Proton Conductive Polyimide Electrolytes Containing Fluorenyl Groups: Synthesis, Properties, and Branching Effect

Kenji Miyatake, Hua Zhou, and Masahiro Watanabe*

Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan

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ABSTRACT: Novel sulfonated polyimide copolymers as electrolytes for high-temperature fuel cell applications are reported. A series of sulfonated polyimide copolymers (SPIH-*X*; *X* refers to molar percentage of fluorenyl content) containing 0−60 mol % of fluorenyl groups as hydrophobic component were synthesized, of which electrolyte properties were investigated and compared to those of the perfluorinated ionomer (Nafion 112). High-molecular-weight copolymers with good film-forming capability were obtained. Thermal stability with decomposition temperature of ca. 280 °C and no glass transition temperature was confirmed for the copolymers. SPIH shows unique water uptake behavior with the maximum value of 57 wt % at $X = 30$. Water molecules absorbed in the electrolyte membrane with this specific composition do not evaporate easily so that the high proton conductivity of 1.67 S cm^{-1} was obtained at 120 °C and 100% RH. The branching and cross-linking of SPIH-30 were carried out by applying 2 mol % of trifunctional monomer (melamine) in the polymerization and by electron beam irradiation upon the membrane. The branching and cross-linking are effective to improve oxidative stability and mechanical strength. Although the proton conductivity decreases slightly by the branching and cross-linking, it still remains at the comparable level to that of Nafion 112.

Introduction

Fuel cells have been receiving considerable attention as electrical power sources in the 21st century because of their high efficiency and low pollution levels.[1−3] Polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) are the most promising candidates for electric vehicles and portable devices.[4−6] However, the current state-of-the-art performance is not high enough for the practical applications. To improve their performance, it is desirable to operate PEFCs and DMFCs at higher temperature than 100 °C, since it would result in increased tolerance of Pt anode catalyst to CO (contaminated in re-formed H_2 fuel or formed during methanol oxidation reaction), better catalytic activity of cathode for oxygen reduction, and higher efficiency of heat exchange for waste heat recovery.[7,8]

The requirements for the electrolyte membranes are proton conductivity (at least 0.01 S cm^{-1}), high mechanical strength, impermeability of hydrogen, oxygen and methanol, and stability to heat, oxidation, and hydrolysis. Perfluorosulfonic acid polymers such as Nafion (Du Pont) have been used as the best available material; however, some of the above criteria have not been met. At elevated temperatures above 100 °C, the proton conductivity of perfluorosulfonic acid polymers decreases due to the desorption of water molecules and the destruction of hydrophilic nanoclusters. Lack of interaction (or cross-linking) among polymer chains causes insufficient mechanical strength. The high cost of these polymers is another serious drawback. Therefore, there has been a great demand for alternative electrolyte membranes for higher temperature fuel cells.[9]

Functionalization of aromatic polymers with acidic groups is one of the available options for the purpose. Sulfonated poly(ether ether ketone)s (PEEK),[10] polysulfones (PSF),[11] poly(arylene ether)s (PAE),[12] poly(*p*-phenylene)s (PPP),[13] and phosphoric acid-doped polybenzimidazole (PBI)[14] have been developed for examples. Recently, sulfonated polyimides have been claimed to display high proton conductivity at high temperatures.[15] In our preliminary communication, we have reported that the sulfonated polyimide copolymers containing fluorenyl groups show the conductivity of 1.67 S cm^{-1} at 120 °C.[16] The value is an order of magnitude higher than that of Nafion membrane and is the highest ever proton conductivity reported for a proton conductive polymer electrolyte. Herein, we describe further investigation on properties of the sulfonated polyimide copolymers for high-temperature fuel cell applications. The effect of branching and radiochemical cross-linking have also been investigated.

Experimental Section

Materials. 4,4′-Diamino-2,2′-biphenyldisulfonic acid (DAPS) (80%, Acros Organics) was purified in the manner as previously reported.[17] Triethylamine (TEA) (99.5%, Aldrich Co., Inc.), 1,4,5,8-naphthalenetetracarboxylic dianhydride (TCND) (99.0%, Aldrich Co., Inc.), 4,4′-(9-fluorenylidene)dianiline (FDA) (99.0%, Aldrich Co., Inc.), melamine (>98.0%, Kanto Chemical Co., Inc.), and benzoic acid (99.5%, Aldrich Co., Inc.) were used as received. *m*-Cresol (>98.0%, Kanto Chemical Co., Inc.) was dried over molecular sieves 3A prior to use. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

Polymerization. The polymerization procedure for unbranched polymers was described previously.[16] Sulfonated polyimide copolymers SPIH-*X* (where *X* refers to the molar percentage of fluorenyl groups) containing 0−60 mol % of fluorenyl groups were synthesized (Table 1).The procedures for chemical branching polymerization are as follows: A 100 mL four-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with DAPS (2.8 mmol, 0.964 g), FDA (1.08 mmol, 0.376 g), melamine (0.08 mmol, 0.010 g), TEA (6.2 mmol, 0.86 mL), and 18 mL of *m*-cresol. The mixture was stirred at 160 °C for 5 min under a N_2 atmosphere. After a clear solution was obtained, TCND (4.0 mmol, 1.073 g), benzoic acid (16.0 mmol, 1.954 g) and 30 mL of *m*-cresol were added while stirring. The

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* To whom correspondence should be addressed. E-mail: m-watanabe@yamanashi.ac.jp.

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Table 1. Composition, Equivalent Weight (EW), and Ion-Exchange Capacity (IEC) of SPIH-*X*

polymer	*X* (mol %)	EW	IEC (mequiv/g)
SPIH-0	0	288	3.47
SPIH-10	10	321	3.12
SPIH-20	20	361	2.77
SPIH-27M[a]	27	402	2.49
SPIH-30	30	413	2.42
SPIH-40	40	482	2.07
SPIH-50	50	579	1.73
SPIH-60	60	724	1.38

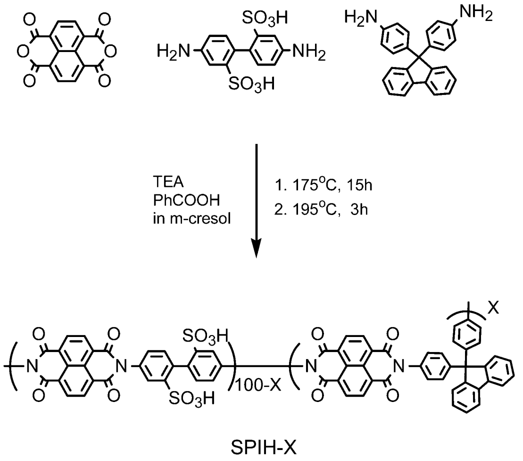
[a] Branched polymer with 2 mol % of melamine.

Table 2. Electron Beam Irradiation Conditions

polymer	current (mA)	acceleration voltage (keV)	conveyer speed (m/min)	intensity (kGy)
SPIH-30EB1[a]	5.0	125	10	100
SPIH-30EB2[b]	6.6	225	5	200

[a] Both faces were irradiated through a 75 μm PET film so that 10 μm of each surface was affected. [b] Electron beam was transmitted through the membrane so that the whole membrane was affected.

Scheme 1. Synthesis of Sulfonated Polyimide Copolymers SPIH-*X*



reaction was continued at 175 °C for 15 h and at 195 °C for 3 h to obtain a dark brown viscous solution.

Membrane Preparation. The above polymerization mixture was cooled to about 60−80 °C and then cast onto a clean glass plate. Drying the solution at 80 °C under atmospheric pressure for several hours and under reduced pressure for overnight gave a brown membrane. The membrane was immersed in a mixture solution of concentrated HNO_3 and ethanol (1/12 by volume) for 12 h. The acidification process was repeated three times until the ^{1}H NMR spectrum of the membrane showed no trace of triethylamine. Washing with ethanol several times and drying under vacuum at 40 °C for 8 h gave a membrane of SPIH-X. The branched membrane is indicated as SPIH-27M.

Cross-Linking by Electron Beam Irradiation. The SPIH-30 membrane with a thickness of 50 μm in acid form was prepared as above. Electron beam irradiation was performed using a universal electron beam accelerator (Iwasaki Electric EC 250/15/180L). The sample was placed on a tray on a conveyer and irradiated in air at room temperature. The conveyer speed was kept constant at 5 or 10 m/min. An acceleration voltage of 125 or 225 keV was used with a current of 5.0 or 6.6 mA in order to obtain an irradiation dose of 100 or 200 kGy per pass (Table 2). Two different samples were prepared by changing the irradiation conditions: one irradiated on both faces through a 75 μm PET film to affect 10 μm of each surface (SPIH-30EB1) and the other irradiated thoroughly to affect the whole membrane (SPIH-30EB2).

Measurement. ^{1}H NMR experiments were performed on a Bruker AVANCE 400S spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the internal reference. Infrared (IR) spectra were recorded on a Jasco FT/IR-500 spectrometer as KBr pellets in the range of 400−4000 cm^{-1}. Molecular weight measurement was performed via gel permeation chromatography equipped with two Shodex KF-805 columns and a Jasco 875 UV detector set at 300 nm. *N*,*N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL/min. M_w and M_n were calibrated with standard polystyrene samples. Thermal analyses were performed on a Mac Science TG-DTA 2000 instrument. For each run, the temperature was increased from room temperature to 400 °C at a heating rate of 20 °C/min under N_2.

Water Uptake. The membrane was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was placed in a humidor set at 93% relative humidity and 85 °C. After 2 h, the membrane was placed in a closed vial and quickly weighed.

Oxidative Stability. A small piece of membrane samples with a thickness of 50 μm was soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. The stability was evaluated by recording the time when membranes began to dissolve and dissolved completely.

Proton Conductivity. A four-point-probe conductivity cell with two gold plate outer current-carrying electrodes and two platinum wire inner potential-carrying electrodes were fabricated. Membrane samples were cut into strips that were 0.5 cm wide and 4.5 cm long and 50 μm thick prior to mounting in the cell. The cell was placed in a stainless steel chamber where the temperature and the humidity were controlled by flowing humidified N_2. Impedance measurements were made using a Solartron SI1280 electrochemical impedance analyzer. The instrument was used in galvanostatic mode with current amplitude of 0.005 mA over a frequency range from 10 to 20 000 Hz.

Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) was recorded on a Mac Science model MXP3. The X-ray beam produced by a rotating anode at 2 kW with a Cu Kα target coming out of the monochromator crossed the sample and then was analyzed. Membrane sample with a thickness of 300 μm was treated with water for 2 h and then contained in a Mylar bag under wet conditions. Background scattering from Mylar bag was determined and found to be negligible. The intensities were multiplied by the square of scattering wave vector (h).

Mechanical Strength. Mechanical tensile testing was performed with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a chamber in which the temperature and the humidity were controlled by flowing humidified air. Stress vs strain curves were obtained at a speed of 10 mm/min for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)).

Results and Discussion

Synthesis and Branching of Sulfonated Polyimide Copolymers. The copolymerization of DAPS, FDA, and TCND proceeds well under the given conditions described in the Experimental Section. The resulting dark red viscous solution was cast onto a plane glass plate and dried to obtain a membrane in salt form, which was washed with ethanol containing 1.0 N HNO_3 three times. Flexible and self-standing membrane in acid form (SPIH-X in Scheme 1 and Table 1) with a thickness of ca. 50 μm was obtained in quantitative yield after drying in a vacuum. Copolymer membranes with different composition have brown color typical for aromatic polyimides and are soluble in polar organic solvents such as DMAC, NMP, and DMSO.

The chemical structure of SPIH-*X* was analyzed by ^{1}H NMR spectra. The characteristic peaks for aromatic

Chart 1. Molecular Structure of the Branched Sulfonated Polyimide Copolymer SPIH-27M

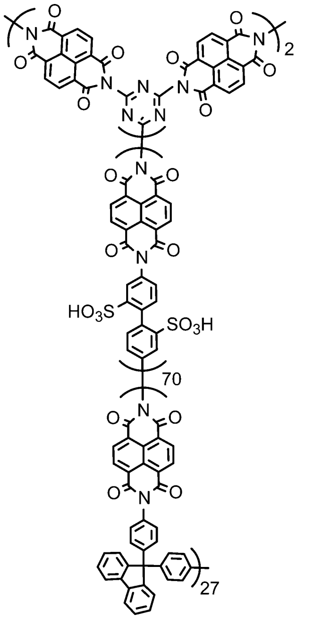


Table 3. Molecular Weight of SPIH-30 and Its Branched and Cross-Linked Equivalents

polymer	M_n (10^3)	M_w (10^3)	M_w/M_n
SPIH-30	64.7	141.0	2.2
SPIH-27M	52.7	136.5	2.6
SPIH-30EB1	61.5	139.3	1.9
SPIH-30EB2	62.8	140.2	2.1

protons were well-assigned to the supposed structure. Copolymer compositions as expected from the feed monomer ratios were confirmed from the integration ratio of the peaks. The IR spectrum also supports the structure in which imide and sulfonic acid groups were detected. The complete cyclization (or imidization) for these copolymers was supported by the absence of absorption peak around 1430 cm^{-1} assigned to NH groups. The characteristic peaks for $\nu_{SO,sym}$ and $\nu_{SO,asym}$ were observed at 1200 and 1254 cm^{-1}, respectively. No evidence for impurities or residual solvent was obtained from both spectra. The ion exchange capacity (IEC) of SPIHs was confirmed by back-titration using 0.005 N NaOH aqueous solution and 0.005 N hydrochloric acid.

Branching of SPIH was carried out by adding 2 mol % of trifunctional monomer (melamine) in the polymerization reaction. In Chart 1 is illustrated the chemical structure of branched material (SPIH-27M). Branched polyimide membrane in acid form was obtained in the same manner as for SPIH-30. There were no distinguishable differences observed in the ^{1}H NMR and IR spectra between SPIH-30 and -27M. We have also performed radiochemical cross-linking of SPIH-30 to give SPIH-30EB1 and SPIH-30EB2. Electron beam irradiation conditions for the preparation are summarized in Table 2. In both cases, appearances of the membranes did not practically change by the irradiation. The IR spectra of SPIH-30EB1 and SPIH-30EB2 are the same as that of SPIH-30, indicating that there was no serious damage on the chemical structure. GPC analyses revealed that SPIH-30, -27M, -30EB1, and -30EB2 have almost same molecular weight of M_w = ca. 140 × 10^3 and M_n = of ca. 60 × 10^3 relative to polystyrene standards (Table 3).

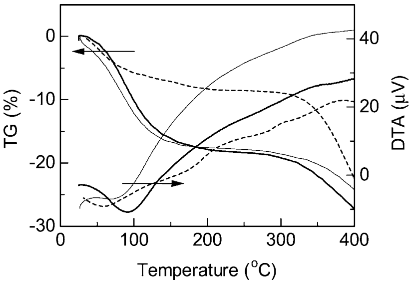


Figure 1. TG/DTA curves of SPIH-30 (thin), SPIH-27M (thick), and Nafion 112 (dashed).

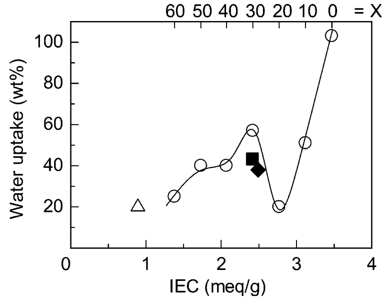


Figure 2. Water uptake of SPIH-*X* (○), SPIH-27M (◆), SPIH-30EB2 (■), and Nafion 112 (△) at 85 °C and 93% RH.

Thermal Properties. In Figure 1 are shown the TG/DTA curves of SPIH-30, SPIH-27M, and Nafion 112. In the TG curves of SPIH-30 and -27M, two-step weight loss is observed: the first one from 20 °C to ca. 170 °C is ascribed to the evaporation of absorbed water, while the second one from 280 °C is due to the loss of sulfonic acid groups. For both of SPIH-30 and -27M, the decomposition temperature is almost the same and is comparable to that of Nafion 112, suggesting that sulfonic groups attached to aromatic polyimide skeleton have high thermal stability. In DTA analyses, no glass transition and melting temperatures were observed for SPIHs due to their whole aromatic rigid structures. The comparison between SPIH-30 and -27M revealed that 2 mol % of branching does not practically affect the thermal properties of the sulfonated polyimides.

Water Uptake. The water uptake of SPIH-*X*, SPIH-27M, SPIH-30EB2, and Nafion 112 is plotted as a function of ion-exchange capacity (IEC) in Figure 2. As expected, the water uptake of SPIH-*X* decreases from 102 wt % (X = 0, IEC = 3.47 mequiv/g) to 20 wt % (X = 20, IEC = 2.77 mequiv/g) with increasing fluorenyl content. The water uptake, however, shows its maximum of 57 wt % at X = 30 despite the enhanced hydrophobicity. It is assumed that the bulky fluorenyl groups force each polymer chain separate to produce large interchain space in which water molecules could be confined. The water uptake decreases with further increase in fluorenyl content. SPIH-60 (IEC = 1.38 mequiv/g) displays 23 wt % of water uptake, which is comparable to that (20 wt %) of Nafion 112 (IEC = 0.91 mequiv/g). The branched and cross-linked membranes SPIH-27M and -30EB2 display lower water uptake (38 and 43 wt %, respectively) than the corresponding un-cross-linked membrane SPIH-30 (57 wt %). The branching and cross-linking should depress the molecular motion and the swelling of the membrane, resulting in the lower water uptake.

Oxidative Stability. Oxidative stability of the membranes (50 μm) was evaluated by observing the dissolving behavior in Fenton's reagent at 80 °C as an

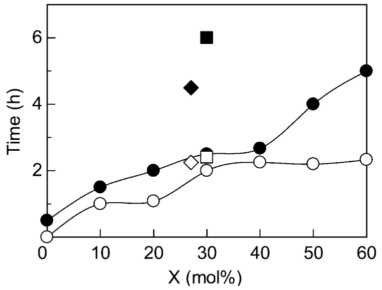


Figure 3. Oxidative stability of SPIH-*X* (○, ●), SPIH-27M (◇, ◆), and SPIH-30EB2 (□, ■) at 80 °C in Fenton's reagent. Open symbols represent the dissolving time, and the solid symbols represent the dissolved time.

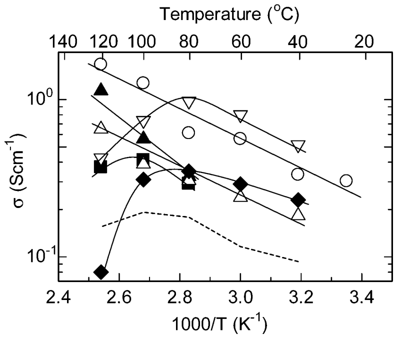


Figure 4. Temperature dependence of the proton conductivity of SPIH-10 (▽), -30 (○), -50 (○), -27M (◆), -30EB1 (▲), and -30EB2 (■) and Nafion 112 (dashed line) at 100% RH.

accelerated testing (Figure 3). Since the oxidative species such as HO$^\bullet$ and HOO$^\bullet$ accompany some water molecules when reacting to the substances, the oxidative stability of SPIH-*X* is improved as increasing in the hydrophobic fluorenyl content. It took almost 2 h before the SPIHs with $X > 30$ started to dissolve in the solution. This oxidative stability is high for an electrolyte membrane based on hydrocarbon polymer.[17] Unlike the water uptake behavior, there was no maximum peak observed in the oxidative stability to the fluorenyl content. The branched and cross-linked membranes SPIH-27M and -30EB2 have better stability to oxidation than SPIH-30, enduring for more than 4 h in Fenton's reagent. A small amount of branching and cross-linking was very effective in improving the oxidative stability.

Proton Conductivity. Temperature dependence of the proton conductivity of SPIH membranes and Nafion 112 at 100% RH is summarized in Figure 4. For uncross-linked membranes, only three (SPIH-10, -30, and -50) of them are included since we have discussed in detail in the previous report.[16] A short summary is that SPIHs with $X > 30$ mol % display a linear dependence of the logarithmic conductivity upon the reciprocal of the temperature even above 100 °C, suggesting that the membranes have capability of holding water at high temperature. The highest conductivity of 1.67 S cm^{-1} was obtained for SPIH-30 at 120 °C and 100% RH. The conductivity is 1 order of magnitude higher than that of Nafion 112 under the same conditions. Although detailed mechanism for the high proton conduction of the SPIH membrane has not yet been well understood, we assume the same mechanism involving hydronium ions as for Nafion membrane because the activation energy estimated from the slopes in Figure 4 is the same (21 kJ/mol) for both samples.

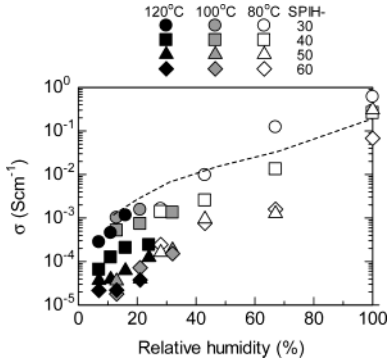


Figure 5. Humidity dependence of the proton conductivity of SPIH-*X* at 80, 100, and 120 °C and of Nafion 112 (dashed line) at 100 °C.

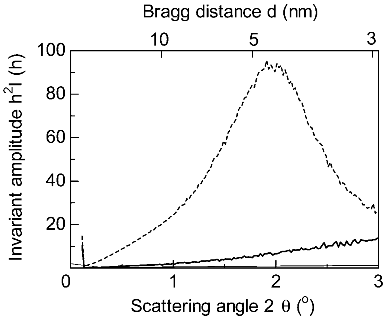


Figure 6. Small-angle invariant X-ray scans from SPIH-30 (thin), SPIH-27M (thick), and Nafion 112 (dashed) under wet conditions.

SPIH-27M showed lower proton conductivity than that of SPIH-30. The decrease is more pronounced at higher temperatures than 100 °C; the conductivity of SPIH-27M at 120 °C is 0.08 S cm^{-1}. The branching lowers not only the water uptake (Figure 2) but also the water holding capability. For the electron beam irradiated membranes, a higher conductivity was obtained than the branched SPIH-27M at 80−120 °C. The SPIH-30EB1 membrane irradiated only on its both surfaces displayed similar (linear) temperature dependence of the proton conductivity as that of SPIH-30, showing the highest value of 1.16 S cm^{-1} at 120 °C. The thoroughly irradiated membrane SPIH-30EB2, however, showed a rather lower conductivity of 0.36 S cm^{-1} at 120 °C. These proton conducting properties seem to reflect the above water uptake behavior. The conductivity results imply that the electron beam irradiation causes less than 2 mol % of the branching. It is noticeable that lowered conductivities for the branched and cross-linked membranes are still higher than those of Nafion 112.

Figure 5 shows the humidity dependence of the proton conductivity of SPIH-30 to -60. Among these membranes, SPIH-30 showed the highest conductivity at any RH from 80 to 120 °C. At RH lower than 30%, the conductivity is practically independent of the temperature, since the carrier (hydronium ions) concentration must be more crucial than its mobility. The conductivity of SPIH-30 at 120 °C and RH < 40% is almost comparable to and is higher at 80 °C and RH > 40% than that of Nafion 112.

Small-Angle X-ray Scattering. To investigate the hydrophilic/hydrophobic separation in the membranes, the small-angle X-ray scattering (SAXS) experiment was performed under the wet conditions (Figure 6). For Nafion 112, the SAXS peak associated with hydrophilic cluster was observed at $2\theta =$ ca. 2.0°, which corresponds to the Bragg distance $d = 4.5$ nm. This agrees well with

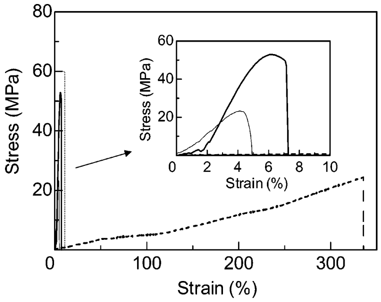


Figure 7. Stress vs strain curves for SPIH-30 (thin), SPIH-27M (thick), and Nafion 112 (dashed) at 85 °C and 93% RH. Inset is enlarged of the dotted region.

the previously reported value.[18] On the other hand, no distinct peak was confirmed for SPIH-30 and -27M up to 2θ of 3.0°. Unlike the perfluorosulfonic acid polymers, uniform size hydrophilic clusters might not form in SPIH membranes because of the less pronounced hydrophilic/hydrophobic separation and the smaller flexibility of aromatic hydrocarbon electrolytes than those of perfluorosulfonic acid polymers, as suggested in the literature.[19]

Mechanical Properties. It is essential for electrolyte membranes to retain the mechanical strength under humidified conditions in light of membrane electrode assembly (MEA) to be used in fuel cells. In general, electrolyte membranes become weaker under wet conditions than under dry conditions. To evaluate the mechanical properties of SPIH membranes, a tailor-made universal testing instrument equipped with a temperature/humidity controllable chamber was used. As a reference, Nafion 112 was subjected to the testing at 85 °C and 93% RH. The membrane extended considerably with its strain reaching to 334% and the maximum stress at break of 24 MPa (Figure 7). These results are reasonable from the comparison with the data released by Du Pont.[20] While the maximum stress at break of SPIH-30 was comparable to that of Nafion 112, SPIH-30 showed small elongation at a break of 5%. The small strain is advantageous since the MEA should display little changes in its size under fuel cell operating conditions. SPIH-27M displayed even higher strength with the maximum stress at break of 52 MPa and the elongation at break of merely 7%. Young's modulus estimated from the slope of the initial linear region in Figure 7 was 0.6 and 1.1 GPa for SPIH-30 and -27M, respectively, which are much higher than 7 MPa for Nafion 112. These results also confirm that the branching effectively improves the strength and stiffness of the sulfonated polyimide membranes.

Conclusions

A series of sulfonated polyimide copolymers (SPIH-*X*) having 0−60 mol % of fluorenyl groups as bulky and hydrophobic moieties have been synthesized and subjected to thermal and oxidative stability testing, conductivity, and mechanical strength measurements to evaluate its possible availability as electrolyte membranes for PEFCs and DMFCs. The optimum composition of fluorenyl groups was found to be 30 mol %, at which the maximum water uptake and the highest proton conductivity were achieved. The SAXS results imply that the SPIHs do not display distinct nanosize hydrophilic/hydrophobic separation even under wet conditions, different from the perfluorinated ionomer with hydrophilic clusters of $d = 4.5$ nm. Branching by using melamine and cross-linking by electron beam irradiation do have a positive effect on the oxidative stability and mechanical strength without losing much of the good conductivity properties. The branched and cross-linked membranes (SPIH-27M and -30EB2) endure in Fenton's reagent for more than 4 h at 80 °C. Its maximum stress at break is more than twice as that of un-cross-linked one and of Nafion 112. These electrolyte properties of the SPIHs are promising for the application to high-temperature PEFCs. The effect of trifluoromethyl groups as more hydrophobic and less bulky moieties on the electrolyte properties of polyimides and DMFC performance using the membrane are described in a following paper.

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(20) From the product information by Du Pont, the maximum tensile strength for Nafion membrane when soaked in water at 100 °C is 25 MPa in the machine direction (MD) and 24 MPa in the transverse direction (TD).

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