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Copolymers Composed of Perfluoroalkyl and Ammonium-functionalized Fluorenyl Groups as Chemically Stable Anion Exchange Membranes

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Abstract

We report synthesis and properties of a novel series of ammonium-functionalized perfluoroalkylene/aromatic copolymers. In particular, effect of number and position of ammonium groups on the properties of the copolymer thin membranes was investigated. Fluorenylidene biphenylene groups were used as a scaffold for the ammonium groups. By controlling the chloromethylation reaction conditions, the ammonium groups could be introduced up to 4.0 per fluorenylidene biphenylene unit, resulting in the ion exchange capacity (IEC) of the resulting copolymers ranging from 1.0 to 1.8 meg g^{-1} . The copolymers provided bendable and transparent membranes by solution casting. The membranes exhibited phase-separated morphology based on the hydrophilic/hydrophobic differences in the copolymer components. The copolymer membrane with IEC = 1.0 meq g^{-1} showed high hydroxide ion conductivity (ca. 70 mS cm⁻¹) at 80 °C in water and good alkaline stability in 1 M KOH aq. over 1000 h at 60 °C. The membrane showed only minor degradation after the long-term alkaline stability test.

1. Introduction

Anion exchange membranes (AEMs) have attracted much attention for applications to energy devices such as electrodialysis¹, redox flow batteries², electrolyzers³, and fuel cells⁴. In particular, alkaline fuel cells using AEMs offer advantages over those with proton exchange membranes; alkaline fuel cells could use non-precious metals (Ni, Co, Fe etc.) as electrocatalysts⁵. However, chemical stability and anion conductivity of the existing AEMs do not meet the criteria for practical use. In order to address these issues, a wide variety of polymer structures such as poly(arylene ether)s⁶ and polystyrenes⁷ functionalized with quaternary ammonium groups have been studied. Ammonium-substituted hydrophilic groups are the key components both for the conductivity and stability of the AEMs.

Cardo structures such as phenolphthalein and fluorene derivatives seem attractive as a scaffold for the ammonium groups because multiple ammonium groups could be easily substituted on them. In addition, because of their bulky structures, a large free volume forms in the polymer membranes serving as an ion-conducting pathway.⁸ For example, Liu et al.⁹ reported poly(arylene ether sulfone) containing phenolphthalein or fluorene groups with up to four ammonium groups per cardo unit that showed high hydroxide

ion conductivity in water. Lin et al.¹⁰ also reported that poly(fluorene arylene ether sulfone) with pendant imidazolium ions exhibited high hydroxide ion conductivity (ca. 60 mS cm⁻¹) and good chemical stability in 1 M KOH at 60 °C for 400 h. We have also developed a series of AEMs based on fluorene-containing poly(arylene ether)s.¹¹ The combination of high ammonium density (each aromatic ring in the fluorenylidene biphenylene unit was functionalized with an ammonium group) and block copolymer structure provided highly anion conductive AEMs. The resulting AEMs (QPE-bl-1) exhibited high ion conductivity (144 mS cm⁻¹ at 80 °C in water) and good fuel cell performance with no precious metal catalysts. The maximum power density of the fuel cell with QPE-bl-1 AEM was 297 mW cm 2 at a current density was 826 mA cm⁻².¹² However, chemical stability of the QPE-bl-1 AEMs was not sufficient and degraded in strongly alkaline conditions.

More recently, we have developed another series of AEMs (QPAF-1) containing perfluoroalkyl groups in the polymer main chain.¹³ Because of the absence of heteroatom linkages (e.g., ether and sulfone) in the polymer main, QPAF-1 AEMs were much more alkaline durable and no mechanical failure was observed during the accelerated alkaline stability test for 1000 h. The objective of the present study is to combine the structure of QPE-bl-1 and QPAF-1 copolymers and to evaluate the effect of the ammonium-functionalized fluorenyl and perfluoroalkyl groups on the properties of the resulting QPAF-2 AEMs. Synthesis, structural analyses, and properties measurements (hydroxide ion conductivity, mechanical strength, alkaline stability) were investigated in detail. Two different monomers, 9,9-bis(4-chlorophenyl)fluorene (p-BCF) and 9,9-bis(3-chlorophenyl)fluorene (m-BCF), were used in order to evaluate the effect of the linking positions in the main chain on the polymer properties.

2. Experimental

Materials. 9,9-Bis(4-aminophenyl)fluorene (> 98%, TCI), 9,9-bis(4-amino-3-chlorophenyl)fluorene (> 97%, TCI), hydrochloric acid (35-37%, Kanto Chemical), sodium nitrite (> 98.5% TCI), copper(I) chloride (> 95%, Kanto Chemical), acetic acid (> 99.7%, Kanto Chemical), phosphinic acid (30-32%, Kanto Chemical), 2,2'-bipyridine (> 99%, TCI), bis(1,5-cyclooctadiene)nickel(0) (Ni(cod)₂) (> 95%, Kanto Chemical), *N*,*N*-dimethylacetamide (DMAc) (> 99%, Kanto Chemical), chloromethyl methyl ether (CMME) (> 95%, TCI), 0.5 M zinc chloride (ZnCl₂) in THF solution (TCI), 1,1,2,2-tetrachloroethane (TCE) (> 98%, Kanto Chemical), and 45 wt% trimethylamine (TMA) aqueous solution (Aldrich) were used as received. Bis(3-chlorophenyl)perfluorohexane (PAF monomer) was synthesized according to the literature.¹³

Synthesis of 9,9-Bis(4-chlorophenyl)fluorene (p-BCF). А 500 mL one neck round-bottomed flask equipped with a magnetic stirrer bar was charged with 9,9-bis(4-aminophenyl)fluorene (BAF: 16.5 g, 47.2 mmol) and 6% hydrochloric acid (190 mL). To this white suspension, sodium nitrite (7.84 g, 114 mmol) aqueous solution (25 mL) was added. The mixture was stirred at room temperature and the solid was gradually dissolved to afford an orange solution. The resulting solution was added dropwise to the mixture of copper(I) chloride (16.8 g, 170 mmol) and concentrated hydrochloric acid (130 mL). During the addition of diazonium salt, a yellow solid was precipitated with an evolution of gas. After stirring overnight, the resulting solid was dissolved in EtOAc and the layers were separated. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with deionized water and diluted hydrochloric acid, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 19/1) to afford *p*-BCF as a white solid (10.8 g, 59% yield). ¹H and ¹³C NMR spectra of the obtained solid are shown in Figure S1. ¹H NMR (500 MHz, CDCl₃): δ 7.12 (d, J = 8.1 Hz, 4H), 7.20 (d, J = 8.1 Hz, 4H), 7.29 (dd, J = 7.6, 7.6 Hz, 2H), 7.35 (d, J = 7.6 Hz, 2H), 7.39 (dd, J = 7.6, 7.6 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 64.4, 120.4, 125.8, 127.9, 128.0, 128.5, 129.4, 132.8, 140.0, 144.0, 150.3.

Synthesis of 9,9-Bis(3-chlorophenyl)fluorene (m-BCF). A 300 mL one neck round-bottomed flask equipped with a stirrer charged magnetic bar was with 9,9-bis(4-amino-3-chlorophenyl)fluorene (10.0 g, 24.0 mmol), acetic acid (88 mL), deionized water (38 mL) and concentrated hydrochloric acid (10 mL). To this white suspension, sodium nitrite (3.91 g, 56.7 mmol) aqueous solution (12.6 mL) was added. The mixture was stirred at room temperature and the solid was gradually dissolved to afford an orange solution. To the resulting diazonium salt solution, phosphinic acid (32~34%, 70 mL) was added. During the addition of phosphinic acid, an orange solid was precipitated with an evolution of gas. After stirring for 24 hours, the resulting solid was recovered by filtration and dissolved in EtOAc. This EtOAc solution was washed with saturated aqueous solution of sodium hydrogen carbonate, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 19/1) to afford *m*-BFC as a white solid (7.01 g, 76% yield). 1 H and ¹³C NMR spectra of obtained solid are shown in Figure S2. ¹H NMR (500 MHz, CDCl₃): δ 7.09 (m, 2H), 7.12 (m, 2H), 7.17 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.20 (m, 2H), 7.29 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.37 (d, J = 7.3 Hz, 2H), 7.39 (dd, J = 7.3, 7.3 Hz, 2H), 7.77 (d, J = 7.3 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 64.9, 120.4, 126.0, 126.3, 127.1, 127.9, 128.0 (C*2), 129.6, 134.2, 140.0, 147.4, 149.6.

Synthesis of Precursor Copolymers (PAF-2). Precursor copolymers were synthesized by Ni promoted Ullmann coupling reaction. A typical procedure is as follows. PAF monomer 1.879 g (3.60 mmol), *p*- or *m*-BCF 0.457 g (1.19 mmol), 2,2-bipyridine (*para* : 1.495 g, 9.57 mmol, *meta* :

1.869 g, 11.9 mmol), DMAc (*para* : 9.6 mL, *meta* : 12 mL) were charged in 100 mL three-necked flask with nitrogen inlet. The mixture was heated at 80 °C and stirred until complete dissolution. Then, Ni(cod)₂ (*para*: 2.634 g, 9.57 mmol, *meta* : 3.291 g, 11.9 mmol) was added to the mixture, and heated at 80 °C for 3 h. After the reaction, the mixture was poured into 300 mL of methanol to precipitate a black powder. The crude product was stirred in concentrated hydrochloric acid overnight, washed with water and methanol several times, and dried at 50 °C in vacuum oven overnight to obtain the product as a white powder (PAF-2) in 85% yield.

Chloromethylation of PAF-2. The chloromethyl groups were introduced in the precursor copolymers by Friedel-Crafts reaction. A typical procedure is as follows. A pressure proof bottle was charged with PAF-2 (0.2 g), TCE (1.3 mL, 0.1 M biphenylfluorene unit in PAF-2), CMME (2.3 mL, 240 equimolar to biphenylfluorene unit in PAF-2) and heated at 80 °C to dissolve the solid. Then, ZnCl₂ solution (0.25 mL, equimolar to biphenylfluorene unit in PAF-2) was added into the mixture. After 5 days reaction, the mixture was poured into 200 mL of methanol to precipitate a product. The crude product was washed with water and methanol several times and dried at 40 °C in vacuum oven overnight to obtain a pale yellow powder (CMPAF-2).

Membrane Preparation and Quaternization of CMPAF-2. A typical procedure is as follows. CMPAF-2 (0.9 g) was dissolved in 9.0 mL of DMAc. After filtration with a syringe stuffed with cotton, the obtained homogeneous solution was cast onto the flat glass plate. The solution was dried at 50 °C overnight to obtain a transparent pale yellow membrane. The resulting membrane was soaked in 5 wt% TMA aqueous solution for 48 h at 40 °C, washed with 1 M HCl and water to obtain a transparent pale brown membrane (QPAF-2).

Measurements. ¹H (500 MHz), ¹³C (125 MHz), and ¹⁹F (471 MHz) NMR spectra were obtained on a JEOL JNM-ECA/ECX500 using deuterated chloroform (CDCl₃), 1,1,2,2-tetrachloroethane (TCE- d_2), or dimethyl sulfoxide $(DMSO-d_6)$ as a solvent and tetramethylsilane (TMS) as an internal reference. The molecular weight was estimated by a gel permeation chromatograph (GPC) equipped with Shodex K-805 L columns and a Jasco 805 UV detector (270 nm) with DMF containing 0.01 M LiBr as an eluent. The molecular weight was calibrated with polystyrene standards. Ion exchange capacity (IEC) was estimated by titration in a method reported in the literature.¹³ Scanning transmission electron microscopic (STEM) images were taken for membrane samples stained with tetrachloroplatinate ions on a Hitachi HD-2700 with an accelerating voltage of 200 kV. Small angle X-ray scattering (SAXS) data were obtained using a Nano-Viewer (Rigaku) equipped with а temperature/humidity controlled chamber. Cu Ka ($\lambda = 0.154$ nm) was used as an X-ray source. The scattering patterns were collected using a Rigaku high speed 2D detector PILATUS 100K/R. The SAXS measurement was performed at 40 °C under humidified N2 atmosphere at 30-90% RH. The AEMs in the chloride-ion forms were placed in an SAXS cell and equilibrated in the humidified N2 for 2 h before each measurement. Properties of QPAF-2 membranes such as hydroxide ion conductivity and mechanical properties were measured according to the methods in the literature.¹³ The hydroxide ion conductivities of the membranes were measured

in carefully degassed and deionized water (18 M Ω) to preclude the effect of carbon dioxide from the atmosphere.

3. Results and Discussion

Synthesis of Quaternized Copolymers (QPAF-2). QPAF-2 was synthesized as shown in Scheme1. The precursor copolymers (PAF-2p, m) were synthesized by Ni-promoted polycondensation reaction of PAF-monomer and p-BCF or *m*-BCF. The copolymerization reaction proceeded successfully as evidenced by NMR and GPC measurements. In the ¹H NMR spectra (Figure 1a and 2a), peaks at 7.6 and 7.7 ppm were assigned to the aromatic protons derived from PAF component and the other peaks were assigned to those derived from BCF component, respectively. The copolymer compositions were calculated from the integral ratios to be m : n = 1.00 : 0.33 (PAF-2p) and 0.35 (PAF-2m), which were in fair agreement with the feed comonomer ratio (m : n = 1.00: 0.32). The molecular weights of the copolymers estimated from the GPC analysis were $M_{\rm n} = 22.4 - 28.3$ kDa and $M_{\rm w} =$ 100 - 125 kDa, respectively (Table 1), which were high enough to form self-standing membranes by solution casting. The polydispersity indices (M_w/M_p) were 4.4 - 4.7, typical for this kind of polycondensation reaction.

The Friedel-Crafts chloromethylaion reaction of the precursor copolymers (PAF-2p, m) was carried out with CMME using $ZnCl_2$ as a Lewis acid catalyst.¹⁴ To control the chloromethylation reaction, effect of several parameters including the reaction temperature and concentration of the reactants (BCF and CMME) were carefully investigated. Under the tested conditions, the obtained products were soluble in many organic solvents implying no or little cross-linking reaction. In addition, phenylene groups attached to the perfluoroalkyl groups (derived from PAF) were intact as evidenced by the ¹H NMR spectra (Figure 1b and 2b). The degree of chloromethylation (DC) per BCF unit was estimated from the integral ratio of the aromatic peaks (7.0-8.0 ppm) to methylene peaks of the introduced chloromethyl groups (4.6-5.0 ppm). The peaks at lower magnetic field (ca. 4.0-4.5 ppm) were assignable to chloromethyl groups on the main chain and those at higher magnetic field were chloromethyl groups on fluorenyl groups. The chloromethyl groups were substituted on the fluorenyl groups at the early stage of the reaction, and then on the main chain as the reaction proceeded. Polymer (or BCF) concentration was the most crucial to determine the DC (Table 2). The highest DC value (4.0) was achieved under the concentrated conditions with QPAF-2p, in which each aromatic ring of BHF unit was substituted with a chloromethyl group. CMPAF-2s were cast from DMAc solution to obtain thin and bendable membranes, which were then quaternized by typical Menschutkin reaction with trimethylamine (TMA) aqueous solution. The resulting membranes were soluble in polar organic solvents such as DMSO and DMAc, but not in nonpolar solvents such as chloroform and TCE. The quaternization reaction was confirmed by the appearance of the methyl protons (ca. 3.0 ppm) in the ¹H NMR spectra of the products (Figure 1c and 2c). Complete quaternization was confirmed from the integral ratio of the aromatic peaks (7.0-8.0 ppm) to the methyl peaks (ca. 3.0 ppm) for all samples. The IEC values obtained by titration were comparable to those estimated from the ¹H NMR spectra within acceptable errors (Table 2).



QPAF-2 (R = H or $CH_2N^+Me_3 OH^-$)

Scheme 1. Synthesis of QPAF-2. **Table 1.** Composition and molecular weight of PAF-2.

| Polymer | Composit | Molecular weight | | | |
|---------|-------------|-----------------------|----------------------------|-----------------------------------|-------------------------|
| | Feed | Obtained ^a | $\frac{M_{\rm n}}{(10^3)}$ | $M_{\rm w}$ (10 ³) | ${M_{ m w}}/{M_{ m n}}$ |
| PAF-2p | 1.00 : 0.32 | 1.00 : 0.33 | 28.3 | 125 | 4.4 |
| PAF-2m | 1.00 : 0.32 | 1.00 : 0.35 | 22.4 | 105 | 4.7 |

^a Obtained by the ¹H NMR spectra.

Table 2. Chloromethylation reaction conditions, DC, and IECof QPAF-2.

| Polymer | Chloromethylation conditions | | | 2 | IEC (meq g^{-1}) | |
|-------------|------------------------------|------------|-------------------|-----|---------------------|------------------------|
| | Temp. (°C) | BCF (M) | CMME (eq./BCF) | DC" | NMR ^b | Titration ^c |
| QPAF- 2p | 50 | 0.01 | 80 | 1.7 | 1.0 | 1.0 |
| | 80 | 0.01 | 240 | 2.0 | 1.1 | 1.1 |
| | 80 | 0.05 | 240 | 3.0 | 1.5 | 1.5 |
| | 80 | 0.1 | 240 | 4.0 | 2.0 | 1,8 |
| QPAF- 2m | 50 | 0.01 | 80 | 1.7 | 1.0 | 1.0 |
| | 80 | 0.01 | 240 | 2.0 | 1.2 | 1.2 |

^a Degree of chloromethylation calculated from the integral ratio of the aromatic peaks to methylene peaks in the ¹H NMR spectra. ^b Calculated from the ¹H NMR spectra of CMPAF-2 assuming complete quaternization reaction. ^c Determined by titration.



Figure 1. ¹H NMR spectra of (a) PAF-2p, (b) CMPAF-2p, and (c) QPAF-2p.

Morphology. Morphology of QPAF-2p (IEC = 1.1, 1.0, and 1.8 meq g⁻¹) membranes was observed by STEM (Figure 3). The membranes with IEC = 1.1 and 1.0 meq g⁻¹ exhibited similar phase-separated morphology with hydrophilic (dark areas) and hydrophobic (bright areas) domains of ca. 5 to 10 nm in width. In contrast, QPAF-2p membrane with higher IEC (1.8 meq g⁻¹) and higher DC (= 4) contained smaller hydrophilic and hydrophobic domains. In addition to the larger ones (ca. 5 to 8 nm), smaller and spherical hydrophilic domains (1 to 2 nm in diameter) were also observed within the hydrophobic domains. It is considered that ammonium groups on the rigid polymer main chains did not contribute much to the development of the phase separation but caused such unique morphology.



Figure 2. ¹H NMR spectra of (a) PAF-2m, (b) CMPAF-2m, and (c) QPAF-2m.

Then, effect of humidity on the morphology was investigated via SAXS measurements for QPAF-2p with IEC = 1.0 meq g^{-1} (Figure 4). The membrane showed a clear ionomer peak at d = 8-9 nm at 30% RH, which developed more as increasing the humidity. The periodic structure observed by SAXS patterns could be reasonably related with the hydrophilic domains. The domain sizes obtained by SAXS curves were similar to or slightly larger than those in STEM images because of the swelling with the absorbed water. Compared to our previous AEMs (QPAF-1)¹³ sharing the same perfluoroalkylene hydrophobic components but oligophenylene hydrophilic components, the hydrophilic domains of QPAF-2 were larger probably because of the bulky fluorenyl groups as a scaffold for the ammonium groups.



Figure 3. STEM dark-field images of QPAF-2p (a) DC = 2.0, IEC 1.1 meq g^{-1} , (b) DC =1.7, IEC 1.0 meq g^{-1} , (c) DC = 4.0, IEC 1.8 meq g^{-1} membranes in PtCl₄²⁻ ion forms.

Hydroxide Ion Conductivity. Hydroxide ion conductivity of the QPAF-2 membranes were measured in water at 30 °C and plotted as a function of IEC in Figure 5. Unlike typical AEMs that show higher ion conductivity with higher IEC, the conductivity of QPAF-2 membranes was less dependent on IEC and nearly constant. QPAF-2p and -2m membranes exhibited similar conductivity and its IEC dependence. The highest conductivity (55 mS cm⁻¹) was obtained for QPAF-2p with IEC = 1.5 meq g^{-1} . The results suggest that the ammonium groups substituted on the main chain contributed less to the hydroxide ion conduction, than those on the fluorenyl groups. The ammonium groups on less hindered fluorenyl groups are more likely to participate in hydroxide ion conduction. As discussed above in the STEM images, the ammonium groups on the main chains (in the case of DC = 4) contributed less to the development of the hydrophilic domains and thus the hydroxide ion conduction. Similar behavior was observed in our poly(arylene ether)-based AEMs containing quaternized fluorenyl groups.¹⁵

Temperature dependence of the hydroxide ion conductivity of the selected QPAF-2 membranes in water is shown in Figure 6. The conductivity showed approximate Arrhenius type temperature dependence. Both membranes exhibited ca. 70 mS cm⁻¹ of hydroxide ion conductivity at 80 °C. The apparent activation energies calculated from the slopes were $E_a = 12.6$ and 11.5 kJ mol⁻¹ for QPAF-2p (IEC = 1.0 meq g⁻¹) and -m (IEC = 1.0 meq g⁻¹), respectively. These values were similar to those of our previous AEMs sharing the perfluoroalkylene groups or quaternized fluorenyl groups,^{13,15} indicating that these membranes shared similar ion conduction mechanism involving the migration of hydrated hydroxide ions.



Figure 4. Humidity dependence of SAXS patterns of QPAF-2p (DC = 1.7, IEC 1.0 meq g^{-1}) membrane in Cl⁻ ion form at 40 °C.



Figure 5. Hydroxide ion conductivity of QPAF-2 membranes in water at 30 °C as a function of IEC.



Figure 6. Temperature dependence of the hydroxide ion conductivity of QPAF-2 membranes in water.



Figure 7. DMA profiles of QPAF-2 (in Cl⁻ form) membrane at 60% RH as a function of temperature.



Figure 8. Time course of the hydroxide ion conductivity of QPAF-2m (IEC = 1.0 meq g^{-1}) membrane in 1 M KOH aqueous solution at 60 °C.



Figure 9. IR spectra of QPAF-2m (IEC = 1.0 meq g^{-1}) membrane before and after the stability test; (a) 4000-500 cm⁻¹ and (b) 2000-500 cm⁻¹.

Mechanical Properties. The mechanical properties of QPAF-2 membranes were evaluated by dynamic mechanical analyses (DMA) at 60% RH from room temperature to 95 °C (Figure 7). QPAF-2p membrane showed slightly higher storage moduli than those of -2m membrane probably because of the symmetric 1,4-phenylene main chain structure in the hydrophilic component. Both membranes exhibited a peak at ca. 60-70 °C in loss moduli. Compared to our previous AEMs containing the same hydrophobic but different hydrophilic (ammonium-substituted phenylene) groups (QPAF-1), the peaks appeared at lower temperature for QPAF-2 membranes than for QPAF-1 membrane (ca. 85 °C), indicating that quaternized fluorenyl groups were responsible for the DMA properties.

Alkaline Stability. The alkaline stability of QPAF-2m (IEC = 1.0 meq g⁻¹ in Cl⁻ form) membrane was examined in 1 M KOH aqueous solution at 60 °C (Figure 8). During the test, ion exchange reaction (from Cl⁻ to OH⁻) and degradation could occur competitively with counteractive effects on the ion conductivity. Nevertheless, the QPAF-2m membrane exhibited high alkaline stability with no practical loss in the conductivity after 1100 h. The conductivity after the test was 26 mS cm⁻¹, which was comparable to or higher than that of the initial membrane. The post-test membrane retained its shape and flexibility. The results suggest that the QPAF-2m membrane did not experience severe degradations under the tested conditions.

However, since the post-test membrane became insoluble, FT-IR spectrum was measured (Figure 9). The peaks at 2850-3000 cm⁻¹ assignable to aliphatic C-H stretching vibration and at 3000-3100 cm⁻¹ assignable to aromatic C-H stretching vibration did not change after the stability test. In addition, the broad and large peak at 3200-3500 cm⁻¹ assignable to OH stretching vibration did not change after the test. The results suggest that both polymer main chain and ammonium groups hardly decomposed. IEC of the post-test membrane was measured by titration. The residual IEC was 0.95 meq g⁻¹ (95% remaining). Furthermore, the mechanical properties were measured (Figure 10). The DMA curves showed minor changes after the stability test. The peak temperature in loss moduli was similar, reflecting the

chemical stability of the polymer main chain. Nevertheless, the change in the solubility after the test might be caused by minor chemical changes such as cross-linking via a slight decomposition of the ammonium groups.



Figure 10. DMA profiles of QPAF-2m (in Cl⁻ forms) membrane before and after the alkaline stability test, at 60% RH as a function of temperature.

4. Conclusion

In order to improve the properties of anion conductive membranes, a novel series of ammonium-functionalized perfluoroalkylene/aromatic copolymer (QPAF-2) membranes were designed and synthesized. Effects of the ionic density and its position substituted on fluorenylidene biphenylene group on the properties were studied in detail. Unlike the conventional AEMs, high ionic density or high IEC did not contribute to the development of the phase-separated morphology and hydroxide ion conductivity for the QPAF-2 membranes. The results suggest that the ammonium groups on less hindered fluorenyl groups functioned better as ion exchange groups than those on the polymer main chains. Accordingly, the QPAF-2 membrane with DC =2 and IEC = 1.0 meq g^{-1} exhibited high hydroxide ion conductivity in water. Because of the absence of heteroatom linkages (e.g., ether, sulfide, and sulfone) in the polymer main chains, QPAF-2 membrane was chemically stable with practical no changes in the ion conductivity and chemical structure after 1000 h alkaline stability test in 1.0 M KOH at 60 °C.

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Graphical Abstract

Copolymers Composed of Perfluoroalkyl and Ammonium-functionalized Fluorenyl Groups as Chemically Stable Anion Exchange Membranes

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A novel series of ammonium-functionalized perfluoroalkylene/aromatic copolymers were designed and synthesized. The obtained membrane with 1.0 meq g⁻¹ of ion exchange capacity exhibited high hydroxide ion conductivity (ca. 70 mS cm⁻¹) at 80 °C in water and good alkaline stability in 1 M KOH aq. over 1000 h at 60 °C.

