



Syntheses of sulfonated star-hyperbranched polyimides and their proton exchange membrane properties

Touru Suda, Kouta Yamazaki, Hiroyoshi Kawakami*

Department of Applied Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

We synthesized novel sulfonated star-hyperbranched polyimides composed of a hydrophobic hyperbranched polymer for polymer stability and a hydrophilic sulfonated polyimide as the proton-transport site in the core-shell structure. The proton conductivities of the star-hyperbranched polyimide membranes were measured as functions of the relative humidity and temperature using electrochemical impedance spectroscopy. Although the water uptake and IEC value for the sulfonated star-hyperbranched polyimide membranes were almost constant, the proton conductivity of the membrane strongly depended on the molecular weight of the hydrophilic sulfonated polyimide as the shell. Especially, the conductivity of the high molecular weight star-hyperbranched polyimide membranes was significantly superior to that determined in Nafion® at all temperatures and was 0.51 S cm^{-1} at 80°C and 98% RH, which may suggest that a good proton-transport pathway in the core-shell structure is formed. Consequently, this material proved to be promising as a proton exchange membrane and may have potential applications for use in fuel cells.

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1. Introduction

The proton exchange membrane fuel cell converts chemical energy directly into electrical energy with a high efficiency and low emission of pollutants, and is the most promising power source for portable and automotive applications. Proton exchange membranes are one of the key components in the fuel cell systems [1–3]. An ideal membrane should possess both good chemical and thermal stabilities, a high mechanical strength, and a high proton conductivity. Although perfluorosulfonate ionomer membranes, such as Nafion®, have been the most widely used for the polymer electrolyte membrane because of their high proton conductivities, there are some drawbacks, such as high cost and low conductivity at high temperature or low humidity [4,5].

Recently, much effort has gone into the development of novel polymer electrolyte membranes based on the sulfonated aromatic hydrocarbon polymers and many sulfonated polymers, such as the sulfonated polyimide, sulfonated polysulfone, sulfonated polyphenylene, and sulfonated poly(ether ether ketone), have been widely synthesized as alternate candidates [6–10] due to their excellent chemical and thermal stabilities, and good mechanical strength. Generally, the proton conductivities for the membranes based on these polymers strongly depend on their ion exchange capacities (IECs) [11]. However, these linear polymers, in which

the sulfonic acid groups are attached to the polymer main chain, sometimes show huge water uptake by the enhanced IEC, resulting in unfavorable swelling of the membranes and a dramatic loss in their mechanical properties. To overcome these problems, the sulfonated block copolymers, which had ion transport channels formed by phase-separated hydrophilic and hydrophobic domain structures, were synthesized, and the efficiency of their proton conductivities was investigated [12–14].

In recent years, polymers with highly branched, globular macromolecular structures, such as dendritic and hyperbranched polymers, have attracted increasing attention, because they are expected to have unique properties when compared to their linear analogues [15–18]. Unlike dendritic polymers, hyperbranched polymers do not have a well-defined architecture, but can be simply prepared, e.g., from bifunctional and trifunctional monomers, and are much more readily available at lower costs than dendritic polymers, which is highly desirable for many applications. Hyperbranched polymers show a low viscosity and high solubility in organic solvents, however, they lack a significant entanglement in the solid state, indicating that it is very difficult to prepare tough membranes with a good mechanical strength [19].

Surface modification of the dendritic and hyperbranched polymers is one important strategy for improving their properties and finding new applications. For example, the polymers with terminal reactive groups can easily react with the functional group on the surface of the hyperbranched polymers, yielding star-hyperbranched polymers. The star-hyperbranched polymers contained core-shell structures, and were composed of a hyper-

* Corresponding author. Tel.: +81 426 77 1111x4972; fax: +81 426 77 2821.
E-mail address: kawakami-hiroyoshi@c.metro-u.ac.jp (H. Kawakami).

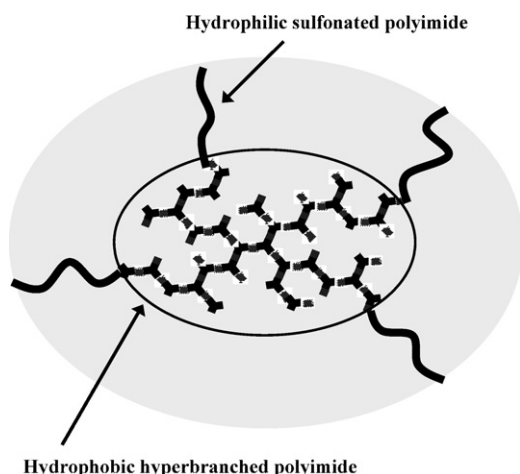


Fig. 1. Structure of star-hyperbranched polyimide (SHB-PI).

branched polymer as the core and one type of linear polymer as the shell [20,21]. That is, the resulting polymers can have extremely different characteristics, such as a hydrophilicity and hydrophobicity.

This paper first describes the syntheses and characterizations of a series of sulfonated star-hyperbranched polyimides for the proton exchange membrane. The star-hyperbranched polyimides were composed of a hydrophobic hyperbranched polymer for polymer stability and a hydrophilic sulfonated polyimide as the proton-transport site (Fig. 1) and their membranes were prepared without any crosslinking. Specifically, we focused on the influence of the molecular weight of the sulfonated polyimide as the shell on the proton conductivity.

2. Experimental

2.1. Materials

2,2'-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from the Clariant Co., Shizuoka, Japan, and purified by sublimation prior to use. The diamine monomer, tris(4-aminophenyl)amine (TAPA), was synthesized from tris(4-nitrophenyl)amine, which was purchased from the Sigma–Aldrich Co., Tokyo, Japan, and purified by sublimation prior to use as reported in a previous paper [14].

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) was purchased from the Sigma–Aldrich Co., Tokyo, Japan. 4,4'-Diamino-

biphenyl 2,2'-disulfonic acid (BDSA) was purchased from the Tokyo Kasei Co., Tokyo, Japan, and was purified by dissolution in a triethylamine aqueous solution and then precipitated in 1N H₂SO₄. Finally, the BDSA was dried in a vacuum oven at 70 °C for 12 h. Nafion® 117 was used in this study as the control membrane. The membranes were obtained from the DuPont Co., Ltd. (Tokyo, Japan) and were as-received for use.

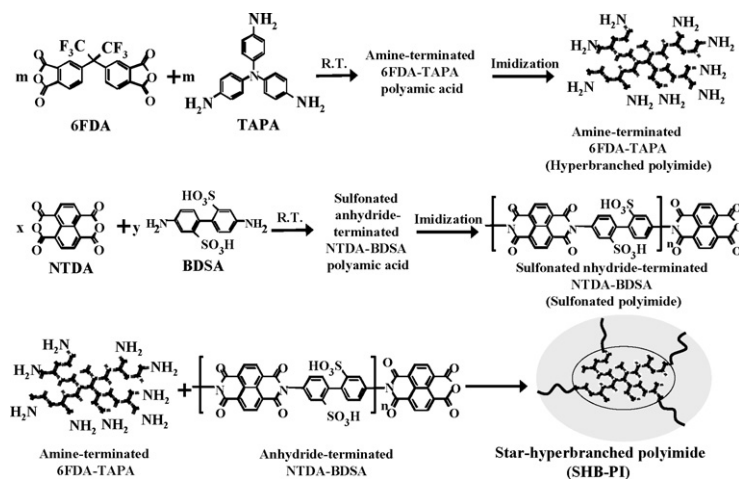
2.2. Syntheses of sulfonated star-hyperbranched polyimides

A novel sulfonated star-hyperbranched polyimide was synthesized as shown in Scheme 1. The hyperbranched polymer as the core, an amine-terminated polyimide, was prepared by the same method reported by Okamoto and co-workers [22].

The linear polymer as the shell, a sulfonated anhydride-terminated polyimide, was prepared by the same method as described in previous papers [13,14]. Sulfonated anhydride-terminated polyimides with the different molecular weights, NTDA–BDSA(1), (2), and (3), were synthesized using the different molar ratios of BDSA:NTDA. After the sulfonated anhydride-terminated polyimide solution was cooled to 80 °C, 0.1 g of the amine-terminated polyimide, 6FDA–TAPA, dissolved in 10 ml of *m*-cresol was added dropwise through a syringe over 1 h. The mixture of the sulfonated anhydride-terminated polyimide and amine-terminated polyimide was stirred at 70 °C for 4 h and at 180 °C for 24 h. After cooling to room temperature, the solution was poured into methanol several times to remove the residual sulfonated anhydride-terminated polyimide. In addition, the precipitated polyimide was collected by filtration and was re-dissolved in *m*-cresol. The solution was poured into ethyl acetate, and the precipitated sulfonated star-hyperbranched polyimide was washed several times with ethyl acetate and dried under vacuum at 150 °C.

2.3. Preparation of sulfonated star-hyperbranched polyimide membranes

The sulfonated star-hyperbranched polyimide membranes were prepared using a solvent-cast method. The dimethyl sulfoxide solution of the polyimide was carefully cast on a glass plate, and then the plate was placed in a vacuum oven at 110 °C for 24 h to slowly remove most of the solvent. The membranes were immersed in ethanol and deionized water for 4 h each, then acidified with a 0.1 M HCl solution for 24 h, and finally washed with deionized water. The resulting membranes were dried in a vacuum oven at 80 °C for 24 h. The thickness of the membranes was approximately 50 μm.



Scheme 1. Synthetic scheme of star-hyperbranched polyimide (SHB-PI).

2.4. Characterization of sulfonated star-hyperbranched polyimide membranes

The molecular weights (M_w and M_n) of the amine-terminated polyimide, sulfonated anhydride-terminated polyimide, and sulfonated star-hyperbranched polyimide were determined by gel-permeation chromatography (detector: Jasco 830-RI monitor, Tokyo, Japan) using two Shodex SB-806HQ and SB-804 HQ columns. Dimethylformamide containing 0.01 M lithium bromide was used as the eluent at the flow rate of 1.0 ml min^{-1} . The molecular weights were estimated by comparing the retention times on the columns to those of standard polystyrene [14]. The ionic-exchange capacity (IEC) was measured by classical titration using NaOH and HCl solutions [14].

The water uptake of the sulfonated star-hyperbranched polyimide was gravimetrically measured from the dried and humidified membranes [14]. The sulfonated star-hyperbranched polyimide membranes were dried in a vacuum oven at 80°C for 10 h and then immersed in liquid water at room temperature. After 24 h, the membrane was then wiped dry and quickly weighed. The water uptake was calculated using Eq. (1):

$$W(\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_s and W_d are the weights of the wet and dry membranes, respectively.

Radical stability of the membranes was measured by soaking in Fenton's reagent (30 ppm FeSO_4 in 30% H_2O_2) at 25°C as an accelerated testing. The stability was evaluated by recording the time when membranes dissolved completely.

The size change of the sulfonated star-hyperbranched polyimide membranes was measured in water at 30°C for 5 h [23]. The changes in the thickness and diameter were calculated from

$$\Delta T(\%) = \frac{T_s - T_d}{T_d} \times 100 \quad (2)$$

$$\Delta L(\%) = \frac{L_s - L_d}{L_d} \times 100 \quad (3)$$

where T_s and L_s are the thickness and diameter of the wet membranes, respectively, and T_d and L_d are the thickness and diameter of the dry membranes, respectively.

The thermal behavior of the polyimide membranes in a nitrogen atmosphere was evaluated by thermogravimetric analysis (TGA: Seiko TG/DTA300, SSC/5200H, Tokyo, Japan). The thickness of the membranes was approximately $50 \mu\text{m}$.

The proton conductivity in plane direction of membrane was measured by electrochemical impedance spectroscopy over the frequency range from 50 Hz to 50 kHz (Hioki 3532-50, Tokyo, Japan) as reported in previous papers [12,14]. The membranes ($1.0 \text{ cm} \times 3.0 \text{ cm}$) and two blackened platinum plate electrodes were placed in a Teflon cell. The distance between the two electrodes was 1.0 cm. The cell was placed in a thermocontrolled humidity chamber to measure the temperature and humidity dependence of the proton conductivity.

3. Results and discussion

3.1. Syntheses of sulfonated star-hyperbranched polyimide membranes

The amine-terminated polyimide as hyperbranched polymer was prepared by the same method reported by Okamoto and co-workers [22]. The structural perfection of the hyperbranched polymers is generally characterized by the degree of branching

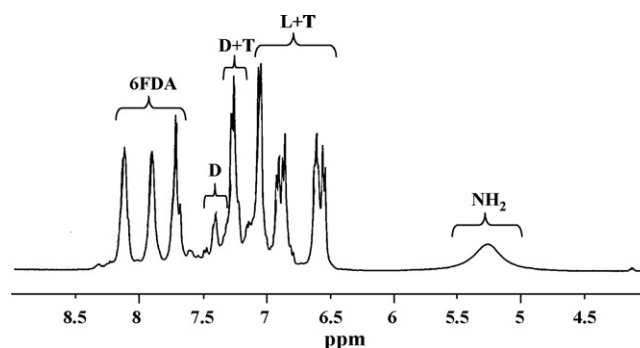


Fig. 2. ^1H NMR spectrum of amine-terminated 6FDA-TAPA.

(DB), which was defined by Frechet as follows:

$$\text{DB} = \frac{D + T}{D + T + L}$$

where D , T , and L refer to the number of dendritic, terminal, and linear units in the polymer, respectively. Generally, DB is determined from NMR spectroscopy by the integration of the peaks for the respective units in the hyperbranched polymers. Fig. 2 shows the ^1H NMR spectrum of the amine-terminated 6FDA-TAPA polyimide. The broad peak at 5.48 ppm is assigned to the hydrogens of the free amine groups in the terminal and linear units. The DB value of the 6FDA-TAPA was calculated from the ^1H NMR spectra of the model compounds for the dendritic, terminal, and linear units as reported by Okamoto and co-workers [22] and was estimated to be 0.64, indicating that the 0.6 was typical value as hyperbranched structure.

The sulfonated anhydride-terminated polyimide, NTDA-BDSA, was synthesized by the same method as described in previous papers [14], and three kinds of NTDA-BDSA polyimides with different molecular weights were obtained. The degree of imidization of the 6FDA-TAPA, and NTDA-BDSA was determined by ^1H NMR spectroscopy. The ^1H NMR spectra of the poly(amic acid)s of 6FDA-TAPA and NTDA-BDSA completely disappeared (data not shown), indicating that 6FDA-TAPA and NTDA-BDSA polymers were completely imidized.

The SHB-PI was synthesized from the mixture of the sulfonated anhydride-terminated polyimide and amine-terminated polyimide stirred at 70°C for 4 h and at 180°C for 24 h. The obtained SHB-PI was washed several times in methanol to completely remove the residual sulfonated anhydride-terminated polyimide, which easily dissolves in methanol. The yield of the resulting polymer was approximately 26%. The SHB-PI was soluble in aprotic polar solvents, such as DMAc, DMSO, DMF and NMP, as shown in Table 1. In general, a hyperbranched polymer membrane was very difficult to prepare tough membranes because of low entanglement between polymer chains [19,24]. The 6FDA-TAPA membrane had very poor membrane strength and easily broken. On the other hand, the SHB-PI membrane as star-hyperbranched polymer, which is composed of a hyperbranched polymer as the core and one type of linear polymer as the shell, indicated good membrane formability because of the enhanced entanglement between linear polymers. In addition,

Table 1
Solubilities of 6FDA-TAPA, NTDA-BDSA, and SHB-PI for organic reagents.

Polyimide	DMAc	DMSO	DMF	NMP	Methanol	Water
6FDA-TAPA	+	+	+	+	–	–
NTDA-BDSA	+	+	+	+	+	–
SHB-PI(1)	+	+	+	+	–	–
SHB-PI(2)	+	+	+	+	–	–
SHB-PI(3)	+	+	+	+	–	–

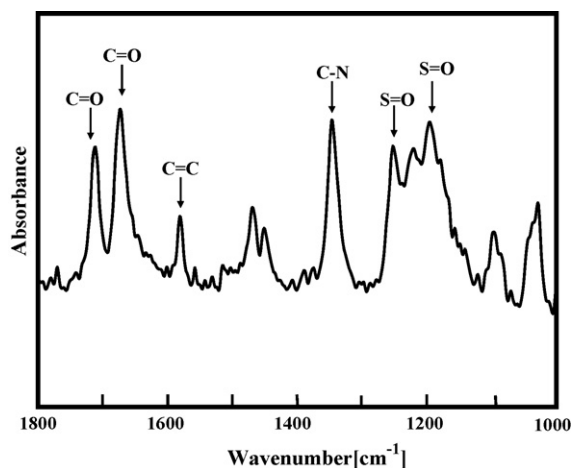


Fig. 3. IR spectrum of SHB-PI.

it was found that the toughness of the SHB-PI membrane increased with the molecular weight of NTDA-BDSA.

Fig. 3 shows the IR spectra of SHB-PI. The peaks at 1710 and 1670 cm^{-1} were assigned to the carbonyl group absorption and the peak at 1350 cm^{-1} was attributed to the imide absorption. The bands that appeared at 1250 and 1180 cm^{-1} were assigned to the sulfonic acid groups. In addition, it was found that the peak of the amine at 5.48 ppm measured by ^1H NMR significantly decreased due to the reaction between the amine of 6FDA-TAPA and the anhydride of NTDA-BDSA (data not shown).

The molecular weights of the amine-terminated 6FDA-TAPA, sulfonated anhydride-terminated NTDA-BDSA, and sulfonated star-hyperbranched polyimide (SHB-PI) are shown in Table 2. The actual molecular weights of the 6FDA-TAPA and SHB-PI may be even greater than the value estimated using the standard polystyrene, because the dendritic polymers are generally smaller than linear polymers with the same molecular weight [22]. Imidization reaction between NTDA-BDSA(1) as the low molecular weight and 6FDA-TAPA was efficiently accelerated rather than NTDA-BDSA(2) and (3) as the high molecular weight, and the apparent NTDA-BDSA(1), (2) and (3) chain numbers attached on 6FDA-TAPA were approximately 5, 3, and 2, respectively.

3.2. Characterization of sulfonated star-hyperbranched polyimide membranes

The thermal stability of the synthesized polyimides was investigated by TGA measurements. Fig. 4 shows the TGA curves of SHB-PI, NTDA-BDSA, and 6FDA-TAPA. The curve of SHB-PI was similar to that measured in the sulfonated homopolyimide, NTDA-BDSA. The loss above 280 $^{\circ}\text{C}$ was due to the desulfonation of the SHB-PI and NTDA-BDSA. The weight loss above 550 $^{\circ}\text{C}$ was ascribed to the decomposition of the polymer main chain. The decomposition temperature was almost as high as that of Nafion[®] [25]. The TGA curves

Table 2
Molecular weights of 6FDA-TAPA, NTDA-BDSA, and SHB-PI.

Polyimide	M_w	M_w/M_n
6FDA-TAPA ^a	44,000	5.3
NTDA-BDSA(1)	59,000	2.9
SHB-PI(1) ^a	320,000	9.0
NTDA-BDSA(2)	200,000	2.8
SHB-PI(2) ^a	500,000	3.0
NTDA-BDSA(3)	300,000	2.4
SHB-PI(3) ^a	830,000	4.9

^a Apparent molecular weight estimated from standard polystyrene.

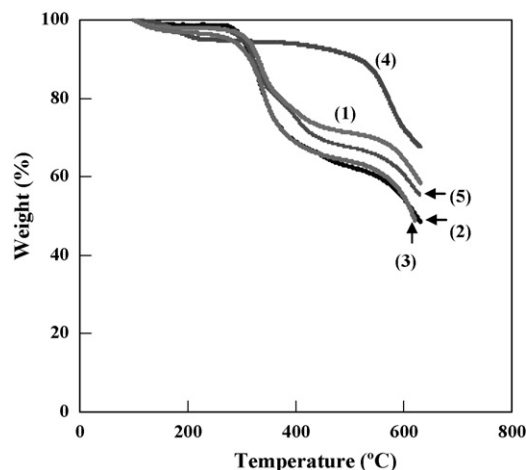


Fig. 4. TGA curves of 6FDA-TAPA, NTDA-BDSA and SHB-PI. (1) SHB-PI(1); (2) SHB-PI(2); (3) SHB-PI(3); (4) 6FDA-TAPA; (5) NTDA-BDSA.

of SHB-PI(2) and (3) indicated a completely similar thermal stability compared to that measured in SHB-PI(1).

On the other hand, the TGA curve of 6FDA-TAPA was thermally stable up to 550 $^{\circ}\text{C}$. The decomposition starts between 560 and 580 $^{\circ}\text{C}$. This indicates that 6FDA-TAPA has a high-temperature resistance compared to SHB-PI and NTDA-BDSA.

Table 3 shows the proton conductivity, ion exchange capacity (IEC), and water uptake for SHB-PI membranes. This value depended on the molecular weight of the sulfonated anhydride-terminated NTDA-BDSA and slightly increased with the molecular weight. In most polymer electrolyte membranes, the proton conductivities of the membranes are strongly related to the water content of the membrane, and the polymer electrolyte membranes absorbing a large amount of water typically have a high proton conductivity [26,27]. Therefore, there is good correlation between the IEC and water uptake, and the water uptake for the SHB-PI membranes also increased with the molecular weight of the NTDA-BDSA. It was clarified that the proton conductivities of the SHB-PI membranes indicated significantly higher values when compared to those of Nafion[®] under the same conditions [14]. One reason is that SHB-PI has a large number of sulfonic groups so that it can significantly adsorb the water compared to Nafion[®] as apparent from the results of the IEC and water uptake. In addition, it was found that the SHB-PI membrane indicated a higher proton conductivity than the other linear sulfonated polyimide membranes with the same IEC values and uncontrolled microstructures such as random sulfonated polyimide, as reported in previous papers [28,29]. This may be due to the fact that the hydrophilic domain formed by the sulfonated polyimide as a shell efficiently transports the protons. That is, the sulfonated star-hyperbranched polyimide has many NTDA-BDSA chains containing sulfonic acid groups as hydrophilic domain at the core surface so that the entanglement of NTDA-BDSA chains between star-hyperbranched polyimides may form ionic channels.

Table 3
Proton conductivity, IEC, and water uptake of SHB-PI membranes.

Polymer	Proton conductivity ^a (S cm^{-1})	IEC (mequiv. g^{-1})	Water uptake ^b (%)
SHB-PI(1)	0.34	2.5	79
SHB-PI(2)	0.46	2.8	82
SHB-PI(3)	0.51	2.8	83
Nafion [®] 117	0.15	0.9	21

^a At 80 $^{\circ}\text{C}$ and 98% relative humidity.

^b In water at room temperature.

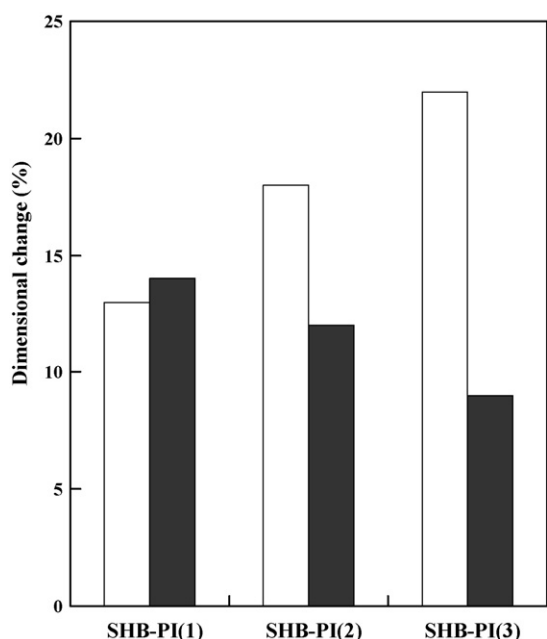


Fig. 5. Dimensional changes of SHB-PI membranes immersed in water at 80 °C. (□) ΔT is the dimensional increase in thickness direction; (■) ΔL is the dimensional increase in plane direction.

Radical stability of the SHB-PI membranes was immersed in Fenton's reagent (30 ppm FeSO_4 in 30% H_2O_2) at 25 °C. All the SHB-PI membranes broke within 1 h and their radical stabilities were not sufficient. We consider that NTDA–BDSA as shell attached on 6FDA–TAPA was mainly attacked by radicals produced from Fenton's reagent.

Fig. 5 shows the results of the dimensional changes (thickness, ΔT , and plane direction, ΔL) of the SHB-PI membranes immersed in water at 80 °C. The ΔT changes of the SHB-PI membranes increased with an increase in the molecular weight of the sulfonated anhydride-terminated NTDA–BDSA, on the other hand, their ΔL changes decreased with the molecular weight. The DB value as the degree of branching of the synthesized star-hyperbranched polyimide was approximately 0.6, therefore, the polyimide structure is not spherical and may form an asymmetric structure. In addition, it may be considered that the hydrophilic domain formed by NTDA–BDSA chain containing sulfonic acid groups were swollen in the thickness direction due to the disordered structure of the star-hyperbranched polyimide. As a result, the through-plane swelling in the thickness direction of the SHB-PI membrane might have occurred. However, these hypotheses require validation by another measurement.

Fig. 6 shows the temperature dependence of the proton conductivity of the SHB-PI membranes at a 98% relative humidity. It was found that the SHB-PI(3) membrane showed higher proton conductivity compared to the other membranes at all temperatures. In addition, it should be noted that the SHB-PI(2) and (3) membranes indicated a significantly higher conductivity compared to that determined in Nafion® at all temperatures.

Fig. 7 shows the relative humidity dependence of the proton conductivity for the SHB-PI membranes at 80 °C. The conductivities of the SHB-PI membranes were similar to or higher than those of Nafion® from 70 to 98% relative humidity. In general, the proton conductivity for most polymer electrolyte membranes based on the sulfonated polyimide is well known to significantly decrease compared to that determined in Nafion® [30]. In this study, the conductivities of the SHB-PI membranes are also much lower than Nafion® at the lower humidities. However, the conductivities of the

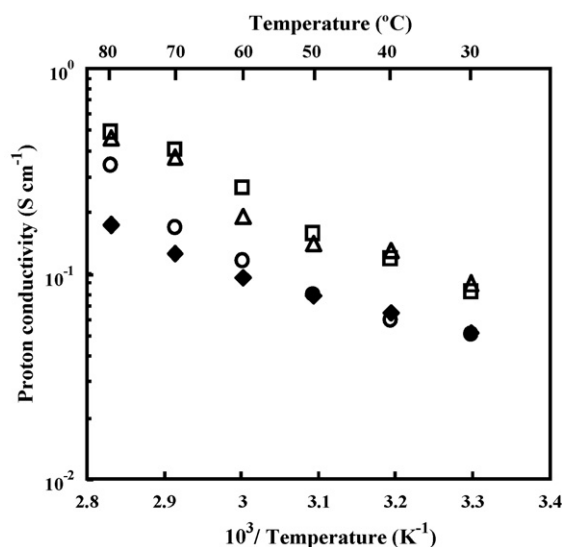


Fig. 6. Temperature dependence of proton conductivity for SHB-PI membrane at 98% RH. (○) SHB-PI(1); (△) SHB-PI(2); (□) SHB-PI(3); (◆) Nafion® 117.

SHB-PI(2) and (3) membranes indicated much higher values than the SHB-PI(1) membrane at the low humidities.

As already mentioned, the proton conductivities of the membranes are strongly related to the water content of the membrane, and polymer electrolyte membranes absorbing a large amount of water typically have a high proton conductivity. The water uptake has been expressed as the number of water molecules per sulfonic group (λ).

$$\lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3^-)} = \frac{\text{WS}}{18 \text{IEC}}$$

where $n(\text{H}_2\text{O})$ is the H_2O mole number, $n(\text{SO}_3)$ is the SO_3 group mole number, WS is the water uptake value by weight, IEC is the ion exchange capacity, and 18 corresponds to the molecular weight of water.

Fig. 8 shows the relative humidity dependence of λ for the SHB-PI membranes at 80 °C. The λ values of all the membranes were enhanced with the relative humidity, however, the comparison of the λ values among the membranes with different molecular weights of the sulfonated anhydride-terminated NTDA–BDSA do

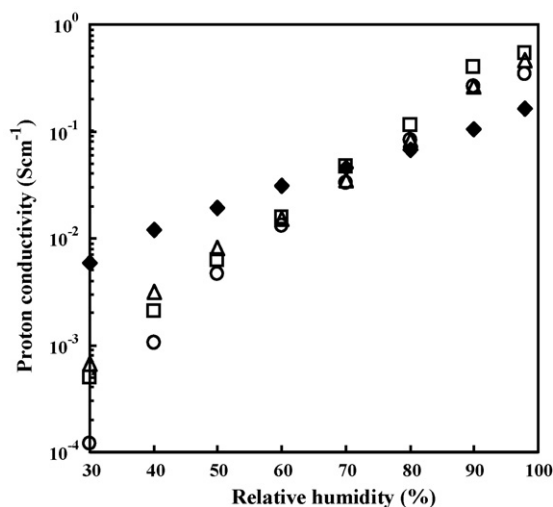


Fig. 7. Relative humidity dependence of proton conductivity for SHB-PI membrane at 80 °C. (○) SHB-PI(1); (△) SHB-PI(2); (□) SHB-PI(3); (◆) Nafion® 117.

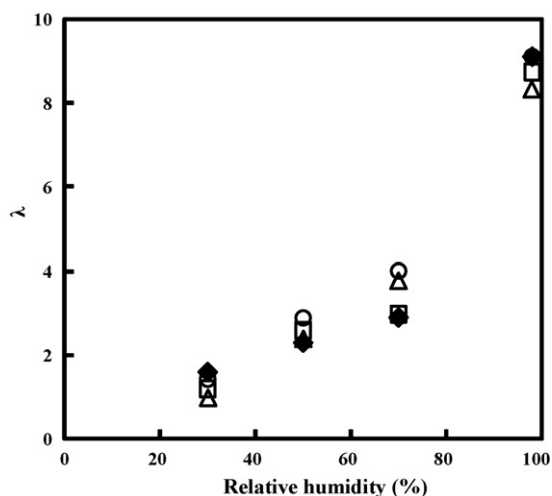


Fig. 8. Relative humidity dependence of water molecules per sulfonated group (λ) for SHB-PI membranes at 80 °C. (○) SHB-PI(1); (△) SHB-PI(2); (□) SHB-PI(3); (◆) Nafion® 117.

not indicate significant differences. In general, the λ value and water uptake have significant influence on the proton conductivity of polymer electrolyte membranes. Although the proton conductivity of SHB-PI(3) at 80 °C and 98% RH was 1.5 times larger than that determined in SHB-PI(1), the λ value and water uptake of the former polymer were almost similar to those in the latter polymer. Therefore, it is difficult to explain the difference in the proton transport among sulfonated star-hyperbranched polyimides using the λ value and water uptake. A most plausible explanation of the proton conductivity behavior in the sulfonated star-hyperbranched polyimide may be that the core-shell structure led to a phase separation between the hydrophilic proton transport sites and the hydrophobic domain so that ionic channels for the proton transport might be formed. If the ionic channels are formed by phase separation in the star-hyperbranched polyimide membranes, it is considered that the channels efficiently transport the proton at lower humidity. It is well known that Nafion® indicates the high proton conductivity at low humidity due to ionic channels. Unfortunately, the proton conductivity of sulfonated star-hyperbranched polyimide membranes prepared in this study did not reach that measured in Nafion® at low humidity. However, as mentioned above, the SHB-PI(2) and (3) indicated much higher proton conductivity at low humidity when compared to SHB-PI(1). That is, we believed that the entanglement of NTDA-BDSA chains as shell between the sulfonated star-hyperbranched polyimides induced the formation of the ionic channel and that, especially, the formation in the star-hyperbranched polyimide with larger molecular weight of NTDA-BDSA was accelerated. In the future research, we will elucidate phase separation produced in the sulfonated star-hyperbranched polyimide membrane using TEM.

4. Conclusions

This paper is the first report concerning with the syntheses and proton exchange membrane properties of a sulfonated star-hyperbranched polyimide membrane. We succeed in preparing the tough membrane without any crosslinking. Although the water uptake and IEC value for the sulfonated star-hyperbranched polyimide membranes were almost constant, it was found that the proton conductivity of the membrane strongly depended on the

molecular weight of the hydrophilic sulfonated polyimide as the shell. Especially, the conductivity of the high molecular weight star-hyperbranched polyimide membranes was significantly superior to that determined in Nafion® at all temperatures. This may be due to the fact that ionic channels in the sulfonated star-hyperbranched polyimide membrane are formed. However, these arguments require validation by observation of the ionic channels and phase separation measurements. Future research will have to elucidate these influences on the proton conductivity.

Unfortunately, although the obtained membranes were tough, the membranes immersed in Fenton's reagent (30 ppm FeSO₄ in 30% H₂O₂ at 25 °C) broke within 1 h and their radical stabilities were not sufficient. Therefore, to improve the membrane stability, such as mechanical strength and radical and hydrolytic stabilities, we are going to prepare organic-inorganic hybrid membranes composed of the star-hyperbranched polyimides and silica that possess desirable membrane stability, then estimate their fuel cell properties. Consequently, the polyimides may prove to be promising as a proton exchange membrane and may be potentially useful for application in fuel cells.

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