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Description	

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Alkaline stability of ether bond free fluorene-based anion exchange polymer containing cycloaliphatic quaternary ammonium groups

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ABSTRACT

Quaternary piperidinium cation was incorporated into aryl-ether-bond-free fluorene-based polymer by flexible alkyl side chains to synthesize a highly conductive and chemically stable anion exchange membrane (AEM). The membrane of the OH^- form shows good solubility in dimethyl sulfoxide and methanol but not soluble in water. In a fully hydrated state, the OH^- conductivity reached 58 mS cm^{-1} at 80 °C. The results of ^1H NMR spectra revealed that the alkyl-substituted N-methylpiperidinium cationic group was excellent alkaline stable as only 13% cationic group was degraded after 168 h storage in 1 M NaOH solution at 80 °C.

Keywords: Anion exchange membrane, alkaline stability, polyfluorene, quaternary ammonium, degradation

1. Introduction

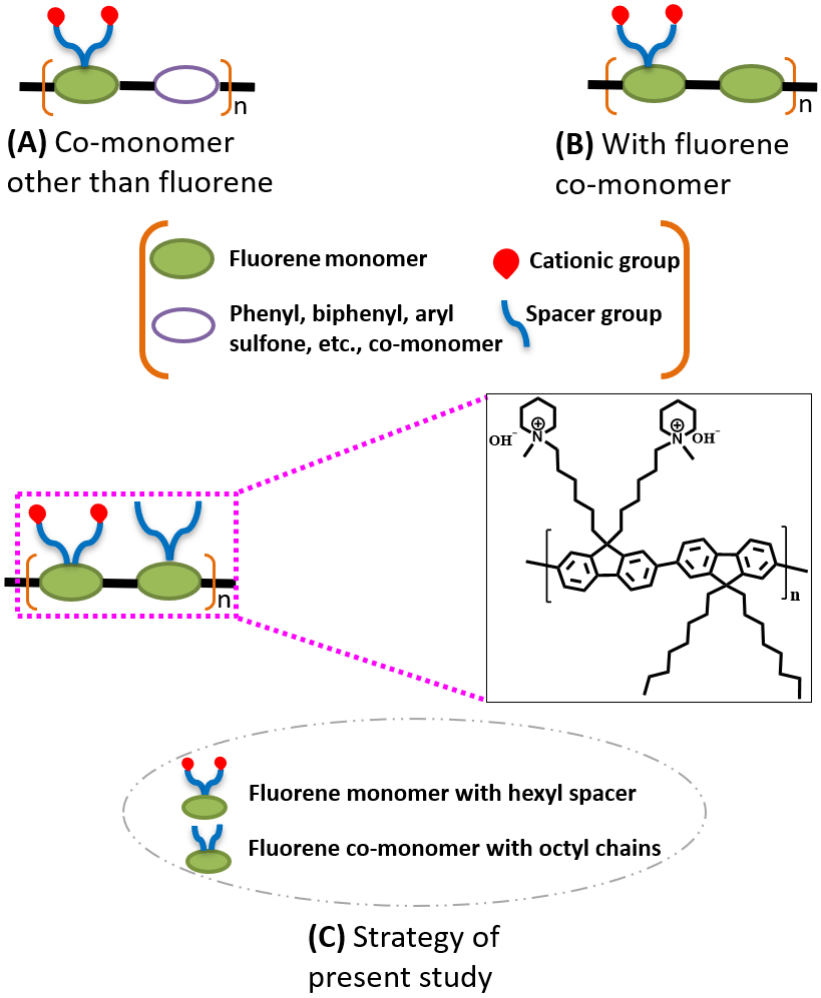
Due to our modern lifestyle, the demand for energy is increasing day by day. In recent years, worldwide attention is growing on the conversion and storage of electricity from renewable energy to protect the environment and depletion of fossil fuel [1]. Alkaline anion exchange membrane fuel cells (AEMFCs) generate electricity directly from the stored energy in fuels, for example, MeOH, H_2. AEMFCs do not rely on the platinum catalyst, and the kinetics of oxygen reduction reaction is faster in comparison to the other sorts of fuel cells [2]. So researchers are extensively motivated to develop catalyst materials and membranes for AEMFCs [3-9]. In the AEMFCs, a molecular design is one of the main challenges to synthesize the new AEM with high durability, high ionic conductivity, and longtime alkaline stability at 80 ^{o}C [10].

In AEMFCs, the attack of nucleophilic OH^- degrades the cationic groups and the polymer backbones of AEMs. For example, if polymer backbones contain electron-withdrawing sulfone and/or ketone groups, these groups stimulate the nucleophilic attack by OH^- groups and resulting in chain scission of backbones [11, 12]. On the other hand, AEMs without electron-withdrawing sulfone and/or ketone groups, for example, polyphenylene oxide (PPO), are practically stable in the alkaline environment [13]. Polymers without aryl ether links, for instance, polyarylene alkylenes [12, 14-16] and

polyphenylenes [17] are potentially even more stable. Lee *et al.* and Hibbs *et al.* [14, 18-21] synthesized some AEMs without any aryl-ether-bond in the main chain and observed much improved alkaline stability.

Aromatic backbones containing fluorenyl groups have attracted much attention due to the possibility of diverse chemical modifications. Before the polymerization reaction, alkyl or dialkyl groups are introduced to the C-9 position of the fluorene to increase the solubility of the polymer. The water uptake (WU) plays an important role in ionic conductivity. Adequate amounts of WU are necessary for the formation of a hydrated ionic domain and faster ionic migration through the membrane. Bulky fluorene groups could force each polymer chain apart and enhance free volumes or interchain separations in which water molecules might be confined [22, 23]. AEMs containing fluorenyl groups not only exhibited high thermal and alkaline stability but also have high ionic conductivity [24, 25]. Bae *et al.* reported that aryl-ether-bond free polyfluorene AEMs were stable for 30 days in 1 M NaOH solution at 80 ºC [19]. In this study we have chosen a similar type of aryl-ether-bond free polyfluorene backbone as in alkaline conditions it can provide high alkaline stability. And can reduce excessive swelling and water uptake of the AEMs due to higher chain rigidity of polyfluorene backbone. There are some reports of the literature containing fluorenyl group as one of the monomers as shown in Scheme 1A

[26-29] but polyfluorene based literature is rare which contains fluorene as both monomer and comonomer (Scheme 1B).



Scheme 1. Different design strategies of polyfluorene AEMs.

For the design of side chains and cations, long alkyl tethered cationic groups show more thermal stability than benzyl tethered cationic groups under alkaline conditions [30]. So, in our research we have chosen one monomer containing two bromohexyl chains which act as a scaffold for the cationic group as shown in Scheme 1C. A co-monomer containing two octyl chains has been employed as the IEC can be controlled, the solubility

of the polymer can be increased and the flexibility of the membrane can be enhanced.

For the selection of cations as our AEM, often the serious problem is the degradation of quaternary ammonium (QA) cations by several different pathways, such as different rearrangement reactions, Hofmann (β) elimination, and nucleophilic substitution [8]. The degradation pathway is dominated by the cationic structure, and how the cationic group is incorporated into the polymer backbone. Therefore, numerous cationic groups including modified tetraalkylammonium, imidazolium, benzimidazolium, guanidinium, and pyridinium have been extensively studied [8, 30-36]. Some heterocycloaliphatic QA cationic groups have been reported as predominantly long-lived in alkaline conditions. In a systematic study, Marino and Kreuer found a longer half-life time of piperidinium and pyrrolidinium than the benchmark tetramethylammonium (TMA) in 6 M NaOH solution at 160 °C [37]. Cyclic QAs were identified as particularly more alkaline stable because of the rotationally restricted anti-periplanar β-protons in the ring. The combination of low ring strain and conformational restrictions of the ring increases the transition state energy for both Hofmann β-elimination and ring-opening substitution reactions [37]. Larger ring sizes such as azepanium (7-membered ring) and additional heteroatoms e.g., morpholinium destabilize the ring structures and have considerably lower chemical stability than the N,N-dimethylpiperidinium cation [38]. N-spirocyclic QA like 6-azonia-

spiro[5.5]undecane (ASU) cation is even more stable. However, the attachment process of QAs with N-spirocyclic structures into the polymer backbone is rather complicated; as a result, a few reports are available [39-45]. In contrast, the incorporation of aliphatic monocyclic QA cations is relatively straightforward and less expensive. The ether-free AEM with alkyl N-methylpiperidinium groups were synthesized by Ren and co-workers and they observed no measurable degradation of the AEM in 1 M NaOH solution at 80 °C for 1200 h [46]. Jannach *et al.* also reported alkali stable PPO based alkyl N-methylpiperidinium functionalized AEMs [10, 47].

To combine high alkaline stability and high ionic conductivity in this study, we have incorporated N-methylpiperidinium (Pip) cations to the polyfluorene backbone via alkyl side chains and evaluated the properties of ion exchange capacity (IEC), hydroxide conductivity, thermal and chemical stability, and WU. The synthesized solvent-processable membrane exhibited adequate hydroxide conductivity, well-controlled IEC, and good thermal and alkaline stability. The major advantage of this study is the facile synthetic strategy that avoids any complicated modifications.

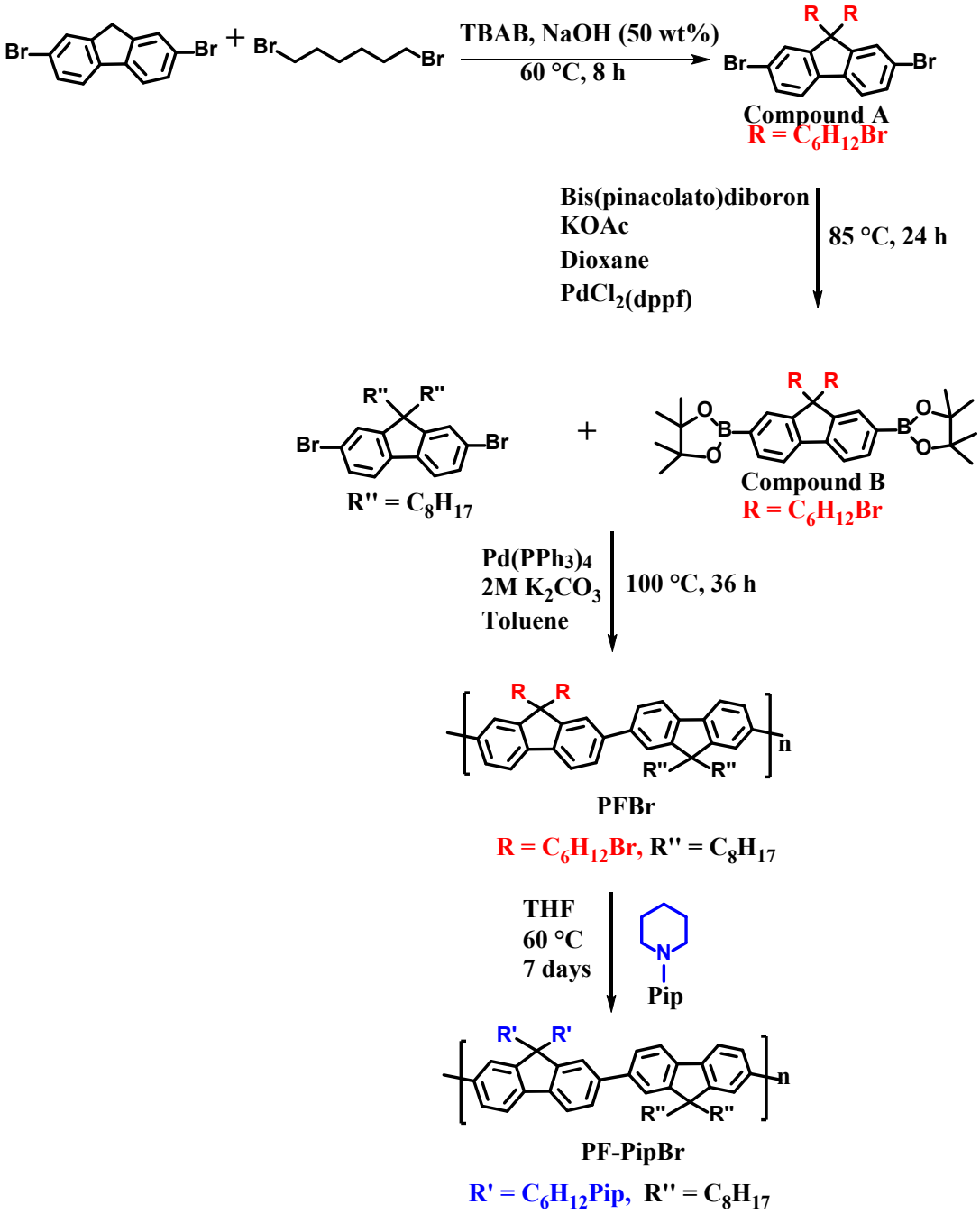
2. Experimental

2.1. Materials

1,6-Dibromohexane, 2,7-dibromofluorene, bis(pinacolato)diboron, tetrabutylammonium bromide (TBAB), 2,7-dibromo-9,9-dioctyl fluorene, tetrakis(triphenylphosphine)palladium(0) denoted as $Pd(PPh_3)_4$ were purchased from Tokyo Chemical Industry Co. Ltd., Japan. [1,1-Bis(diphenylphosphino)ferrocene] dichloropalladium(II) ($PdCl_2$)(dppf) (Sigma-Aldrich Corp.) was used. N-methylpiperidine, dioxane, dichloromethane, chloroform, toluene, ethanol, tetrahydrofuran (THF), diethyl ether, N,N-dimethylformamide (DMF), potassium carbonate, hexane, acetonitrile, ethyl acetate, methanol, ethanol, sodium chloride, sodium hydroxide, potassium hydroxide, anhydrous magnesium sulfate, potassium acetate, and hydrochloric acid were obtained from Fujifilm Wako Pure Chemical Corp., Japan. For all experimental work, deionized (DI) water was used.

2.2. Synthesis of Monomers and Polymers

In this study, we have presented a facile synthetic procedure for the synthesis of piperidinium functionalized fluorene based AEM. The synthetic strategy for monomers and polyfluorenes (PF) is shown in Scheme 2.



Scheme 2. Synthesis route of piperidinium functionalized polyfluorenes. Red means alkyl side chains containing bromine atom and the blue stands for piperidinium functionalized alkyl side chains.

2.2.1. Synthesis of 2,7-dibromo-9,9-bis(6'-bromohexyl)fluorene (Compound A), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-(6'-dibromohexyl)fluorene (Compound B), poly[(9,9-bis(6'-bromohexyl)fluorene)-co-(9,9-bis(6'-octyl)fluorene)] (PFBr)

2,7-Dibromo-9,9-bis(6′-bromohexyl)fluorene (Compound A) was synthesized by the reaction between 2,7-dibromofluorene and 1,6-dibromohexane [48]. 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-(6′-dibromohexyl)fluorene (Compound B) was prepared from compound A and bis(pinacolato)diboron [49]. And by using Pd-catalyzed Suzuki cross-coupling reaction the polymer poly[(9,9-bis(6′-bromohexyl)fluorene)-co-(9,9-bis(6′-octyl)fluorene)] (PFBr) was synthesized from compound B and 2,7-dibromo-9,9-dioctyl fluorene [19]. The detail synthetic procedures are provided in Supporting Information.

2.2.2. Synthesis of poly[(9,9-bis(6'-(N-methylpiperidinium)hexyl)fluorene)-co-(9,9-bis (6'-octyl)fluorene)]bromide (PF-PipBr)

A solution was prepared by dissolving brominated polymer PFBr (200 mg, 0.2 mmol) in 5 mL THF. To this, 8 mL N-methylpiperidine was added and the solution was heated at 60 °C for 7 days with the continuous stirring condition under argon. The solvents were evaporated in a vacuum evaporator. The concentrate was dissolved in 2 mL of MeOH,

precipitated in THF. The desired PF-PipBr polymer (217 mg, 88%) was dried at 60 °C under vacuum condition. The polymer was characterized by ^{1}H NMR spectrum in CH_3OH-d_4.

2.3. Membrane Casting

The PF-PipBr membrane was fabricated by a 4 wt% solution of the polymer in DMF. The solution was poured on a clean PTFE sheet. Then slowly dried for 48 h at 60 ºC to avoid the air bubbles and finally dried the membrane under vacuum for 48 h at 60 ºC. The membrane thickness was 70-80 μm.

2.4. Ion Exchange of Polymers in Hydroxide Ion form

To obtain the OH^- ion form membranes we have immersed the PF-PipBr membranes in argon saturated 1 M NaOH aq. solution at room temperature for 48 h. Within this time, we have exchanged three times the NaOH solution with fresh solution. Then the membranes were soaked in argon saturated DI water and finally, the OH^- ion form AEMs (PF-Pip) were washed by degassed DI water until the pH becomes neutral.

2.5. Characterization and Measurements

The experimental details of each measurement including ^{1}H and ^{13}C NMR spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, mass spectrometry, gel permeation chromatography (GPC), energy dispersive X-ray spectroscopy (EDX),

scanning electron microscopy (SEM), ion sputter equipment, transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), thermogravimetric analyzer (TGA), mechanical properties, WU, SR, IEC, hydroxide ion conductivity, and alkaline stability are included in Supporting Information.

3. Results and Discussions

3.1. Synthesis and Characterization of Monomers and Polymers

The chemical structure of the compound A and B was confirmed by ^{1}H and ^{13}C NMR, and mass spectra (shown in Supporting Information). The PFBr polymer was characterized by ^{1}H NMR spectrum as shown in Fig. 1A. The signals for the aromatic protons (Ar-*H*) of fluorene units were observed at 7.30 - 7.80 ppm. The signal appeared at 3.20 - 3.25 ppm due to the protons of methylene bromide (-CH_2Br), the chemical shifts found between 0.75 - 2.06 ppm for the additional methylene (-CH_2-) protons. The integral ratio and peak position confirmed that the polymerization reaction was successful. The PFBr polymer was soluble in THF and chloroform but insoluble in water. The molecular weight (M_w) of PFBr was 2.2 x 10^4 g mol^{-1} in Table S1. Fig. 1B shows the ^{1}H NMR spectrum of the PF-PipBr polymer. The new signals appeared at 2.90 ppm and 3.20 ppm due to the protons of -N^+CH_3 and -N^+CH_2 of the cyclopiperidinium group. The ratio of the peak area between protons of -N^+CH_3 at 2.90 ppm and the aromatic protons from 7.30

to 7.80 ppm determined the full substitution of N-methylpiperidine in PFBr polymer. The Br^- form polymer, PF-PipBr, was soluble in organic solvents, for example, DMF, CH_3OH, and DMSO at room temperature but was not soluble in H_2O.

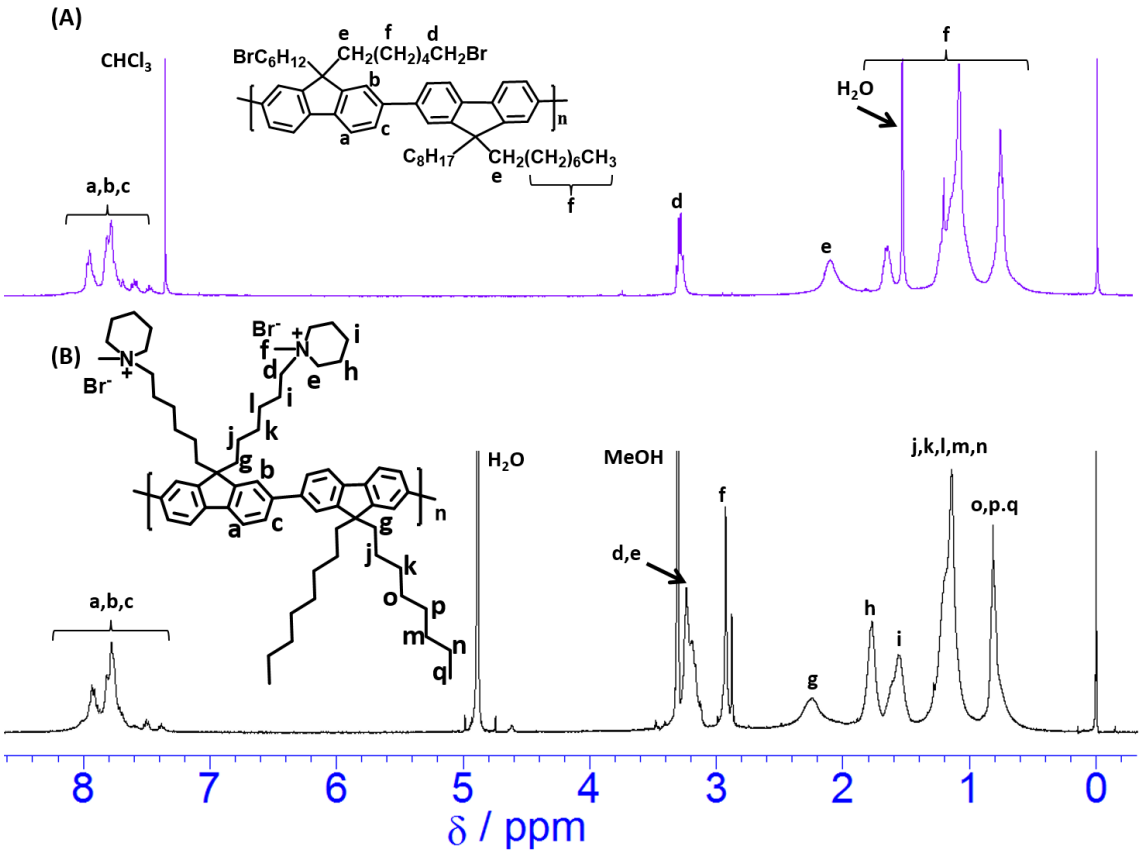


Fig. 1. ^1H NMR spectra of PFBr and PF-PipBr.

The EDX spectra before and after ion exchange of Br^- form to OH^- form as shown in Fig. 2A and 2B confirmed that Br^- ions almost disappeared or declined after the alkalization. More than 92% of Br^- ions have been exchanged by OH^- ions. The remaining bromine elements in Fig 2B may come from the end group of the polymer.

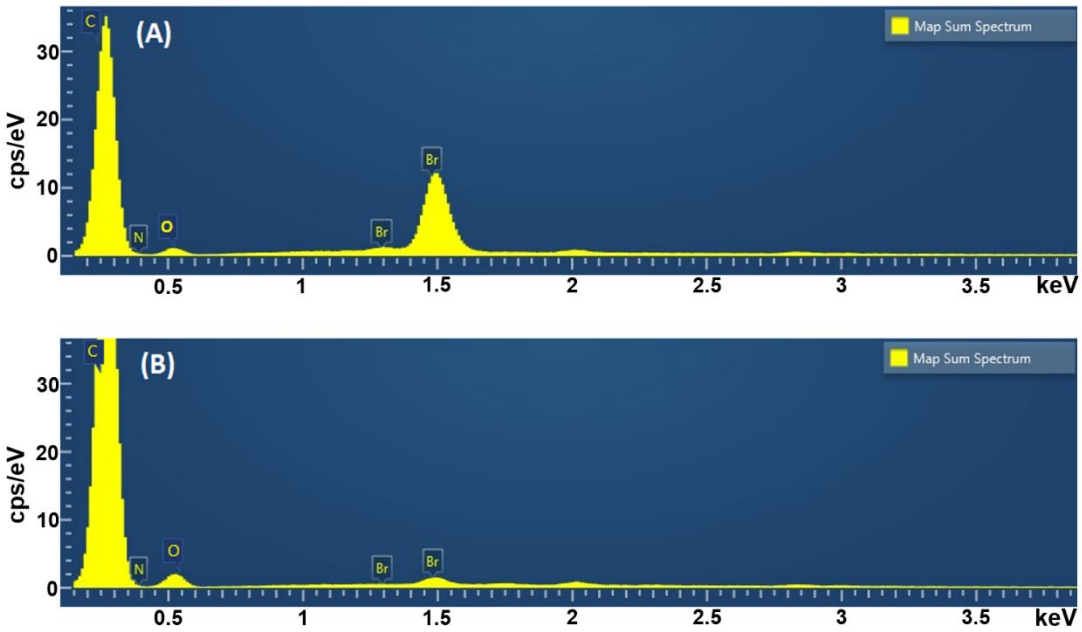


Fig. 2. EDX spectra for (A) PF-PipBr and (B) PF-Pip

3.2. Membrane Morphology

The PF-PipBr membrane was fabricated from 4 wt% solutions in DMF and was cast on a flat PTFE sheet. The resultant membrane becomes transparent as shown in Fig. 3A after evaporation of the solvent. The SEM images of Fig. 3B and 3C showed that the membrane surface and cross-section were homogeneous, tight and dense, and no pores and crack were visible at this scale.

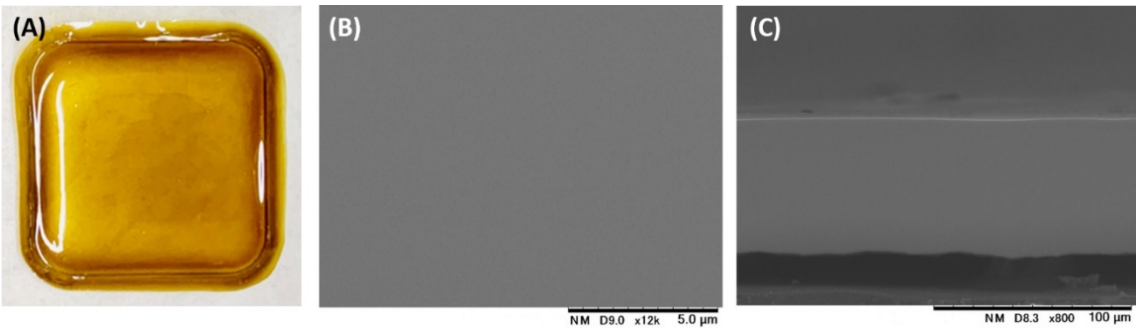


Fig. 3 (A) Photograph, SEM images of (B) membrane surface and (C) cross section of

the PF-PipBr polymer.

TEM was also used to investigate the morphology of the PF-Pip membrane. The cross-sectional TEM image of the membrane was observed after stained with tetrachloroplatinate ion. The bright regions represent the hydrophobic domains and dark regions correspond to the hydrophilic domains. The domain size of the hydrophilic group was observed as 1 to 2 nm as shown in Fig. 4. This morphology is similar to the membranes of literature [50, 51] containing fluorenyl group. The hydrophilic and hydrophobic domains were homogeneously distributed throughout the sight. This microphase-separated morphology would have a great influence on the hydroxide ion conduction through the PF-Pip membrane.

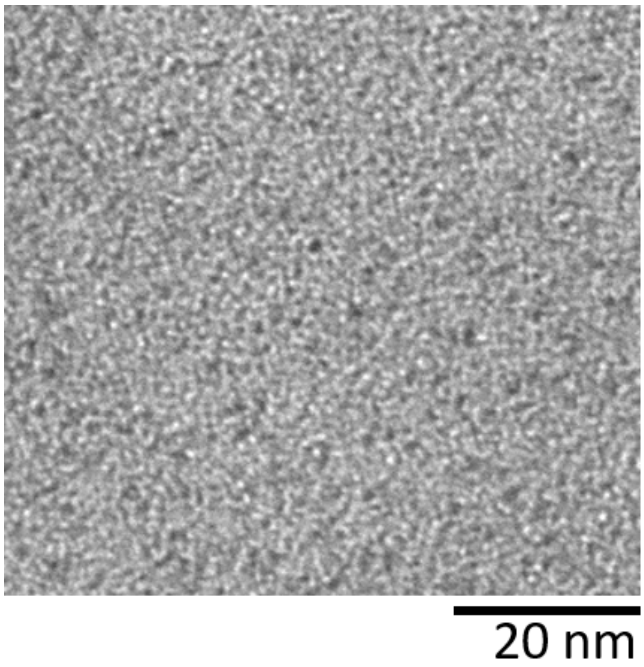


Fig. 4. Cross sectional TEM image of the PF-Pip membrane.

We have tried SAXS measurements to clarify the surface morphology of the membrane in both dry and submerged condition. A weak scattering peak was observed for PF-PipBr AEM in both samples at q = 0.21 $Å^{-1}$ which corresponds to d = 3 nm as shown in Fig. 5. A small broad band between 0.25 – 1.25 $Å^{-1}$ appeared in humidified and water conditions. This could be attributed as the size of ionic domains. No significant profile changes were observed in humidified and submerged conditions.

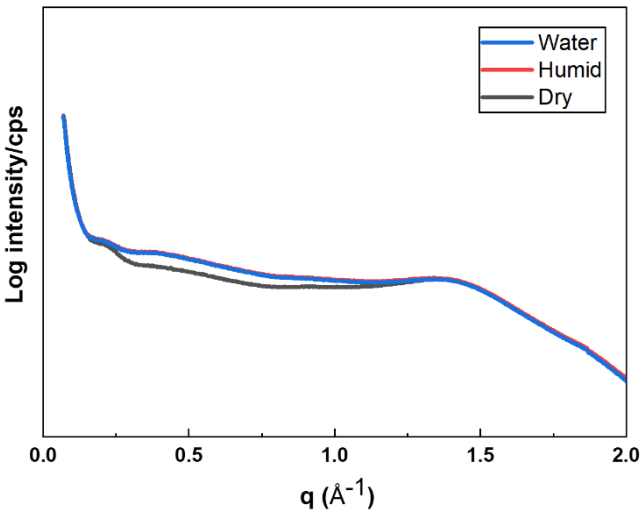


Fig. 5. The SAXS profile of PF-PipBr AEM, measured under dry and submerged conditions.

3.3. Thermal Stability

The thermal stability is always a concern for the AEMs. Aromatic polymers are the preferred candidates for application in high temperature AEMFCs because of outstanding thermal stability. Fig. 6 shows the results of the thermogravimatric analysis. The first weight loss below 150 °C; this weight loss possibly originates from the evaporation of

adsorbed water in the membrane. In the second step, 5% weight loss occurred between 150 ºC to 190 ºC due to the degradation of the methyl group of piperidinium cations of the polymer. The third degradation at temperatures above 390 °C might be due to the decomposition of the polyfluorene backbones. The overall result of thermal analysis implies that the resultant polymer maintains high thermal stability up to 150 ºC, which is higher than benzyl quaternary ammonium cationic groups [52]. The thermal stability is clearly well above the desired temperature range for fuel cell applications.

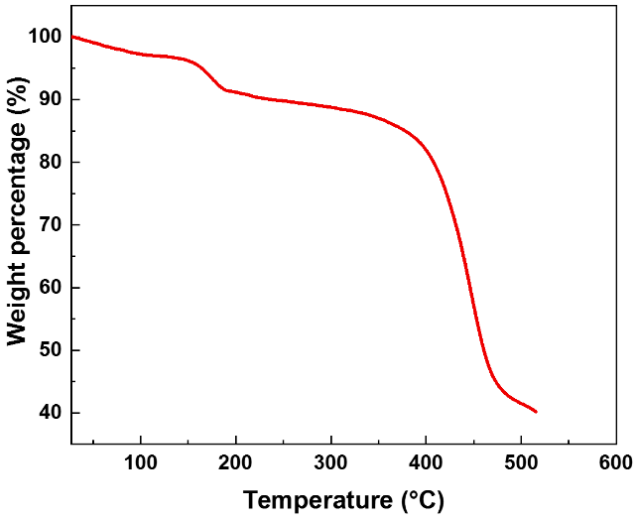


Fig. 6. TGA graph of PF-Pip under N_2 flow. Heating rate: 10 ºC min^{-1}.

3.4. Mechanical Properties

The tensile strength of PF-PipBr polymer was observed as 10.5 MPa with an elongation at break of 2.5% in water (Table S2). The Young's modulus was found to be 354 MPa.

3.5. Water Uptake (WU), Ion Exchange Capacity (IEC), and Swelling Ratio (SR)

For AEMs, sufficient amounts of WU are essential for the formation of hydrated ionic domain phase and faster migration of ions through the membrane [3, 5, 7, 10]. However, the balanced WU is important since excessive WU may influence undesirable membrane swelling and mechanical properties. Furthermore, the charge carriers e.g., anions are diluted due to high water contents, and conductivity decreases [10, 53]. As anticipated, the WU of AEM increases with increasing temperature [47]. The WU of the synthesized PF-Pip membrane is shown in Fig. 7 as a function of temperature from 20 to 80 °C after soaked in water. We found 35 wt% WU at 20 °C and 81 wt% at 80 °C. The WU of the synthesized PF-Pip membrane is comparable with the reported literature [16, 38]. The IEC of the membranes represents the number of exchangeable ions. The back-titration technique was used to determine the IEC of the synthesized membrane (see Supporting Information). It was found to be 1.82 mmol/g. The obtained IEC shows good agreement with the value of 1.89 mmol/g obtained from the ^{1}H NMR result. The SR increased with increasing temperature. The SR of the PF-Pip membrane was 11% at 20 °C and 20% at 80 °C as shown in Fig. 7.

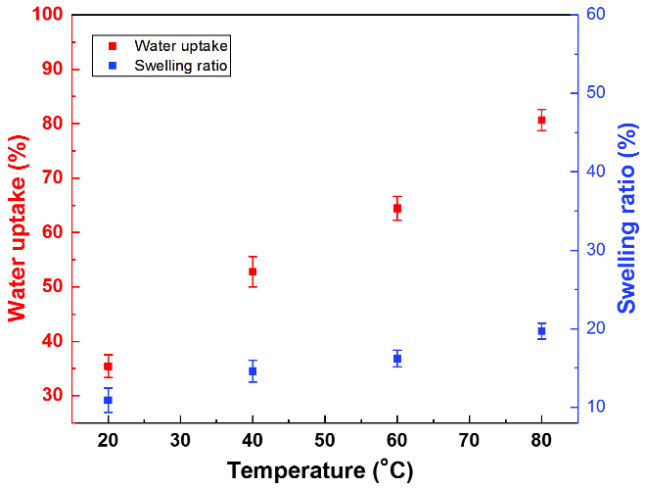


Fig. 7. The WU and SR of the PF-Pip membrane.

3.6. Hydroxide Ion Conductivity and Activation Energy

Hydroxide conductivity is one of the vital performances of AEMs. The hydroxide conductivity of the resultant PF-Pip membrane at different temperatures is shown in Fig. 8A. The PF-Pip membrane exhibited hydroxide conductivity of 9 mS cm^{-1} at 20 ºC and increased to 58 mS cm^{-1} at 80 ºC. The hydroxide conductivity of the AEMs increases with increasing temperature. Higher temperature can cause faster water diffusivity and ionic migrations. The AEMs containing piperidinium cationic groups, have high WU [54] and therefore facilitate the ionic migration through the water clusters. The hydroxide conductivity of the PF-Pip membrane follows the Arrhenius behavior from 20 to 80 ºC as shown in Fig. 8B. The activation energy of polymer PF-Pip was 27 kJ mol^{-1}, which was comparable with some reported AEMs [55-57].

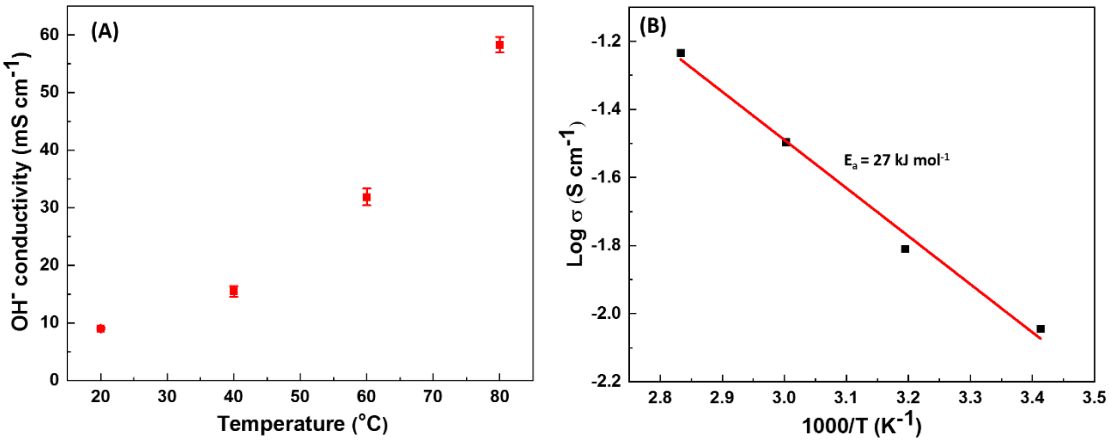


Fig. 8. (A) Hydroxide conductivity and (B) Arrhenius plots of the hydroxide conductivity for the PF-Pip membrane.

3.7. Alkaline Stability

The thermochemical stability of AEMs is the most important challenge for practical application, particularly in the high-pH medium of AEMFCs. Fig. 9 shows the ^{1}H NMR spectra of PF-Pip before and after the alkaline test. After 96 h and 168 h storage in 1 M NaOH aq. solution the peak intensity of the methyl protons (-$N^{+}CH_3$) at 2.9 ppm and methylene protons linked to N atom at 3.2 ppm, was slightly reduced. The reduction of peak intensity at 2.9 ppm indicated the substitution of the methyl group and at 3.2 ppm corresponded to the Hofmann β hydrogen elimination reaction of the N-methylpiperidinium cationic group. According to the literature, the degradation mechanisms of the N-methylpiperidinium group can be suggested as Scheme 3 [16, 37]. Bae *et al.* reported that the degradation of the N-methylpiperidinium cation was caused

by nucleophilic substitution of methyl groups and degradation by ring opening reaction was not observed [36]. Marino and Kreuer [37] confirmed from the results of ^{1}H NMR spectroscopy that the extreme degradation of N,N-methylpiperidinium group was taken by the substitution at the methyl groups in 6 M NaOH solution at 160 °C. In addition, a slight decay comes from the slower ring opening elimination processes. Jannasch *et al.* observed new peaks in the region from 5 to 6.5 ppm for vinylic protons due to the degradation of quaternary piperidinium groups by Hofmann β elimination [16, 38]. However, we did not observe these peaks for the vinylic protons. According to the literature [36, 37] we concluded that the major degradation of N-methylpiperidinium was the methyl substitution by the attack of OH^- ion. The ^{1}H NMR spectra of the PF-Pip membrane revealed that only 13% of the initial cationic group was lost after 96 h of storage in 1 M NaOH solution by following the degradation mechanism of Path A in Scheme 3. Further, no loss of cationic group was observed after stored for 168 h.

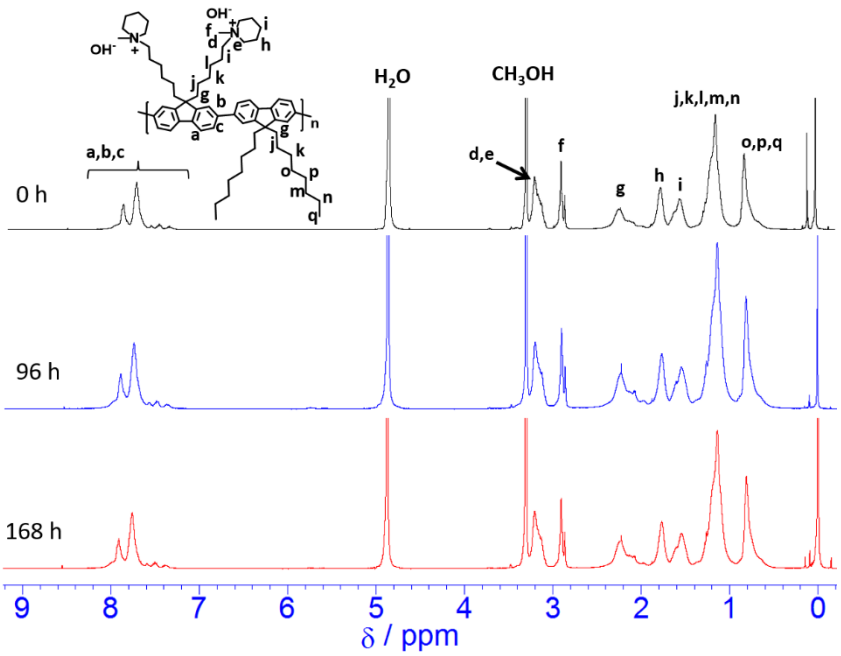
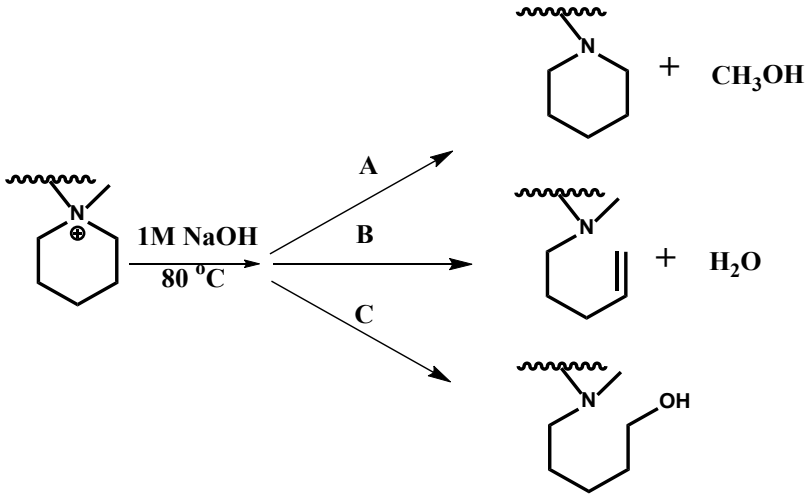


Fig. 9. ^{1}H NMR spectra of PF-Pip (OH^- form) membrane after soaking in 1 M NaOH solution for 80 °C for 96 h and 168 h.



Scheme 3. Reported degradation pathways of N-methylpiperidinium cationic group (A) nucleophilic substitution of the methyl group, (B) Hofmann β elimination, and (C) substitution (ring opening) [37].

To complement the NMR results, we also measured the OH^- conductivity of the PF-

Pip membrane after storage for 168 h in 1 M NaOH solution at 80 °C. The results revealed that only 15% of the initial conductivity was lost in water at 80 °C. Some other literature also observed a slight decline of conductivity [10, 47] after storage in alkaline conditions. The above results on fluorene-based membrane containing alkyl-substituted N-methylpiperidinium cationic groups indicate that this cationic group is relatively alkaline stable at 80 ^{o}C.

4. Conclusions

In summary, we have synthesized ether-bond-free polyfluorene AEM by using Pd catalyzed Suzuki cross-coupling reaction with piperidinium cations at the alkyl side chains. The properties of AEM were investigated including OH^- conductivity, WU and swelling behavior, IEC, thermal and chemical stability. The AEM in OH^- form exhibited good thermal stability. The hydroxide conductivity reached 58 mS cm^{-1} at 80 °C. The piperidinium cationic group of 13% was degraded after 168 h storage in 1 M NaOH solution at 80 °C. This study suggests that the alkyl substituted N-methylpiperidinium cationic group is relatively stable in alkaline conditions at 80 ^{o}C. It should be noted that the N-methylpiperidinium cation group decomposes slightly under alkaline conditions depending on the structure. The simple synthetic procedure presented is the major advantage in this study for synthesizing solvent-processable fluorene based AEM that

avoids any complicated modifications.

Acknowledgments

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Declaration of competing interest

Declarations of interest: none

Research data for this article

Data not available/Data will be available on request.

Supporting Information

Supporting information contains synthesis procedures for Compound A, Compound B, PFBr polymer. Details of characterizations and measurements including ^{1}H and ^{13}C NMR spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, mass spectrometry, gel permeation chromatography (GPC), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), thermogravimetric analyzer (TGA), mechanical properties, water uptake (WU), swelling ratio (SR), ion exchange capacity (IEC), hydroxide ion conductivity, alkaline stability of the membrane. GPC results of precursor PFBr polymer.

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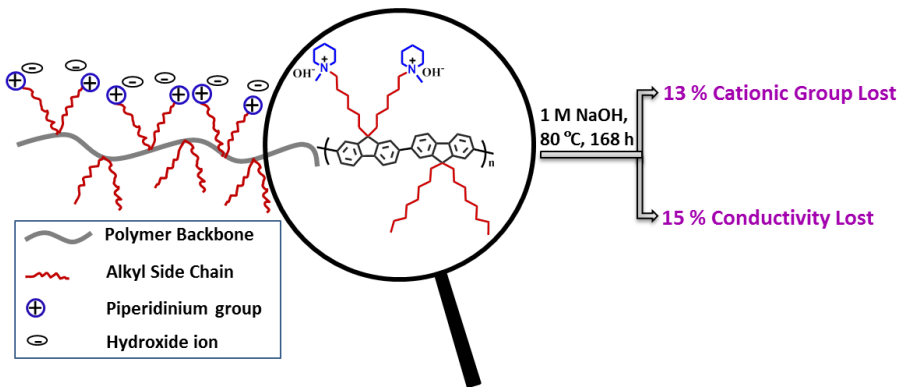
Graphical Abstract

Alkaline stability of ether bond free fluorene-based anion exchange polymer containing cycloaliphatic quaternary ammonium groups

Umme Salma and Yuki Nagao