intermolecular interactions in the copolymers to effectively reduce the water uptake and swelling ratio of the

membranes, which further suppresses the attack of hydroxide ions on hydrophilic groups [36, 37].

Fig. 7 (1) shows the change in hydroxide conductivity over time for the QPP-*co*-PAEK membranes at 80 °C. Over the initial 9-day period, s-QPP-*co*-PAEK showed a continual decline from 21.7 mS cm⁻¹ to 19.8 mS cm⁻¹. When increasing the immersing time in the alkaline solution, s-QPP-*co*-PAEK membrane became brittle and ionic conductivity could not be measured. The possible reason is due to the low molecular weight of the s-QPP-*co*-PAEK (Table 1) and the degradation of the main chain. The new peaks in ¹H NMR spectra in the aromatic proton area from 6.5 ppm to 8.5 ppm emerged (Fig. S6), which could be contributed to the degradation of the main chain. The polar electron-withdrawing nitrile groups could accelerate the hydrolysis of benzonitrile-ether linkages, leading to the degradation of the backbone. Additionally, compared with s-QPP-*co*-PAEK membrane, m-QPP-*co*-PAEK and l-QPP-*co*-PAEK still keep flexible, which is mainly from their better alkaline stability as shown in Fig. 6 and Fig. S6. With the increase of the length of the hydrophobic segments, the dimensional stabilities of these membranes increased, indicating the hydrophobic units of the polymer densely aggregated. The longer and dense nonionic segments around hydrophilic ionic segments contribute to inhibiting the attack from OH⁻, leading to the decrease of the membrane degradation compared with s-QPP-*co*-PAEK. s-QPP-*co*-PAEK also exhibited partial insolubility in the alkaline stability experiments, as shown in Fig. S7, which inhibited additional studies of its molecular structure. For m-QPP-*co*-PAEK and l-QPP-*co*-PAEK, the ionic

conductivity remained constant for 13 days, after which the ionic conductivity slightly decreased. The preserved conductivity in first period was likely a result of membrane swelling caused by the hydrolysis of a small number of the nitrile groups, while the degradation of the ionic groups continued. The decrease in hydroxide conductivity from 13 days to 30 days was largely due to the degradation of the quaternary ammonium ionic groups. Moreover, the conductivity change of m-QPP-co-PAEK during the life test is actually less than that of l-QPP-co-PAEK, which is mainly because of the nitrile groups associated degradation. Judging from hydrophobic segments, l-QPP-co-PAEK has more number of nitrile groups per molecular weight than m-QPP-co-PAEK, leading to more degradation of nitrile groups. To further investigate the extent of degradation in the membranes, we also measured the change in IEC values upon long-term immersion in alkaline solution. As shown in Fig. 7 (2), the IEC values gradually decreased for all QPP-co-PAEK membranes, where the IEC values of s-QPP-co-PAEK was the most reduced. Judging from the changing trend in IEC values, the s-QPP-co-PAEK membrane exhibited lower alkaline stability than either the m-QPP-co-PAEK or the l-QPP-co-PAEK membrane. Based on the analysis above, m-QPP-co-PAEK and l-QPP-co-PAEK exhibited better alkaline stability than s-QPP-co-PAEK. Therefore, controlling the distribution of hydrophilic QA groups in the PP moieties and tuning the block length of hydrophobic nonionic segments are effective methods for improving the hydroxide conductivity and alkaline stability of AEMs.

Fig. 6. The degradation pathways for QPP-co-PAEKs (1), and the ^1H NMR spectra of (2) s-QPP-co-PAEK (3) m-QPP-co-PAEK (4) l-QPP-co-PAEK AEMs after immersed in 1 M NaOH at 60 °C for 30 days.

Fig. 7. (1) The conductivity curves and (2) IEC curves of QPP-co-PAEK AEMs measured at 80 °C after the membrane immersed in 1 M NaOH at 60 °C for 30 days.

3.9 Single fuel cell evaluation

The membrane electrode assembly (MEA) was examined using l-QPP-co-PAEK

due to its high conductivity and alkaline stability compared with s-QPP-*co*-PAEK and m-QPP-*co*-PAEK. A single cell test of a direct methanol alkaline fuel cell was performed according to the method provided in the literature [33]. As shown in Fig. 8, the DMFC assembled with the l-QPP-*co*-PAEK membrane exhibited a peak power density of 12.4 mW cm^{-2} . Compared with our previous work, the DMFC performance of the l-QPP-*co*-PAEK membrane with the lower IEC value of 1.6 exhibited a higher peak power density than a PSf-ImmOH-70 membrane [30] with a higher IEC value of 1.9, which had a peak power density of 6.0 mW cm^{-2} under the same conditions. The open circuit voltage (OCV) is closely related to methanol permeation and it increases when the methanol crossover decreases [38]. Single cells prepared with the l-QPP-*co*-PAEK exhibited high OCVs of 0.76 for 2 M methanol at 40°C . This value is slightly higher than that of PSf-ImmOH-70 (0.70 V). The better cell performance of the l-QPP-*co*-PAEK membrane was mainly due to its higher conductivity and lower methanol permeation.

Fig. 8. Polarization and power density curves of AMFC assembled with l-QPP-*co*-PAEK membrane measured at 40°C .

4. Conclusions

We designed and synthesized a series of quaternized poly (*p*-phenylene-*co*-aryl ether ketone)s (s-, m-, and l-QPP-*co*-PAEK) via a nickel-catalyzed coupling reaction. The environmentally friendly and low-cost synthetic route avoids the use of hazardous chloromethylation reagents and provides good control of the IEC and location of QA groups in the copolymers. The l-QPP-*co*-PAEK copolymer exhibited more distinct hydrophilic-hydrophobic phase separation and more aggregated ionic clusters, as shown by AFM and TEM analyses. This in turn produced flexible and mechanically durable AEMs with high conductivities (hydroxide conductivity of 37.6 mS cm⁻¹ at 80 °C) compared with AEMs made of m-QPP-*co*-PAEK (32.1 mS cm⁻¹ at 80 °C) and s-QPP-*co*-PAEK (21.7 mS cm⁻¹ at 80 °C). The introduction of long hydrophobic nonionic segments into the copolymer backbone constrains membrane swelling and maintains the membrane dimensional stability. The ¹H NMR spectra, FT-IR spectra and hydroxide conductivity indicated that the m-QPP-*co*-PAEK and l-QPP-*co*-PAEK membranes exhibited better alkaline stability (in 1 M NaOH at 60 °C for 30 days) compared with s-QPP-*co*-PAEK. Therefore, controlling the distribution of hydrophilic QA groups in PP moieties and tuning the block length of hydrophobic nonionic segments are effective methods for improving the hydroxide conductivity and alkaline stability of AEMs.

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