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Anion Conductive Aromatic Ionomers Containing Fluorenyl Groups

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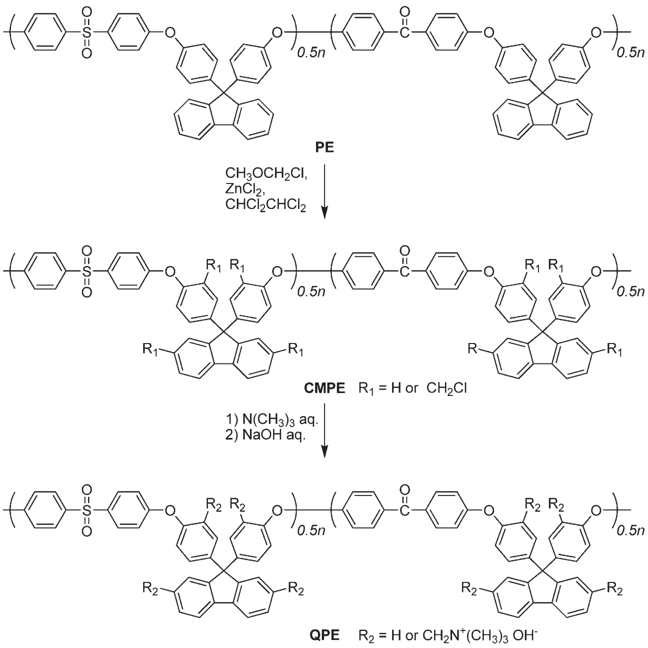
Fuel cells have attracted considerable attention because of their high efficiency and low pollution levels.[1,2] Among the several kinds of fuel cells, most efforts have been directed toward development of polymer electrolyte fuel cells (PEFCs) using proton exchange membranes (PEMs) in the past decade.[3] Perfluorinated ionomers such as Nafion have been most used. Although the PEMs exhibit excellent chemical, mechanical, thermal stability, and high proton conductivity, there are obstacles that impede the commercialization of PEM fuel cells due to the high cost of the perfluorinated PEMs and noble metal based electrocatalysts and insufficient durability of these materials under fuel cell operating conditions.[3] In recent years, interest has grown in the development of anion exchange membranes (AEMs) for alkaline fuel cells, which have advantages over PEM fuel cells including cost and performance.[4,5] In a basic environment using AEMs, sluggish oxygen reduction reaction at the cathode can be significantly improved, leading to high fuel cell efficiency. Catalysts are generally more stable in basic medium so that more options are available for the cathode catalysts from nonprecious metals (such as nickel and silver[6]) and thus potentially reducing the cost of the fuel cells.

A variety of AEMs based on cross-linked polystyrene,[7] radiation-grafted fluorinated polymers,[8] poly(phenylene oxide),[9] poly(ether−imide),[10] poly(arylene ether)s,[11−13] or organic−inorganic hybrid composites[14] have been reported. Poly(arylene ether sulfone)s and poly(arylene ether ketone)s fall into a class of aromatic polymers that have shown good solubility and have been most widely used as a backbone of hydrocarbon PEMs.[15−18] Recently, poly(arylene ether)s bearing quaternized ammonio groups were reported as AEMs by several groups.[11−13] These AEMs were typically prepared by chloromethylation of the pristine poly(arylene ether)s and followed by exposure to trimethylamine to form benzyltrimethylammonio groups.

Although various types of polymer backbones have been investigated for the AEMs, fluorenyl groups have gained little publicity as AEM polymer segments. Over the years, we have synthesized a series of sulfonated poly(arylene ether)s and sulfonated poly(arylene imide)s containing fluorenyl groups as PEMs and have demonstrated the effectiveness of the fluorenyl groups not only on the chemical, thermal, and mechanical stability but also on the proton conductivity.[19−22] Introduction of sulfonic acid groups at the fluorenyl groups renders the PEMs more proton conductive because the fluorenyl groups have the possibility to increase the number of ionic groups per polymer repeating unit. In addition, such PEMs bearing sulfonic acid groups, which were introduced at far from the polymer backbone, showed remarkable chemical stability by preventing the hydrolytic and/or oxidative degradation triggered from the sulfonic acid group-substituted polymer backbones. More recently, we have reported that poly(arylene ether sulfone)s containing sulfofluorenyl groups are highly proton conductive and durable for 5000 h in operating fuel cells.[19,23]

Scheme 1. Synthesis of Poly(arylene ether sulfone ketone)s Containing Quaternized Ammonio-Substituted Fluorenyl Groups



Our idea is that the fluorenyl groups should function in the AEMs as well as PEMs. This Communication describes the synthesis of poly(arylene ether sulfone ketone)s containing quaternized ammonio-substituted fluorenyl groups as novel AEMs. Chloromethyl groups were successfully introduced at the specific positions of the fluorenyl groups of polyethers via Friedel−Crafts reaction and were converted to quaternized ammonio groups (Scheme 1). Ionic conductivity of the polymer membranes bearing various ion exchange capacities (IECs) were evaluated in water at various temperatures.

Precursor poly(arylene ether sulfone ketone) bearing fluorenyl groups (PE) was synthesized by a nucleophilic substitution polymerization of 4-fluorophenyl sulfone (0.5 equiv), 4,4′-difluorophenylbenzophenone (0.5 equiv), and 9,9′-bis(4-hydroxyphenyl)-fluorene (1.0 equiv) in the presence of potassium carbonate in dry *N*,*N*′-dimethylacetamide (DMAc). The random sulfone-*co*-ketone structure was introduced in order for the polymers to have better solubility. The molecular weight of the purified PE was measured by GPC to be $M_w = 2.2 \times 10^5$ and $M_n = 6.3 \times 10^4$. Despite such high molecular weight, PE showed high solubility in many organic solvents including polar aprotic solvents and halogenated solvents due to the bulky fluorenyl groups and random sulfone-*co*-ketone structure. The Friedel−Crafts chloromethylation reaction of the pristine polymers was carefully examined from various angles of the reaction factors, such as concentrations of the polymer and chloromethyl methyl ether (CMME), kinds and amounts of Lewis acid catalyst (e.g., zinc chloride and tin chloride), and reaction time and temperature. The severe reaction conditions and excess reaction time led gelation

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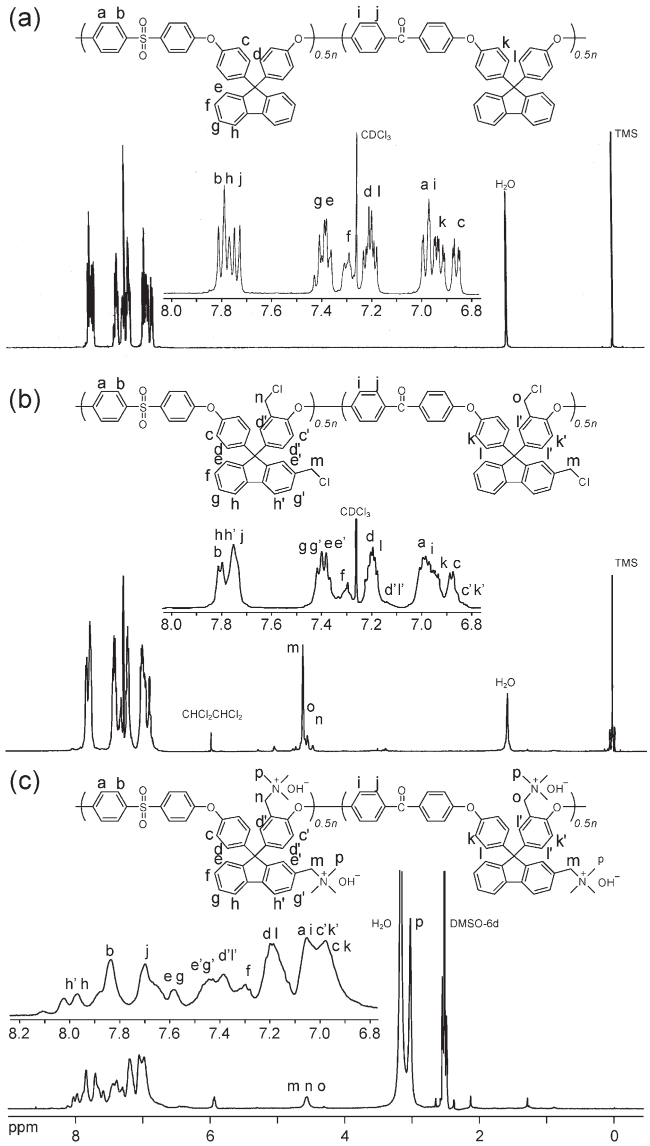

Figure 1. ^{1}H NMR spectra of (a) PE, (b) CMPE, and (c) QPE (IEC = 1.88 mequiv/g).

of the polymers due to undesirable cross-linking reaction. We found that the reaction temperature and the ratio of CMME to PE were particularly important and concluded that 35 °C and 40:1 (CMME:polymer) were the effective conditions without gelation. The detailed study of the chloromethylation reactions on various types of poly(arylene ether)s is beyond the scope of this preliminary report and will be discussed elsewhere.

^{1}H NMR spectra of the precursor PE and the obtained chloromethylated polyether (CMPE) are compared in Figure 1a,b. A new peak, which was observed at 4.59 ppm for CMPE in Figure 1b, was assigned to the methylene protons in the chloromethyl groups. Peaks assigned to the fluorenyl protons at the region between 7.1 and 7.9 ppm also altered after the reaction. The integral values of protons at 7.29 ppm, which corresponds to the protons at 2- and 7-positions of the fluorenyl groups (denoted as f in Figure 1), were smaller in Figure 1b. The integral ratio of the decreasing proton at 7.29 ppm was coincident with the integral ratio of the newly appeared protons at 4.59 ppm. The ^{1}H NMR spectra revealed that the chloromethyl groups were preferentially substituted at the expected specific positions (2- and 7-positions) of the fluorenyl groups in CMPE. Besides the peak at 4.59 ppm, several minor peaks were observed nearby. Adjacent peaks at 4.44 and 4.52 ppm were also assigned to the methylene protons in the chloromethyl groups, not at the fluorenyl groups but at the polymer backbone. The chloromethylation yield in CMPE was estimated from the integral ratio of the methylene protons of chloromethyl groups (4.44−4.59 ppm) to the protons at 7.75−7.81 ppm, which were assigned to 4-positional protons at the fluorenyl groups (denoted as h in Figure 1) and *ortho*-positional phenylene protons (denoted as b and j in Figure 1) and were intact during the chloromethylation reaction. The maximum chloromethylation yield reached to ca. 45% (1.80 chloromethyl groups per repeating unit) under the optimized reaction conditions. CMPE bearing different number of chloromethyl groups, such as 1.24, 0.81, and 0.39 chloromethyl groups per repeating unit, were also obtained under different conditions.

The CMPEs were dissolved in 1,1,2,2-tetrachloroethane and were cast on glass plates to form ca. 50 μm thick membranes by evaporating the solvent slowly on a hot plate. The obtained colorless transparent membranes were tough and ductile. Then, the membranes were immersed in a 35 wt % trimethylamine aqueous solution for 48 h at room temperature to convert the chloromethyl groups into quaternized ammonio groups. These polymer membranes were also strong and became less soluble. The following immersion of the membranes in a 1 M sodium hydroxide aqueous solution for 12 h at room temperature several times provided quaternized polyethers (QPE) with hydroxide counteranions. The ^{1}H NMR spectrum of the QPE bearing the highest amount of quaternized ammonio groups was not available because of its low solubility in most solvents; however, the other QPEs were soluble in DMSO. Figure 1c shows a ^{1}H NMR spectrum of the QPE obtained from the CMPE containing 1.24 chloromethyl groups per repeating unit. The new peaks at 4.54 and 2.98 ppm were assigned to the methylene and methyl groups in the quaternized ammonio groups, respectively. The integral ratio of the proton peaks revealed that the quaternization reaction proceeded quantitatively. The ion exchange capacity (IEC) of the membrane was calculated to be 1.88 mequiv/g from the integral ratio, which was in good agreement with the value supposing that all of the chloromethyl groups were quaternized. As the quaternization and the following ion exchange reactions normally proceeds quantitatively, the IECs of the other insoluble QPE membranes were presumed to be 2.54, 1.31, and 0.68 mequiv/g from the chloromethylation yields in CMPE (1.80, 0.81, and 0.39 chloromethyl groups per repeating unit, respectively).

For fuel cell applications, water uptake and ion conductivity are of particular importance. These properties of the obtained four QPE membranes are summarized in Figure 2. The hydroxide ion conductivity of the QPE membranes was measured at 30 °C by an impedance technique using four gold (ion-blocking) electrodes. Since hydroxide ions are easily transformed to carbonate and bicarbonate ions with the trace amount of carbon dioxide in air,[24] the measurement was carried out in water to obtain possibly pure hydroxide ion conductivity. Water uptake was measured after immersing the membranes into water at 30 °C for 48 h.

As expected, water uptake of the membranes increased with the IEC and the maximum water uptake was 160% (Figure 2a), which was reasonable with other AEMs based on the aromatic polymers bearing quaternized ammonio groups (e.g., ca. 95% at IEC = 1.89 mequiv/g[11] and ca. 115% at IEC = 2.2 mequiv/g[12]). The hydroxide ion conductivity of the QPEs also increased with the increase of their IECs; the highest conductivity of 50 mS/cm was obtained for the QPE membrane with IEC = 2.54 mequiv/g. Compared to the other AEMs based on the aromatic polymers, of which hydroxide ion conductivity ranges from 2.3 to 35 mS/cm under similar conditions,[11−14] our novel QPE membranes achieved much higher conductivity possibly due to their high

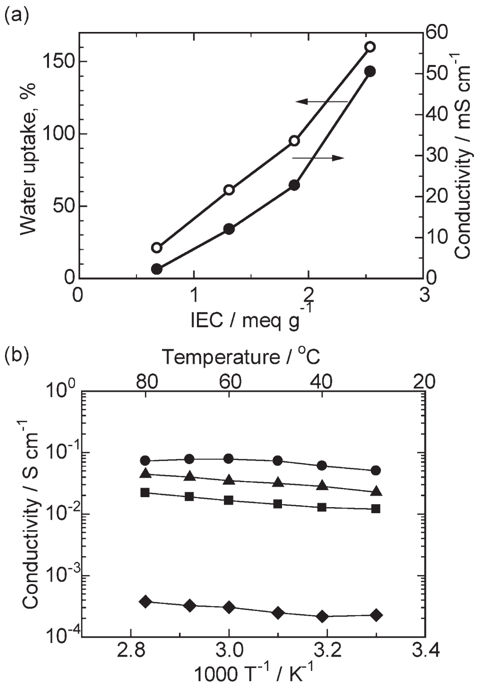

Figure 2. (a) Water uptake and hydroxide ion conductivity as a function of ion exchange capacity (IEC) at 30 °C: (open symbol) water uptake; (closed symbol) conductivity. (b) Temperature dependence of hydroxide ion conductivity of QPEs bearing various IECs (circle: 2.54; triangle: 1.88; inverted triangle: 1.31; diamond: 0.68 mequiv/g).

molecular weights and high IECs. The random sulfone-*co*-ketone structure with fluorenyl groups would be responsible to realize such high IEC (> 2.5 mequiv/g) membranes with insolubility and less swellability in water. Hydroxide ion conductivity is plotted as a function of temperature in Figure 2b. The conductivity showed approximate Arrhenius-type temperature dependency except at 70 and 80 °C of the highest IEC membrane. The apparent activation energy estimated from the slope was 10−12 kJ/mol and seemed independent of the IEC. The activation energy of QPE was similar to or somewhat lower than those of the other reported AEMs (9.92−23.03 kJ/mol).[12,13] The highest conductivity of 78 mS/cm was obtained at 60 °C for the QPE membrane with the highest IEC.

In conclusion, novel high-molecular-weight anion exchange membranes containing fluorenyl groups were synthesized via chloromethylation of poly(arylene ether sulfone ketone) followed by quaternization. By optimizing the reaction conditions, up to 1.80 chloromethyl groups were successfully introduced per repeating unit (or per fluorenylidene biphenylene unit) without significant side reactions. Quaternization and the following ion exchange reactions were quantitative so that the obtained ionomer membranes could have high IEC up to 2.5 mequiv/g. High hydroxide ion conductivity up to 50 mS/cm at 30 °C and 78 mS/cm at 60 °C was achieved with the membrane of the highest IEC. Our polymer design concept based on the high molecular weight aromatic polymers with rigid and bulky fluorenyl groups, which enable the introduction of more ionic groups to achieve high IEC, was revealed to be effective for highly anion-conductive ionomers.

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Supporting Information Available: Detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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