Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Fluorine Chemistry 127 (2006) 1087–1095

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

Synthesis of novel perfluorosulfonamide monomers and their application

Nobuyuki Uematsu [*], Nobuto Hoshi, Takehiro Koga, Masanori Ikeda

Central R&D Laboratories, Asahi Kasei Corporation, 2-1 Samejima, Fuji, Shizuoka 416-8501, Japan

Received 30 March 2006; received in revised form 7 May 2006; accepted 15 May 2006
Available online 26 May 2006

Abstract

The novel perfluorosulfonamide monomers and their preparation methods have been developed. The ternary-copolymer membranes, utilizing the perfluorosulfonamide monomers as the cross-linking site, can be efficiently converted to the cross-linked membranes with the strictly controlled structure. The novel cross-linking method has proved to be effective for the improvement of the mechanical properties at high temperature, while keeping its high proton conductivity.

Keywords: Perfluorosulfonamide; Ternary-copolymer; Cross-linking; Fluorine; Polymer electrolyte

1. Introduction

Polymer electrolyte fuel cell (PEFC) has attracted much attention as an environmentally clean energy source with high efficiency. Although a variety of polymer electrolytes for PEFC have been developed [1], the perfluorosulfonic acid ionomers such as Nafion®, Aciplex® and Flemion® have seemed to be promising for the polymer electrolyte due to their chemical stability (Fig. 1).

However, through the durability test of the PEFC, the durability of these materials at high temperature in practical fuel cell has proved to be insufficient. Therefore, the development of the practical fuel cell membrane requires the improvement of the mechanical strength and the chemical stability at high temperature.

Hydro-Quebec and Toyota Central R&D Laboratories reported that the polymer membrane containing the sulfonyl fluoride group (PSF) reacts with lithium hexamethyldisilazide (LHMDS) or ammonia to form the sulfonimide-cross-linked membrane [2,3]. The sulfonimide-cross-linked membrane was reported to be effective for the suppression of the film-expansion by swelling, as well as the improvement of the creep properties at high temperature. However, the reaction of PSF with LHMDS results in the surface-enriched amidation reaction. On the other hand, the slow reaction of PSF with ammonia enables the uniform amidation reaction though it takes long time as much as 2–10 days [3]. For the practical use, the further improvement in the productivity and the strict control of polymer structure are required. Here we report the synthesis of the novel perfluorosulfonamide monomers (**2a**, **2b**), their ternary-copolymers (**3aa**–**3ac**, **3b**) with the strictly controlled amount of the perfluorosulfonamide unit and their perfluorosulfonimide-cross-linked membranes (**4aa**–**4ac**, **4b**) (Scheme 1).

2. Results and discussion

2.1. Synthesis of perfluorosulfonamide monomers (**2a**, **2b**)

The perfluorosulfonamide monomers (**2a**, **2b**) were prepared by three methods (Methods A–C).

2.1.1. Method A

The cyclic compound **7** was prepared by the modification of Resnick's method [4]. The acyl fluoride **5** was added to Na_2CO_3 in tetraglyme while keeping the temperature below 30 °C to form the sodium salt **6**, and then decarboxylation of the sodium salt **6** at 160 °C was carried out to produce the cyclic compound **7** in high yield. The cyclic compound **7** is the useful synthetic

---

[*] Corresponding author. Tel.: +81 545 62 3058; fax: +81 545 62 3691.
E-mail address: uematsu.nb@om.asahi-kasei.co.jp (N. Uematsu).

0022-1139/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2006.05.015

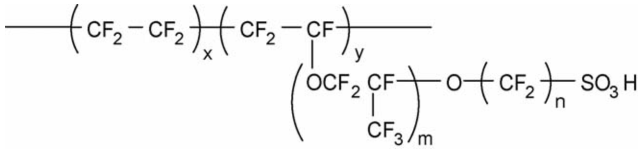
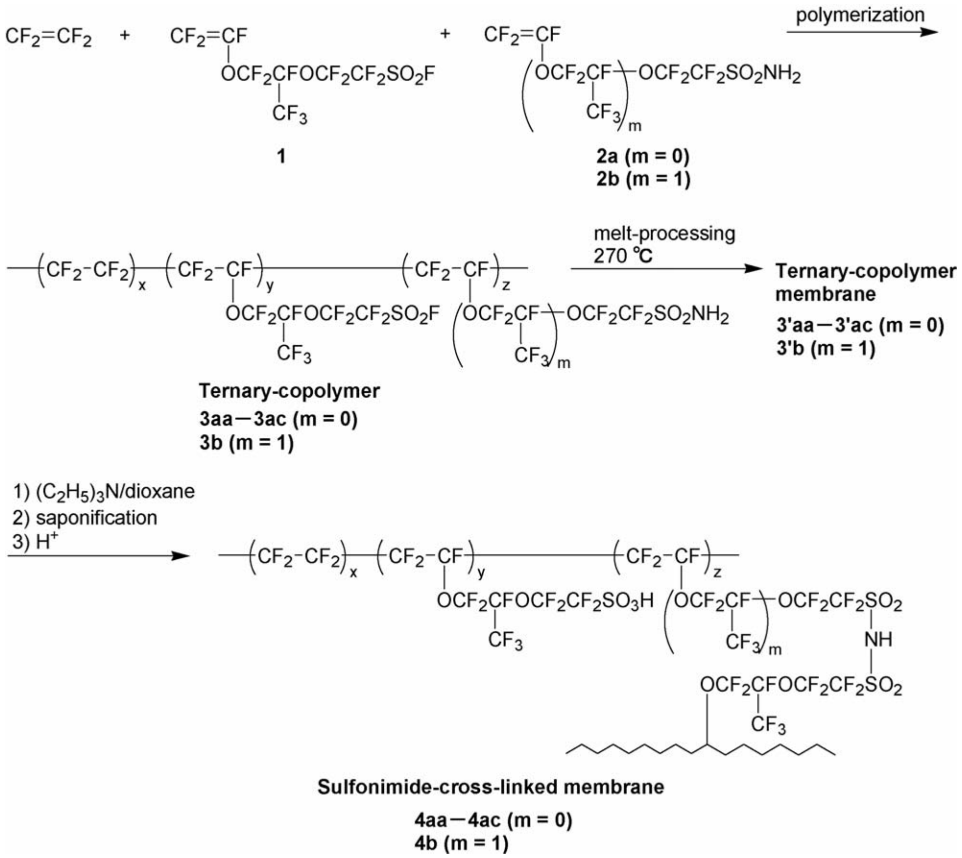


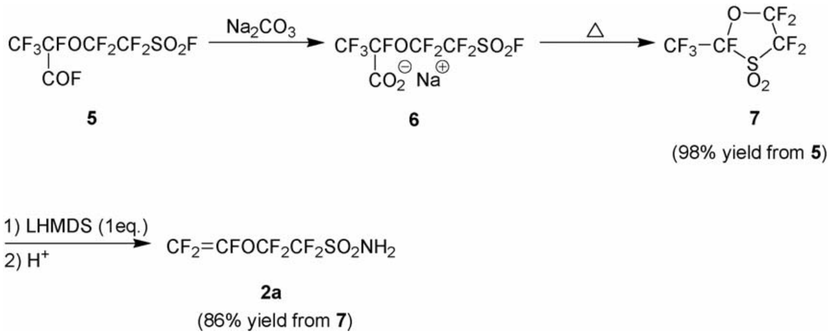
Fig. 1. Perfluorosulfonic acid ionomers.

intermediate for the preparation of the perfluorosulfonamide monomer **2a**. The cyclic compound **7** reacted with one equivalent of LHMDS to produce the perfluorosulfonamide monomer **2a** in high yield (Scheme 2).

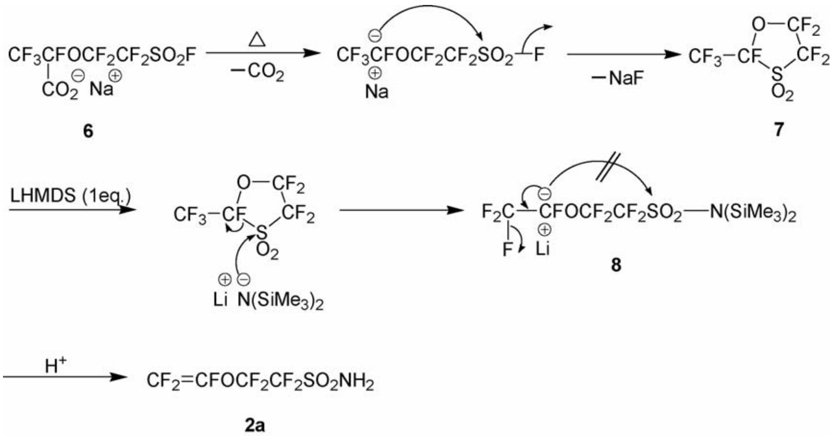
The proposed reaction mechanism is shown in Scheme 3. The pyrolytic decarboxylation of the sodium salt **6** generates the carbanion, which attacks the sulfonyl fluoride group to form the cyclic compound **7** quantitatively. In this reaction, the electron withdrawing of fluorine atom on the sulfonyl fluoride group enhances the nucleophilic attack of the carbanion on SO_2 site. Moreover, the formation of five-membered ring **7** seems to be thermodynamically favorable. By the addition of hexamethyldisilazide ion to SO_2 group in cyclic compound **7**, sulfonamidation and vinylation reactions take place at the same time. The carbanion, generated by the ring opening reaction, does not attack $SO_2N(SiMe_3)_2$ group, because the electron donation from hexamethyldisilazide group to SO_2 group suppresses the nucleophilic attack of the carbanion on SO_2 site. The carbanion in the intermediate **8** abstracts fluoride ion in CF_3 group to form the corresponding perfluorosulfonamide monomer **2a**.



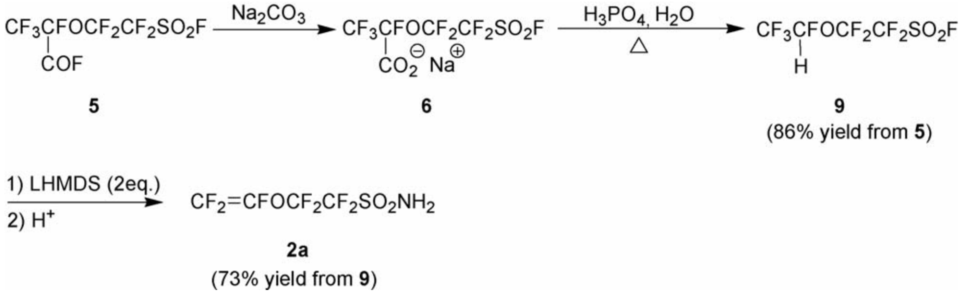
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

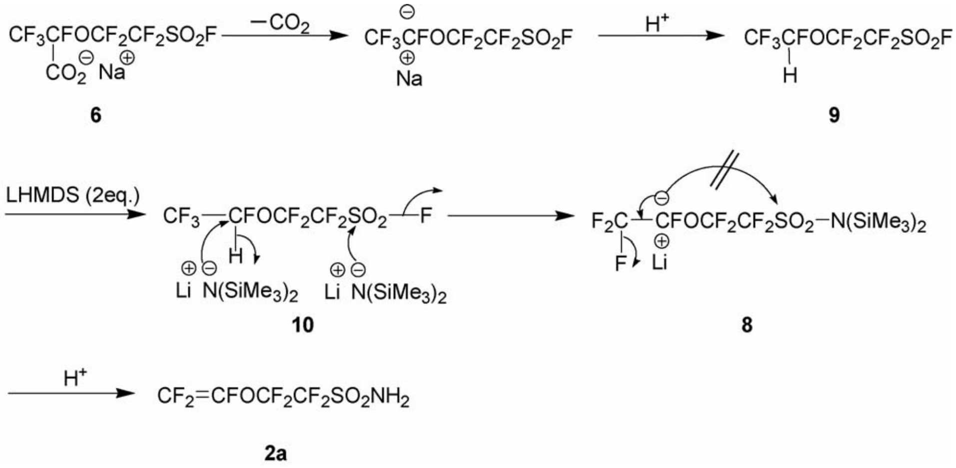
2.1.2. *Method B*

In the presence of the proton source, the pyrolytic decarboxylation of the sodium salt **6** forms the protonated compound **9**. By the reaction with two equivalents of LHMDS, the protonated compound **9** was converted to the perfluorosulfonamide monomer **2a** (Scheme 4).

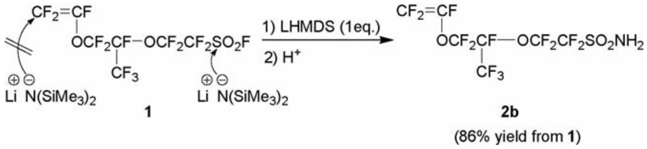
The proposed reaction mechanism is shown in Scheme 5. The protonated compound **9** was produced by the reaction of the proton with the carbanion, which is formed by the decarboxylation of the sodium salt **6**. As the reaction of **9** with LHMDS is shown in **10**, one equivalent of LHMDS is used for the proton abstraction [5] and the other one equivalent of LHMDS is used for sulfonamidation reaction. The intermediate **8** can be converted to the perfluorosulfonamide monomer **2a** in the same manner.

2.1.3. *Method C*

The perfluorosulfonamide monomer **2b** was synthesized from the perfluorosulfonyl fluoride monomer **1** with one equivalent of LHMDS in high yield (Scheme 6).



Scheme 5.



Scheme 6.

Hexamethyldisilazide ion is the bulky nucleophile and it does not attack the vinyl group.

2.2. Copolymerization

The perfluorosulfonamide monomers (**2a**, **2b**) were copolymerized with tetrafluoroethylene (TFE) and the perfluorosulfonyl fluoride monomer **1** to give the ternary-copolymers (**3aa–3ac**, **3b**) by the conventional free radical polymerization in the solution system (Scheme 7, Table 1).

The ternary-copolymers (**3aa–3ac**, **3b**) were obtained as white powders, which were identified by IR and solid-state ^{19}F NMR spectroscopy. The IR spectra of the ternary-copolymers (**3aa–3ac**, **3b**) showed characteristic signals for the sulfonamide (3309 and 3373 cm^{-1}) and the sulfonyl fluoride (1468 cm^{-1}). The solid-state ^{19}F NMR spectra of the ternary-copolymers (**3aa–3ac**, **3b**) showed the peaks for CF_2SO_2F (−104 ppm) and $CF_2SO_2NH_2$ (−108 ppm). The copolymer composition ratio of TFE, **1** and (**2a**, **2b**) was determined by solid-state ^{19}F NMR and IR spectroscopy. The amount of the perfluorosulfonamide monomer units (**2a**, **2b**) in the ternary-copolymers (**3aa–3ac**, **3b**) was 60–80 mol% of that of the monomer composition. The amount of the perfluorosulfonamide monomer units (**2a**, **2b**), as well as that of the perfluorosulfonyl fluoride monomer **1**, in the ternary-copolymers (**3aa–3ac**, **3b**) can be strictly controlled by the monomer composition for the polymerization.

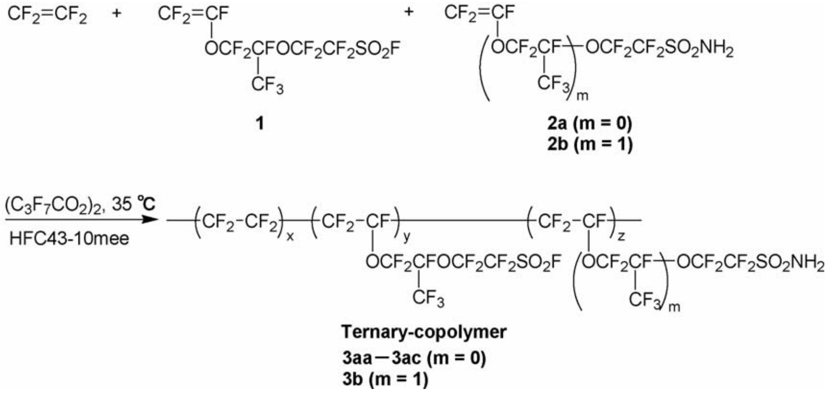
2.3. Cross-linking

The ternary-copolymers (**3aa–3ac**, **3b**) were stable enough to afford the melt-processing at 270 °C to produce the homogeneous membranes (**3′aa–3′ac**, **3′b**). Namely, during the melt-processing, the sulfonamide group and the sulfonyl fluoride group don't react nor are denatured at all.

However, by the heat treatment of the ternary-copolymer membranes (**3′aa–3′ac**, **3′b**) in the presence of triethylamine, the reaction between the sulfonamide group and the sulfonyl fluoride group took place efficiently to form the stable sulfonimide-cross-link (**4aa–4ac**, **4b**) (Scheme 8, Table 2).

When the ternary-copolymer membrane containing a large amount of the sulfonamide units, the formation of the sulfonimide-cross-linkage can be confirmed by the decrease of the sulfonamide band (1389 cm^{-1}) and the appearance of the sulfonimide band (1352 cm^{-1}) in the IR spectra. Fig. 2 shows the IR spectra of the ternary-copolymer membrane (TFE:**1**:**2a** = 530:100:20 (molar ratio)) (**I**) and the corresponding sulfonimide-cross-linked membrane (**II**).

However, when the ternary-copolymer membranes (**3′aa–3′ac**, **3′b**) containing a small amount of the sulfonamide units, the sulfonimide band in the IR spectra was elusive, and hence the amount of the sulfonimide-cross-linking site in (**4aa–4ac**,



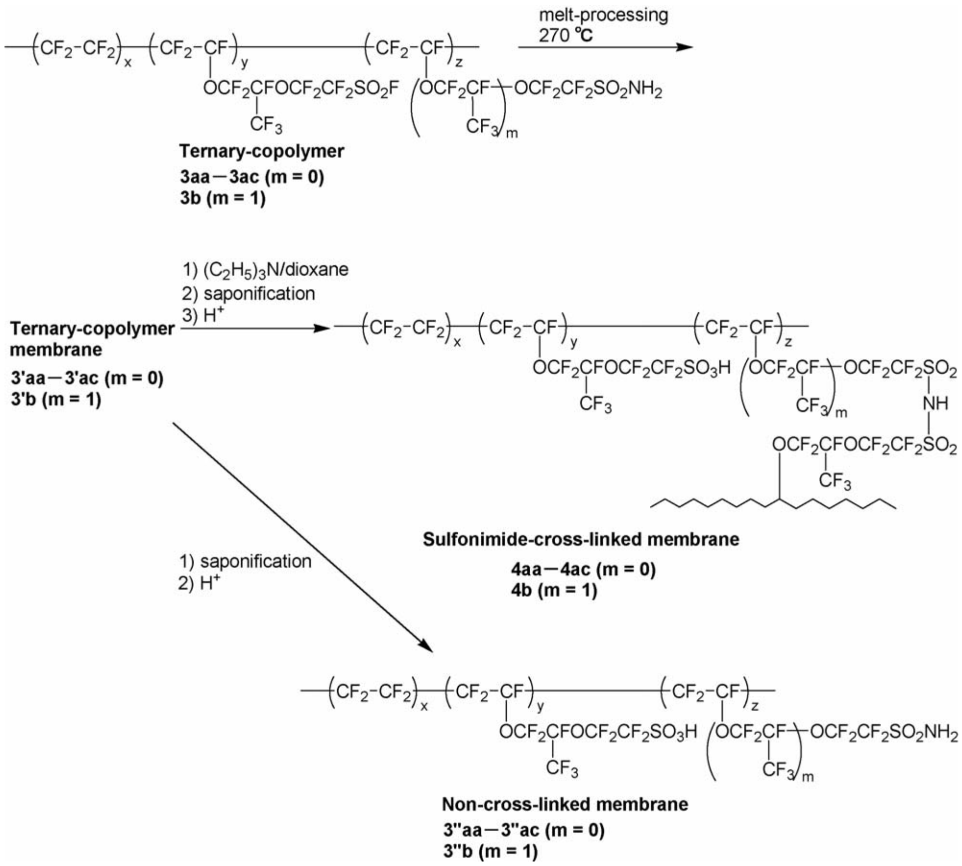
Scheme 7.

Table 1
Copolymerization[a] of TFE, **1** and **2a** (or **2b**)

Monomer composition		Reaction time (h)	Ternary-copolymer		
Sulfonamide monomer	**1**:**2a** (or **2b**) (molar ratio)		Copolymer	Copolymer weight (g)	Copolymer composition[b]; TFE:**1**:**2a** (or **2b**) (molar ratio)
2a (0.0052 mol)	100:1.0	5.0	**3aa**	53.3	360:100:0.6
2a (0.016 mol)	100:3.1	5.4	**3ab**	50.0	320:100:1.9
2a (0.039 mol)	100:7.5	5.5	**3ac**	40.3	360:100:4.5
2b (0.016 mol)	100:3.1	5.1	**3b**	45.3	340:100:2.4

[a] Polymerization was carried out at 35 °C in 1 L autoclave. Reaction conditions: TFE (1.7 kg/cm^2), **1** (0.523 mol), **2a** (or **2b**), HFC43-10mee (700 g), 5 wt.% $(C_3F_7CO_2)_2$ solution in HFC43-10mee (3.7 g).

[b] Determined by solid-state ^{19}F NMR and IR.



Scheme 8.

4b) was estimated by the decrease of the sulfonamide band (1389 cm^{-1}), compared to the IR spectra of the non-cross-linked membranes (ternary-copolymer membranes (**3′aa**–**3′ac**, **3′b**) in the acid form without treating (**3′aa**–**3′ac**, **3′b**) with triethylamine) (**3″aa**–**3″ac**, **3″b**). The disappearance of the sulfonamide units in (**4aa**–**4ac**, **4b**) was confirmed by the IR spectra. Fig. 3 shows the IR spectra of the non-cross-linked membrane (**3″ac**) and the corresponding sulfonimide-cross-linked membrane (**4ac**).

Table 2 shows the equivalent weight (EW) and the proton conductivity (23 °C) of the non-cross-linked membranes (**3″aa**–**3″ac**, **3″b**) and the corresponding sulfonimide-cross-linked membranes (**4aa**–**4ac**, **4b**). The proton conductivity of (**4aa**–**4ac**, **4b**) does not decrease by the sulfoni-

Table 2
EW and proton conductivity of the non-cross-linked membranes and the sulfonimide-cross-linked membranes

Non-cross-linked membrane[a]			Sulfonimide-cross-linked membrane[b]			
Membrane	EW (g/equiv.)	Proton conductivity (S/cm at 23 °C)	Membrane	Cross-linking site[c] (mol%)	EW (g/equiv.)	Proton conductivity (S/cm at 23 °C)
3″aa	994	0.10	**4aa**	0.6	999	0.10
3″ab	992	0.11	**4ab**	1.9	1000	0.10
3″ac	992	0.10	**4ac**	4.5	999	0.10
3″b	995	0.10	**4b**	2.4	1005	0.11

[a] The ternary-copolymer membranes (**3′aa**–**3′ac**, **3′b**) were saponified with the solution (Me$_2$SO:KOH:H$_2$O = 15:30:55 (weight ratio)) at 90 °C for 1 h, and then immersed in deionized water at 90 °C for 1 h, immersed in 4N sulfuric acid at 90 °C for 1 h, washed in deionized water until the wash water was neutral, and dried to produce the non-cross-linked membranes (**3″aa**–**3″ac**, **3″b**).

[b] The ternary-copolymer membranes (**3′aa**–**3′ac**, **3′b**) were immersed in (C$_2$H$_5$)$_3$N–dioxane mixture ((C$_2$H$_5$)$_3$N:dioxane = 3:5 (volume ratio)) at 80 °C for 5 h, and then saponified with the solution (Me$_2$SO:KOH:H$_2$O = 15:30:55 (weight ratio)) at 90 °C for 1 h, immersed in deionized water at 90 °C for 1 h, immersed in 4N sulfuric acid at 90 °C for 1 h, washed in deionized water until the wash water was neutral, and dried to produce the sulfonimide-cross-linked membranes (**4aa**–**4ac**, **4b**).

[c] The disapperance of the sulfonamide units in the membranes (**4aa**–**4ac**, **4b**) was confirmed by IR. The molar ratio of the sulfonimide-cross-linking site to the suifonic acid group and the sulfonimide-cross-linking site in the membranes (**4aa**–**4ac**, **4b**).

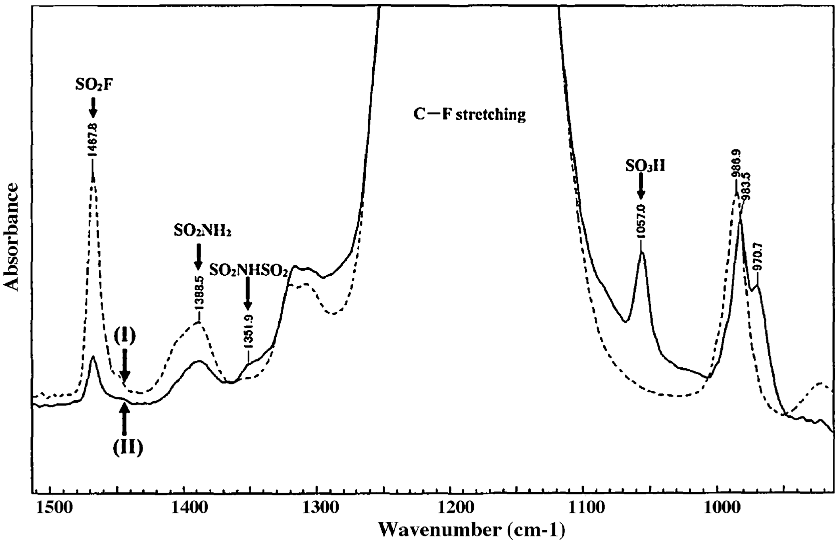


Fig. 2. IR spectra of the ternary-copolymer membrane (TFE:**1**:**2a** = 530:100:20 (molar ratio)) (**I**) and the corresponding sulfonimide-cross-linked membrane (**II**). The ternary-copolymer membrane (**I**) was immersed in triethylamine–dioxane mixture (triethylamine:dioxane = 3:5 (volume ratio)) at 80 °C for 5 h, and then immersed in 4N sulfuric acid at 90 °C for 1 h, washed with deionized water until the wash water was neutral, and dried to produce (**II**).

mide-cross-linking, which seems to be due the fact that the sulfonimide-cross-linking site in (**4aa**–**4ac**, **4b**) acts as a super acid [6].

2.4. Effects of cross-linking

Fig. 4 shows the storage modulus of the sulfonimide-cross-linked membranes (**4aa**–**4ac**, **4b**), the non-cross-linked membrane **3″ab**, and the binary-copolymer membrane **S** (TFE:**1** = 360:100 (molar ratio), having no sulfonamide units (**2a**, **2b**)) against the temperature.

The storage modulus of **S** and **3″ab** is not preserved at high temperature over 200 °C. The preservation of the storage modulus improves with the increasing amount of the cross-linking site. Typically, the sulfonimide-cross-linked membrane **4ac**, which contains 4.5 mol% cross-linking site, preserves the excellent storage modulus even at high temperature around 300 °C.

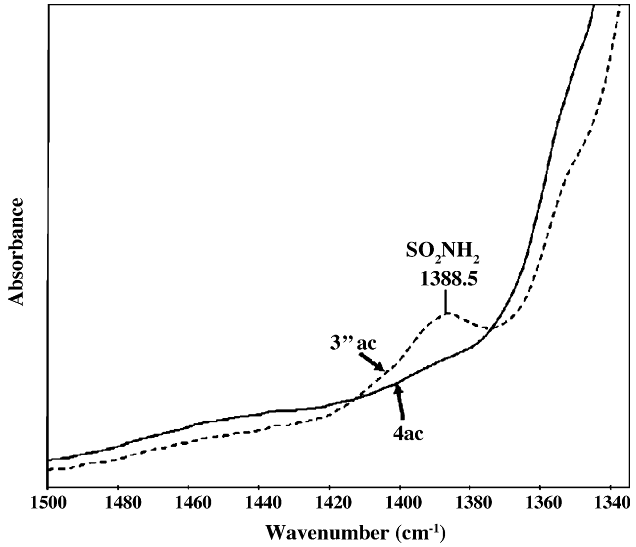


Fig. 3. IR spectra of the non-cross-linked membrane (**3″ac**) and the corresponding sulfonimide-cross-linked membrane (**4ac**).

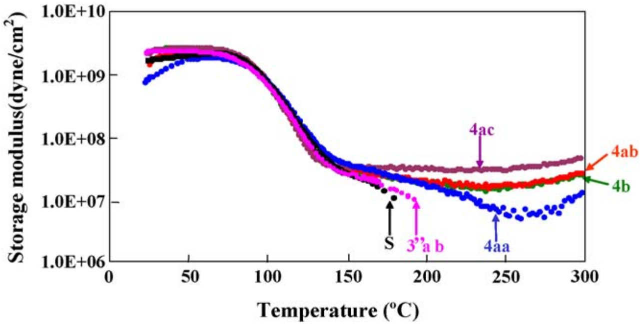


Fig. 4. The storage modulus of the binary-copolymer membrane **S**, the non-cross-linked membrane **3″ab** and the sulfonimide-cross-linked membranes (**4aa**–**4ac**, **4b**). The amount of the sulfonimide-cross-linking site: **4aa**, 0.6 mol%; **4ab**, 1.9 mol%; **4ac**, 4.5 mol%; **4b** 2.4 mol%.

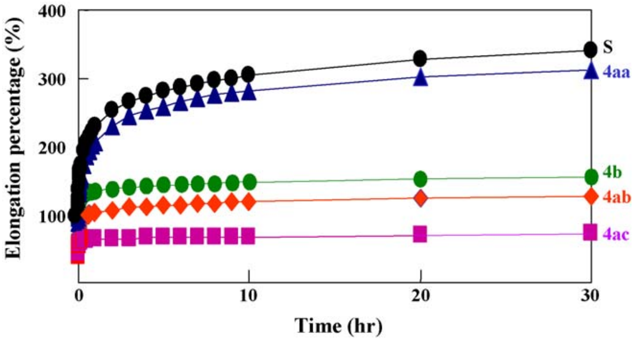


Fig. 5. The creep property of the sufonimide-cross-linked membranes (**4aa**–**4ac**, **4b**) and the binary-copolymer membrane **S** (conditions: 120 °C dry state, 16 kg/cm^2). The amount of the sulfonimide-cross-linking site: **4aa**, 0.6 mol%; **4ab**, 1.9 mol%; **4ac**, 4.5 mol%; **4b**, 2.4 mol%.

Fig. 5 shows the creep property of the sulfonimide-cross-linked membranes (**4aa–4ac**, **4b**) and the binary-copolymer membrane **S** at 120 °C dry state. The creep property of the sulfonimide-cross-linked membranes (**4aa–4ac**, **4b**) improves with the increasing amount of cross-linking site. Typically, the sulfonimide-cross-linked membrane **4ac**, which contains 4.5 mol% cross-linking site, scarcely shows creep property.

3. Conclusion

The novel perfluorosulfonamide monomers and their preparation methods have been developed. The ternary-copolymer membranes, utilizing the perfluorosulfonamide monomers as the cross-linking site, can be efficiently converted to the cross-linked membranes with the strictly controlled structure. The novel cross-linking method has proved to be effective for the improvement of the mechanical properties at high temperature, while keeping its high proton conductivity. As compared to the previous cross-linking method utilizing the reaction of cross-linking reagent with the sulfonyl fluoride type membrane, the present method has various advantages, such as the productivity and the strict control of the membrane structure. Therefore, the present method will be useful for the improvement of the durability of PEFC at high temperature.

4. Experimental

The reagents were obtained from commercial sources and used as received unless otherwise stated. $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) and $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**) were prepared as described in literature [7–8]. Na_2CO_3 was dried *in vacuo* at 180 °C for 6 h before use. The ^1H NMR (400 MHz) spectra and ^{19}F NMR (376 MHz) spectra were recorded in $CDCl_3$ on a JEOL GSX-400 and the chemical shifts (δ) were referred to tetramethylsilane (^1H), and $CFCl_3$ (^{19}F), respectively. Solid-state ^{19}F NMR spectra were obtained with magic angle spinning (MAS) using a Brucker Biospin DSX-400, and the chemical shifts (δ) were references to trifluoroacetic acid. IR spectra were obtained by the transmission method or the attenuated total reflectance method with a Perkin-Elmer Spectrum One or Bio-Rad FTS6000. GC–MS data were obtained on a Hewlett-Packard HP5890 series II gas chromatograph equipped with a HP5973 MSD with chemical ionization (CI) using methane as reagent gas.

4.1. Preparation of $CF_2{=}CFOCF_2CF_2SO_2NH_2$ (**2a**)

4.1.1. Method A

The cyclic compound **7** was prepared by the modification of Resnick's method [4]. To a 3 L round-bottomed flask equipped with a mechanical stirring, a dropping funnel and a reflux condenser were added dry Na_2CO_3 (328.6 g, 3.10 mol), tetraglyme (1000 mL). To the flask was added $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) (934.2 g, 2.70 mol) through a dropping funnel keeping the temperature below 30 °C over 3 h. After the completion of the addition, the reaction mixture was stirred at 40 °C for 1 h to form the sodium salt **6**. The formation of the sodium salt **6** was confirmed by ^{19}F NMR. Then the flask was heated at 160 °C and the volatile component was collected out of the flask at atmospheric pressure, which was cooled by ice bath. The colorless liquid was the cyclic compound **7**, which was confirmed by ^{19}F NMR. The yield of the cyclic compound **7** was determined by ^{19}F NMR (741.9 g, 2.65 mol, 98% yield).

^{19}F NMR δ: −124.71 (d, 1F, $J = 218$ Hz), −120.56 (d, 1F, $J = 218$ Hz), −115.35 (s, 1F), −90.09 (d, 1F, $J = 135$ Hz), −80.50 (s, 3F), −78.01 (d, 1F, $J = 135$ Hz). GC–MS (CI) *m/z* 281 $(MH)^+$.

To a 2 L round-bottomed flask equipped with a mechanical stirring and a dropping funnel were added dry THF (600 mL, no stabilization), hexamethyldisilazane (154.6 g, 0.96 mol) under N_2 atmosphere, and the flask was cooled at −78 °C. To the flask was added 1.6 M *n*-BuLi solution in hexane (600 mL, 0.96 mol) through a dropping funnel at −78 °C over 1 h. After the completion of the addition, the reaction mixture was stirred at 0 °C for 1 h. To the flask was added cyclic compound **7** (245.0 g, 0.88 mol) through a dropping funnel at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with diluted HCl and then HFC43-10mee was added. The organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by reduced distillation to give a colorless liquid **2a** (210.5 g, 0.76 mol, 86% yield).

b.p. 91–92 °C/3 mmHg. ^{19}F NMR δ: −137.90 (dd, 1F, $J = 112, 67$ Hz), −124.07 (dd, 1F, $J = 112, 87$ Hz), −118.13 (s, 2F), −116.70 (dd, 1F, $J = 87, 67$ Hz), −85.21 (s, 2F). ^1H NMR δ: 6.01 (s, 2H). IR (neat) 3392 (NH), 3295 (NH), 1388 (SO_2) cm^{-1}. GC–MS (CI) *m/z* 278 $(MH)^+$.

4.1.2. Method B

The protonated compound **9** was prepared by the modification of Ref. [9]. To a 2 L round-bottomed flask equipped with a mechanical stirring, a dropping funnel and a reflux condenser were added dry Na_2CO_3 (106.0 g, 1.0 mol), tetraglyme (311 mL). To the flask was added $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) (311.0 g, 0.90 mol) through a dropping funnel, while keeping the temperature below 30 °C over 3 h. After the completion of the addition, the reaction mixture was stirred at 40 °C for 1 h to form the sodium salt **6**. The formation of the sodium salt **6** was confirmed by ^{19}F NMR. To the flask was added the mixture of 85% H_3PO_4 (230.0 g, 2.0 mol) and water (230 mL). Then the flask was heated at 160 °C, and the protonated compound **9** and water were collected out of the flask, which was cooled by ice bath. The collected liquid was washed three times with water, dried over Na_2SO_4, and filtered to give a colorless liquid **9**, which was confirmed by ^{19}F NMR. The yield of the protonated compound **9** was determined by ^{19}F NMR (231.1 g, 0.77 mol, 86% yield).

^{19}F NMR δ: −147.91 (d, 1F, $J = 52$ Hz), −114.21 (s, 2F), −86.99 (d, 1F, $J = 134$ Hz), −86.53 (s, 3F), −84.67 (d, 1F, $J = 134$ Hz), 42.73 (s, 1F). ^1H NMR δ: 6.07 (d, 1H, $J = 52$ Hz).

To a 2 L round-bottomed flask equipped with a mechanical stirring and a dropping funnel were added dry THF (500 mL, no stabilization), hexamethyldisilazane (134 g, 0.832 mol). To the flask was added 1.6 M *n*-BuLi solution in hexane (520 mL, 0.832 mol) through a dropping funnel at 0 °C. The reaction mixture was stirred at 0 °C for 1 h. To the flask was added the protonated compound **9** (112 g, 0.373 mol) through a dropping funnel at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was quenched with diluted HCl and then HFC43-10mee was added. The organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by reduced distillation to give a colorless liquid **2a** (75.3 g, 0.272 mol, 73% yield).

*4.2. Synthesis of $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2NH_2$ (**2b**) (Method C)*

To a 2 L round-bottomed flask equipped with a mechanical stirring and a dropping funnel were added dry THF (500 mL, no stabilization), hexamethyldisilazane (79.4 g, 0.493 mol). To the flask was added 1.6 M *n*-BuLi solution in hexane (308 mL, 0.493 mol) through a dropping funnel at −78 °C. The reaction mixture was stirred at −78 °C for 1 h. To the flask was added $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**) (200 g, 0.448 mol) through a dropping funnel at 0 °C. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was quenched with diluted HCl and the solvent was evaporated. To the residue was added diluted HCl until the aqueous and organic layers were separated. The organic layer was separated and the aqueous layer was extracted twice with HFC43-10mee. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by reduced distillation to give a colorless liquid **2b** (170.1 g, 0.384 mol, 86% yield).

b.p. 118–119 °C/3 mmHg. ^{19}F NMR δ: −146.68 (s, 1F), −138.48 (dd, 1F, $J = 113$, 67 Hz), −124.58 (dd, 1F, $J = 113$, 87 Hz), −118.23 (s, 2F), −117.03 (dd, 1F, $J = 87$, 67 Hz), −86.80 (s, 2F), −82.28 (s, 3F), −80.42 (m, 2F). ^1H NMR δ: 5.95 (s, 2H). IR (neat) 3390 (NH), 3299 (NH), 1388 (SO_2) cm^{-1}. GC–MS (CI) *m/z* 444 $(MH)^+$.

*4.3. General procedure for copolymerization of TFE, $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**) and perfluorosulfonamide monomer (**2a** or **2b**)*

The following procedure is typical. $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**) (233.3 g, 0.523 mol), the perfluorosulfonamide monomer (**2a**) (4.43 g, 0.016 mol (0.031 equiv. based on **1**)), HFC43-10mee (700 g) were introduced into a 1 L autoclave under 20 °C. The internal atmosphere of the autoclave was fully purged several times with N_2 gas. After the internal atmosphere of the autoclave was replaced with TFE, the autoclave was elevated at 35 °C. To the autoclave added 3.7 g of 5 wt.% $(C_3F_7CO_2)_2$ solution in HFC43-10mee, and TFE was added to the pressure of 1.7 kg/cm^2. Then the reaction temperature was performed at 35 °C while TFE was added to maintain the pressure of 1.7 kg/cm^2. During the reaction, 1.9 g of 5 wt.% $(C_3F_7CO_2)_2$ solution in HFC43-10mee was added to the autoclave. When the desired amount of TFE (29 g) was consumed, TFE was vented and methanol was added to the reaction mixture to precipitate a white solid. The white solid was filtered, rinsed with HFC43-10mee and dried *in vacuo* at 110 °C for 12 h to give 50.0 g of the ternary-copolymer **3ab**.

The composition of the ternary-copolymer **3ab** was 320:100:1.9 (TFE:**1**:**2a** (molar ratio)) by the solid-state ^{19}F NMR.

The ternary-copolymer **3ab** was compression-molded at 270 °C to give the homogeneous membrane **3′ab** (thickness: 56 μm). The IR spectra of the ternary-copolymer membrane **3′ab** showed the characteristic signals for the sulfonamide (3309, 3373 cm^{-1}) and the sulfonyl fluoride (1468 cm^{-1}).

*4.4. General procedure for the non-cross-linked membranes (**3″aa–3″ac, 3″b**)*

The following procedure is typical. The ternary-copolymer membrane **3′ab** was saponified with the solution (Me_2SO:KOH:H_2O = 15:30:55 (weight ratio)) at 90 °C for 1 h, and then immersed in deionized water at 90 °C for 1 h, immersed in 4 N sulfuric acid at 90 °C for 1 h, washed with deionized water until the wash water was neutral, and dried to produce the non-cross-linked membrane (**3″ab**). The disappearance of the sulfonyl fluoride signal (1468 cm^{-1}), the appearance of the sulfonic acid signal (1057 cm^{-1}), and the sulfonamide signal (1389 cm^{-1}) were confirmed by the IR spectra of the non-cross-linked membrane (**3″ab**).

*4.5. General procedure for the sulfonimide-cross-linked membranes (**4aa–4ac, 4b**)*

The following procedure is typical. The ternary-copolymer membrane **3′ab** was immersed in triethylamine–dioxane mixture (triethylamine:dioxane = 3:5 (volume ratio)) at 80 °C for 5 h, and then the membrane was saponified with the solution (Me_2SO:KOH:H_2O = 15:30:55 (weight ratio)) at 90 °C for 1 h, immersed in deionized water at 90 °C for 1 h, immersed in 4 N sulfuric acid at 90 °C for 1 h, washed with deionized water until the wash water was neutral, and dried to produce the sulfonimide-cross-linked membrane **4ab**. The disappearance of the sulfonamide signal (1389 cm^{-1}) and the sulfonyl fluoride signal (1468 cm^{-1}), and the appearance of the sulfonic acid signal (1057 cm^{-1}) were confirmed by the IR spectra of the sulfonimide-cross-linked membrane **4ab**.

*4.6. Procedure for the binary-copolymer membrane **S***

A polymerization reaction of TFE with $CF_2{=}CFOCF_2CF(CF_3)OCF_2CF_2SO_2F$ (**1**) was performed in the same manner as Section 4.3, except that the perfluorosulfonamide monomer was not used, thereby obtaining 53.4 g of the binary-copolymer. The composition of the binary-copolymer was 360:100 (TFE:**1** (molar ratio)) by the solid-state ^{19}F NMR. The binary-copolymer was compression-molded at 270 °C to give a colorless membrane (thickness: 60 μm). The IR spectra of the colorless membrane showed the characteristic signal for the sulfonyl fluoride ($1469\ cm^{-1}$). The colorless membrane was saponified with the solution (Me_2SO:KOH:H_2O = 15:30:55 (weight ratio)) at 90 °C for 1 h, and then immersed in deionized water at 90 °C for 1 h, immersed in 4 N sulfuric acid at 90 °C for 1 h, washed with deionized water until the wash water was neutral, and dried to produce the binary-copolymer membrane **S**. The IR spectra of the binary-copolymer membrane **S** showed the disappearance of the sulfonyl fluoride signal ($1469\ cm^{-1}$) and the appearance of the sulfonic acid signal ($1057\ cm^{-1}$).

4.7. Characterization

The equivalent weight (EW) of the acidified membrane was measured as follows. The dry membrane (about 2 to $10\ cm^2$) was weighed and dipped in 50 ml of saturated NaCl aq. solution at 23 °C. The solution was left for standing for 10 min while stirring, and then neutralized to an end point of pH 7.0 by titration of 0.01 M NaOH aq. solution. EW (g/eq) was calculated by the following Eq. (1):

$$\mathrm{EW} = \frac{m}{0.01v} \tag{1}$$

where v is the volume (mL) of 0.01 M NaOH aq. solution required to reach the end point, and m is the weight (mg) of the dry membrane.

The proton conductivity of the acidified membrane was measured as follows. The membrane sample in a wet state was cut out and the thickness T (cm) was measured. The sample was loaded on a two terminal conductivity measuring cell for measuring the conductivity in the length direction of a membrane having a width of 1 cm and a length of 5 cm. This cell was immersed in deionized water at 23 °C for 30 min, and then the resistance value R (Ω) of real number component at a frequency of 10 kHz was measured by an AC impedance method. The proton conductivity Z (S/cm) was determined by the following Eq. (2):

$$Z = \frac{L}{RTW} \tag{2}$$

where L (=5 cm) is the length of the sample and W (=1 cm) is the width of the sample.

A creep test specimen having a width of 10 mm and a length of 50 mm was cut out from the acidified membrane and the thickness was measured. The elongation of the test specimen was measured by a Orientec CP3-P-30 (conditions: 120 °C dry state, tensile stress: $16\ kg/cm^2$).

A rectangular test specimen having a width of 3 mm and a length of 30 mm was cut out from the acidified membrane and the thickness was measured. The storage modulus of the test specimen was measured from 23 to 300 °C at the frequency of 35 Hz by a A&D RHEOVIBRON DDV-01FP.

Acknowledgement

We thank Dr. Yasuhiro Hashimoto of Asahi Kasei Corporation for the measurement of the solid-state ^{19}F NMR spectroscopy.

References

[1] O. Savadogo, J. New Mater. Electrochem. Syst. 1 (1998) 47–66.
[2] C. Michot, M. Armand, WO Patent 99/38897 (1999).
[3] H. Tanaka, A. Usuki, M. Kawasumi, Y. Morimoto, JP Patent 2001-319521A (2001).
[4] P.R. Resnick, US Patent 3,560,568 (1971).
[5] R. Anilkumar, D.J. Burton, J. Fluorine Chem. 126 (2005) 1174–1184.
[6] D.D. DesMarteau, J. Fluorine Chem. 72 (1995) 203–208.
[7] B.H. Thomas, G. Shafer, J.J. Ma, M.-H. Tu, D.D. DesMarteau, J. Fluorine Chem. 125 (2004) 1231–1240.
[8] D.J. Connoly, W.F. Gresham, US Patent 3,282,875 (1966).
[9] Y.-H. He, L.-C. Zhang, W.-Q. Li, B.-P. Xu, Acta Chim. Sin. 48 (1990) 1120–1126.