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Synthesis of difluoroethyl perfluorosulfonate monomer and its application

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ABSTRACT

The novel difluoroethyl perfluorosulfonate monomer **20** and its application have been developed. The difluoroethyl perfluorosulfonate monomer **20**, which was prepared by the reaction of the vinyl sulfonic acid **19** with vinylidene fluoride, was copolymerized with tetrafluoroethylene (TFE) to give the difluoroethyl perfluorosulfonate copolymer **21**. The copolymer **21** was easily converted to the perfluorosulfonic acid ionomer **2** in one step by heating and/or alcoholysis. This property of **21** enables the efficient preparation of the polymer solution of **2**.

1. Introduction

Perfluorosulfonic acid ionomers such as DuPont's Nafion® **1** and Dow's short side chain ionomer **2** show the strong acidities and the excellent chemical stabilities (Fig. 1). These ionomers have been used in a variety of electrochemical processes and devices [1–3].

The perfluorosulfonic acid ionomers (**1**, **2**) are prepared through the utilization of the perfluorosulfonyl fluoride monomers (**7**, **8**) (Scheme 1).

The perfluorosulfonyl fluoride monomer **7** is prepared by the decarboxylation reaction of the acyl fluoride **6** with the base such as Na_2CO_3 [4]. On the other hand, the short chain monomer **8** cannot be obtained by the reaction of the short chain acyl fluoride **5** with the base in the same manner, but the cyclic compound **9** is produced. The cyclic compound **9** seems to be formed through the mechanism shown in Scheme 2.

In this case, the carbanion in **15** prefers the nucleophilic attack on the sulfonyl group to form **9** to the elimination of fluoride ion from the adjacent CF_3 group to form the vinyl group.

Ezzell et al. have developed the new method utilizing the epoxide **10** containing the chlorine atom: the adduct **11** is useful for the suppression of the cyclization reaction [5] (Scheme 1). The drawback of this process is that the preparation of **10** is much more complicated than that of hexafluoropropylene oxide **4**, which is commercially available.

The perfluorosulfonyl fluoride monomers (**7**, **8**) are copolymerized with tetrafluoroethylene (TFE) to form the perfluorosulfonyl fluoride copolymers (**12**, **13**). The perfluorosulfonyl fluoride copolymers (**12**, **13**) are hydrolyzed to give the perfluorosulfonic acid ionomers (**1**, **2**) through the saponification and the succeeding acidification. The perfluorosulfonic acid ionomers (**1**, **2**) are added to alcohol–water mixture followed by heating at 200–250 °C to obtain polymer solutions, which are useful for the production of cast films for membrane electrolytes and coating materials for modified electrodes [6–9].

Among the perfluorosulfonic acid ionomers (**1**, **2**), the short side chain ionomer **2** is more preferable because of the higher mechanical properties and the higher concentration of the sulfonic acid group [3]. However, **2** has the drawbacks in its preparation procedures, namely the preparation procedure of **8** and the hydrolysis procedure of **13**, as shown above.

We report here the synthesis and the application of the difluoroethyl perfluorosulfonate monomer **20**, which can overcome the drawbacks of **2**.

2. Results and discussion

2.1. *Synthesis of difluoroethyl perfluorosulfonate monomer (20)*

The novel difluoroethyl perfluorosulfonate monomer **20** was prepared through the procedure shown in Scheme 3. The monomer **20** can be prepared utilizing the conventional intermediate **5**.

The vinyl compound **17** was prepared by the modification of Tatemoto's method [10]. Namely, the acyl fluoride **5** was added to

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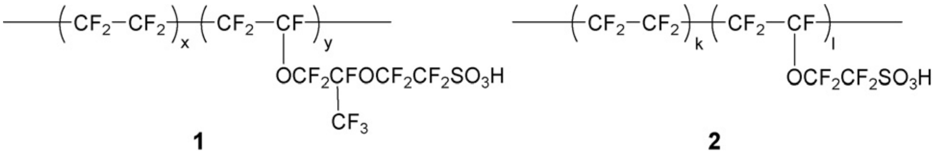
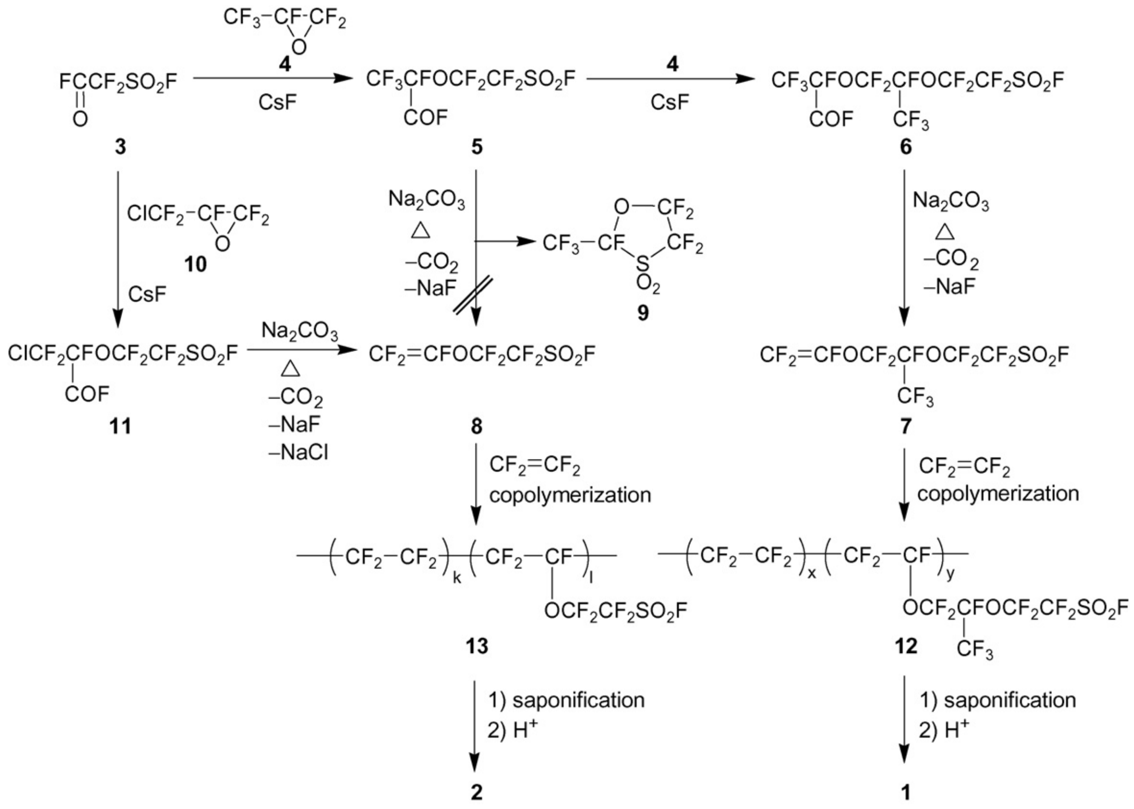


1 **2**

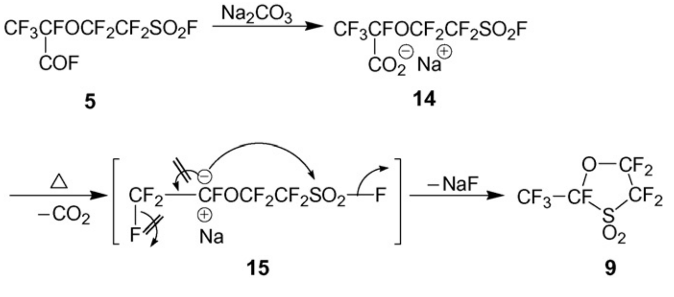
Fig. 1. Perfluorosulfonic acid ionomers.



Scheme 1.

the methanol solution of NaOH to form the disodium salt **16**. After **16** was dried *in vacuo* at 110 °C for 24 h, dry diglyme was added to **16** and then the mixture was heated at 160 °C. Decarboxylation reaction took place to produce the mixture of the vinyl compound **17** and the protonated compound **18** (**17**:**18** = 87:13, molar ratio), which was confirmed by ^{19}F NMR spectroscopy.

It is noteworthy that the decarboxylation of the disodium salt **16** gives the vinyl compound **17**, whereas that of the monosodium salt **14** in Scheme 2 gives the cyclic compound **9**. The estimated reaction mechanism from **16** to the mixture of **17** and **18** is shown in Scheme 4.



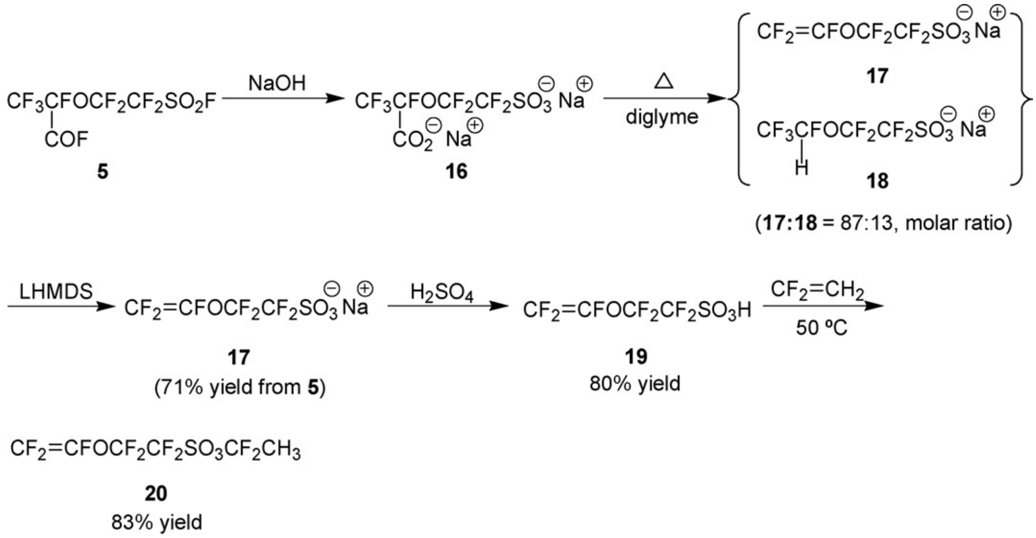
Scheme 2.

The carbanion generated by pyrolytic decarboxylation of **16** does not attack the SO_3^- group, because the SO_3^- group has a negative charge and suppresses the nucleophilic attack of the carbanion on the SO_3^- site. The carbanion abstracts fluoride ion in the CF_3 group to form **17**. However, in the presence of the proton source, the carbanion reacts with the proton to produce **18**. The impurity water seems to cause the formation of **18**, which may be suppressed by the sufficient drying of the hygroscopic salt **16**.

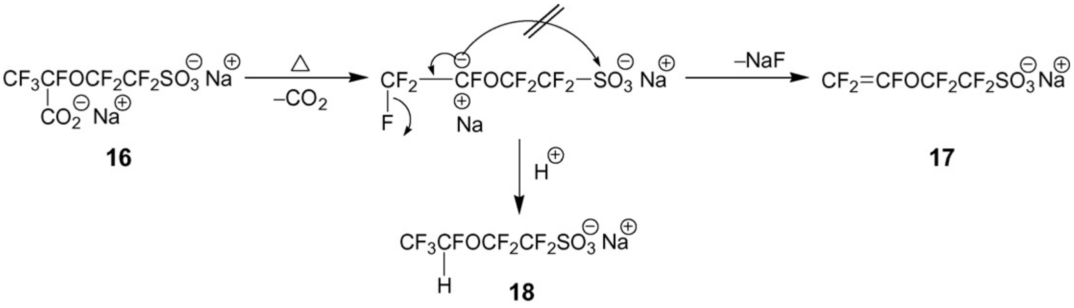
The protonated compound **18** can be converted to the vinyl compound **17** by lithium hexamethyldisilazide (LHMDS) according to our previous reported method [11,12]. The proposed mechanism is shown in Scheme 5. LHMDS is used for the proton abstraction for the conversion to the vinyl compound **17**. $(Me_3Si)_2N^-$ is a bulky nucleophile and does not attack the vinyl group of **17**. After this treatment, the overall yield of **17** from **5** was 71%.

The vinyl compound **17** was suspended in concentrated H_2SO_4 followed by distillation to give the vinyl sulfonic acid **19** in 80% yield.

Wakselman et al. reported the reaction of trifluoromethanesulfonic acid with vinylidene fluoride (VDF) affords 1,1-difluoroethyl triflate in high yield [13]. In the same manner, the vinyl sulfonic acid **19** reacted with VDF under the pressure of 0.8 MPa at 50 °C in an autoclave to give the difluoroethyl perfluorosulfonate monomer **20** in 83% yield. As shown in Scheme 6, the regioselective



Scheme 3.



Scheme 4.

addition of VDF to **19** to form **20** is attributed to the predominant formation of the intermediate carbocation $CH_3CF_2^+$ formed by the protonation of the double bond in VDF [13].

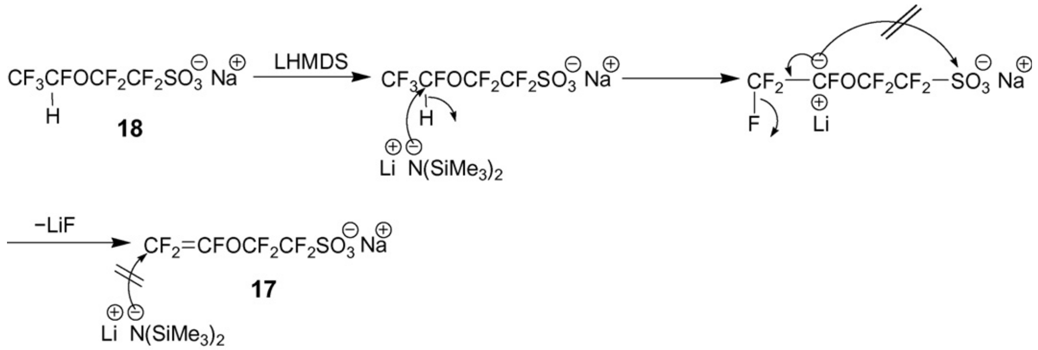
2.2. Copolymerization of difluoroethyl perfluorosulfonate monomer (20) with TFE

The difluoroethyl perfluorosulfonate monomer **20** can be copolymerized with TFE by a conventional free radical polymerization in a solution system. For example, the copolymerization of **20** with TFE was conducted in HFC43-10mee ($CF_3CHFCHFCF_2CF_3$) using $(C_3F_7CO_2)_2$ as a radical initiator under the constant TFE pressure to give the difluoroethyl perfluorosulfonate copolymer **21** (Scheme 7, Table 1). As shown in Table 1, the copolymer composition can be easily controlled by the monomer composition.

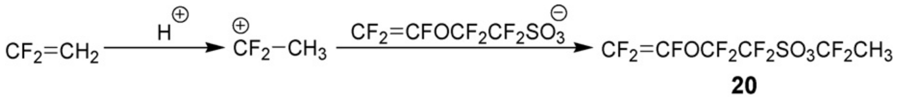
2.3. Conversion of difluoroethyl perfluorosulfonate copolymer (21) to perfluorosulfonic acid ionomer (2)

The difluoroethyl perfluorosulfonate copolymer **21** can be converted to the perfluorosulfonic acid ionomer **2** in one step by heating and/or alcoholysis (Scheme 8).

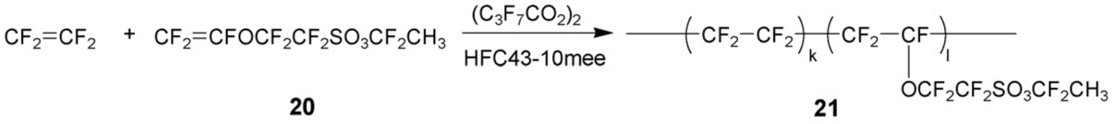
Fig. 2 shows the IR spectra of the original difluoroethyl perfluorosulfonate copolymer **21** and the copolymer **21** after heating at 160 °C. The IR spectrum of the original difluoroethyl



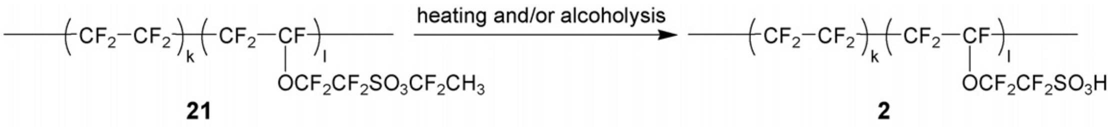
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

perfluorosulfonate copolymer **21** showed the characteristic signal for the sulfonic acid ester band (1436 cm^{-1}). On the other hand, the IR spectrum of the copolymer **21** after heating at 160 °C showed the disappearance of the sulfonic acid ester band (1436 cm^{-1}) and the appearance of the sulfonic acid band (1055 cm^{-1}). These observations indicate that the difluoroethyl perfluorosulfonate copolymer **21** is converted to the perfluorosulfonic acid ionomer **2** by heating.

Fig. 3 shows the thermal gravimetric analysis (TGA) profile of the difluoroethyl perfluorosulfonate copolymer **21** under an argon atmosphere. The first weight loss (approximately 8 wt.%) was observed in the temperature range of 100–230 °C. This result suggests that the first weight loss is attributed to the loss of VDF from the $SO_3CF_2CH_3$ group.

Additionally, the difluoroethyl perfluorosulfonate copolymer **21** can be converted to the perfluorosulfonic acid ionomer **2** by alcoholysis. The mixture of **21** and ethanol was refluxed for 2 h. Ethanol was evaporated and the residue was dried *in vacuo* at room temperature to give **2**, which was confirmed by the disappearance of the sulfonic acid ester band (1436 cm^{-1}) and the appearance of the sulfonic acid band (1055 cm^{-1}) in the IR spectrum.

The reaction scheme was examined as follows: the conversion progress of the difluoroethyl perfluorosulfonate monomer **20** in methanol at room temperature was monitored by ^{19}F NMR spectroscopy. Transformation of **20** into the corresponding vinyl sulfonic acid **19** was confirmed by the shift of the signal of the neighboring fluoromethylene group from −114.7 ppm ($CF_2SO_3CF_2CH_3$) to −119.0 ppm (CF_2SO_3H). At the same time, a signal for the ester group at −59.0 ppm ($SO_3CF_2CH_3$) disappeared while a new quartet at −73.9 ppm (J_{F-H} = 14 Hz) ($CH_3CF_2OCH_3$) appeared [14]. This result shows that 1,1-difluoroethyl group in the copolymer **21** works as the alkylating agent for alcohol while the copolymer **21** converts to the perfluorosulfonic acid ionomer **2**.

2.4. Polymer solution and solution-cast film (2′)

As shown above, the difluoroethyl perfluorosulfonate copolymer **21** was easily converted to the perfluorosulfonic acid ionomer **2** by heating and/or alcoholysis. Utilizing this property, the polymer solution of **2** can be easily prepared from **21** in one step as follows: **21** and ethanol–water mixture (ethanol:water = 1:1, weight ratio) were charged in an autoclave and heated at 180 °C for 3.5 h. After cooling to room temperature, the contents of the autoclave were filtered through a PTFE membrane filter to give a clear polymer solution (**2** content: 2.3 wt.%). We attempted to produce a solution-cast film at 160 °C from this polymer solution. However, the resulting solution-cast film was brittle and cracked. Moore and Martin reported the polymer solutions of **1**, **2** including

Table 1
Copolymerization of **20** with TFE

	Run 1	Run 2
Monomer **20** (g)	20.0	16.0
HFC43-10mee (g)	60.0	32.0
TFE (MPa)	0.26	0.22
5 wt.% $(C_3F_7CO_2)_2$ solution in HFC43-10mee (g)	1.00	1.48
Reaction time (h)	3.7	13.5
Copolymer **21** (g)	4.79	7.27
Copolymer composition[b] TFE:**20** (molar ratio)	7.6:1	4.7:1
Number average molecular weight (M_n)[b]	340000	286000
Equivalent weight (EW)[c] (g/equiv.)	1076	859
Proton conductivity[c] (S/cm, 23 °C)	0.12	0.17

[a] Copolymerization was carried out at 23 °C in a 200 mL autoclave.
[b] **21** was converted to **2** by heating and/or alcoholysis. Copolymer composition and M_n of **2** were determined by solid-state ^{19}F NMR.
[c] Solution-cast films **2′** derived from **21** were measured.

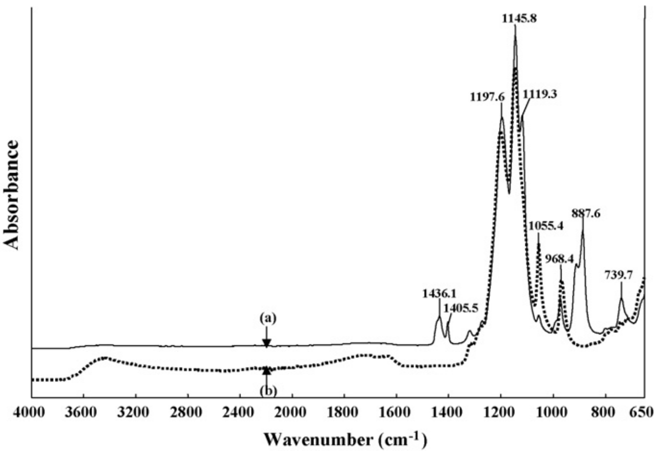


Fig. 2. IR spectra of (a) the original **21** and (b) **21** after heating at 160 °C.

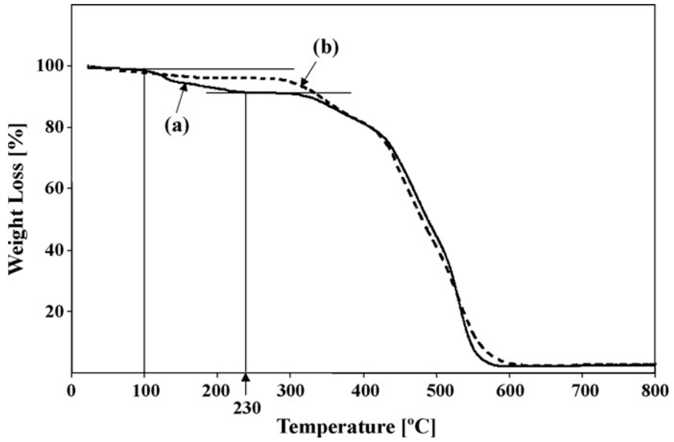


Fig. 3. TGA curves of (a) the difluoroethyl perfluorosulfonate copolymer **21** and (b) the cast film (EW 859) **2′** derived from **21** under an argon atmosphere.

polar organic solvents such as *N*,*N*-dimethylformamide (DMF) and ethylene glycol give solution-cast films with good mechanical properties [8,9]. Therefore, DMF (30 wt.% based on the weight of the polymer solution) was added to the above polymer solution, and the resulting solution was raised to 180 °C for 3 h to give the tough clear film **2′**. Table 1 shows the proton conductivities and the equivalent weights of the cast films **2′** derived from the difluoroethyl perfluorosulfonate copolymers **21**.

Fig. 3 shows TGA profile of the cast film (EW 859) **2′** under an argon atmosphere. After the initial weight loss corresponding to dehydration up to about 180 °C, the onset of thermal decomposition of the cast film (EW 859) **2′** was observed around 300 °C, as well as that of difluoroethyl perfluorosulfonate copolymer **21**.

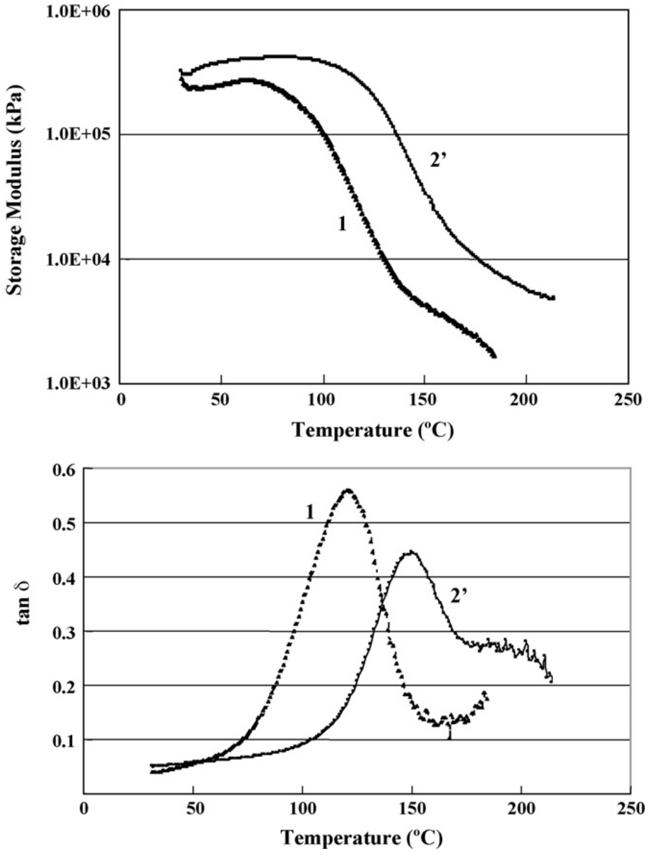


Fig. 4. Storage modulus and tan δ of Nafion® 112 (EW 1100) **1** and the cast film (EW 859) **2′**.

The dynamic mechanical analysis (DMA) results of Nafion® 112 (EW 1100, sulfonic acid form) **1** and the cast film (EW 859) **2′** were shown in Fig. 4. The storage modulus of the cast film **2′** was higher than that of Nafion® **1**. The glass transition temperature (T_g) of the cast film **2′** (150 °C) was also higher than that of Nafion® **1** (120 °C). These results are consistent with those previously obtained in the literature [16,17].

3. Conclusion

The novel difluoroethyl perfluorosulfonate monomer **20** and its application have been developed. The novel monomer **20** shows the excellent productivity and copolymerizability with TFE. The difluoroethyl perfluorosulfonate copolymer **21** can be easily converted to the perfluorosulfonic acid ionomer **2** by heating and/or alcoholysis. This property of **21** enables the efficient preparation process of the polymer solution of **2**, which is useful for the various electrochemical applications.

4. Experimental

The reagents were obtained from commercial sources and used as received unless otherwise stated. Nafion® 112 (EW 1100, sulfonic acid form) was obtained from Sigma–Aldrich. $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) was prepared as described in literature [15]. ^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 Bruker BioSpin DSX-400, and the chemical shifts (δ) were referred to trifluoroacetic acid. The number average molecular weight (M_n) was evaluated by the quantitative analysis of CF_3 end group using solid-state ^{19}F NMR. IR spectra were obtained by the attenuated total reflectance method with a Perkin Elmer Spectrum One or Bio-Rad FTS6000. GC–MS data were obtained on HP5973 MSD coupled to a Hewlett-Packard HP5890 series II gas chromatograph with a 30 m capillary column J&W DB-1 under CI condition (reagent gas: NH_3). MALDI-TOF MS measurements were performed with a Shimadzu AXIMA-CFR *plus* equipped with a N_2 laser (λ = 337 nm) in reflectron mode. α-Cyano-4-hydroxycinnamic acid was used as the matrix. TGA was carried out under an argon atmosphere with a Shimadzu TGA-50 in the temperature range of 20–800 °C at a heating rate of 10 °C/min. The equivalent weight and the proton conductivity were measured as described previously [11]. DMA was performed at a frequency of 35 Hz and a heating rate of 1 °C/min using an A&D RHEOVIBRON DDV-01FP. A rectangular test specimen having a width of 3 mm and a length of 30 mm was cut out and the thickness was measured. The storage and loss modulus and tan δ (ratio of loss to storage modulus) were recorded as a function of temperature. T_g was taken to be the maximum of tan δ versus temperature curve.

4.1. *Preparation of sodium 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)ethanesulfonate (17)*

The vinyl compound **17** was prepared by the modification of Tatemoto's method [10]. To a 1 L round bottom flask equipped with a mechanical stirring, a dropping funnel and a reflux condenser were added methanol (300 mL) and NaOH (50.4 g, 1.26 mol), and then the mixture was refluxed to form the methanol solution of NaOH. After the flask was cooled in an ice-cold water bath, $CF_3CF(COF)OCF_2CF_2SO_2F$ (**5**) (103.8 g, 0.3 mol) was added to the flask through a dropping funnel while keeping the temperature below 20 °C over 2 h. After the completion of the addition, the reaction mixture was stirred at room temperature for 1 h and refluxed for 1 h to form the disodium salt **16**. The formation of the disodium salt **16** was confirmed by ^{19}F NMR. Methanol was evaporated and the residue was dried *in vacuo* at 110 °C for 24 h. Dry diglyme (300 mL) was added to the dry residue and then the mixture was heated at 160 °C for 1 h. The pyrolytic decarboxylation of the disodium salt **16** formed the vinyl compound **17** and the protonated compound **18** (**17**:**18** = 87:13, molar ratio), which was confirmed by ^{19}F NMR. After the reaction mixture was cooled to room temperature, 1 M LHMDS solution in THF (39 mL, 0.039 mol) was added to the flask under a nitrogen atmosphere and stirred at room temperature. The reaction progress was monitored using ^{19}F NMR by sampling a small amount of the reaction mixture. After the protonated compound **18** was completely converted to the vinyl compound **17**, the insoluble material in the reaction mixture was filtered off through Celite®. The filtrate was concentrated under reduced pressure to give a brown solid **17** (121.06 g, 0.21 mol, 71% yield based on ^{19}F NMR).

^{19}F NMR δ −135.92 (dd, J = 111, 64 Hz, 1F, $\mathrm{CF_2{=}}\mathit{CF}\mathrm{O}$), −124.22 (dd, J = 111, 87 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −118.84 (s, 2F, $\mathrm{CF_2}\mathit{CF_2}\mathrm{SO_3}$), −116.89 (dd, J = 87, 64 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −85.32 (s, 2F, $\mathrm{O}\mathit{CF_2}\mathrm{CF_2SO_3}$).

MALDI-TOF MS: 276.9 $[\mathrm{M{-}Na}]^-$ (negative-ion mode), 323.0 $[\mathrm{M{+}Na}]^+$ (positive-ion mode).

4.2. Preparation of 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)ethanesulfonic acid (19)

The vinyl compound **17** (78.64 g, 152 mmol, purity 58%) was suspended in concentrated H_2SO_4 (100 mL) and distilled under reduced pressure (0.12 kPa) to give two fractions A (bp 90 °C, 5.57 g, purity 37%) and B (bp 112–124 °C, 41.03 g, purity 82%). Redistillation of combined A and B gave a colorless oil **19** (38.00 g, 122 mmol, 80% yield based on ^{19}F NMR).

bp 97–100 °C/0.11 kPa.

^{19}F NMR δ −137.78 (dd, J = 111, 67 Hz, 1F, $\mathrm{CF_2{=}}\mathit{CF}\mathrm{O}$), −124.23 (dd, J = 111, 87 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −118.55 (s, 2F, $\mathrm{OCF_2}\mathit{CF_2}\mathrm{SO_3}$), −116.71 (dd, J = 87, 67 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −85.92 (s, 2F, $\mathrm{O}\mathit{CF_2}\mathrm{CF_2SO_3}$).

^{1}H NMR δ 10.92 (s, 1H).

4.3. Preparation of 1,1-difluoroethyl 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)ethanesulfonate (20)

The vinyl sulfonic acid **19** (33.45 g, 120 mmol) was placed in a 200 mL autoclave at room temperature. 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 VDF, the autoclave was elevated at 50 °C, and then VDF was added to the pressure of 0.8 MPa. The reaction temperature was kept at 50 °C while the consumed VDF was compensated by the addition of VDF to keep the pressure of 0.8 MPa. When the consumption of VDF stopped, the remaining VDF was vented. The reaction mixture was distilled under reduced pressure to give a colorless liquid **20** (34.0 g, 99 mmol, 83% yield).

bp 43–45 °C/2.0–3.0 kPa.

^{19}F NMR δ −138.08 (dd, J = 113, 67 Hz, 1F, $\mathrm{CF_2{=}}\mathit{CF}\mathrm{O}$), −123.67 (dd, J = 113, 86 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −116.10 (dd, J = 86, 67 Hz, 1F, $\mathit{CF_2}\mathrm{{=}CFO}$), −115.11 (s, 2F, $\mathrm{OCF_2}\mathit{CF_2}\mathrm{SO_3}$), −85.29 (s, 2F, $\mathrm{O}\mathit{CF_2}\mathrm{CF_2SO_3}$), −59.79 (s, 2F, $\mathrm{SO_3}\mathit{CF_2}\mathrm{CH_3}$).

^{1}H NMR δ 2.14 (t, 3H, J = 14 Hz).

GC–MS (CI) m/z 360 $(\mathrm{M{+}NH_4})^+$.

4.4. Copolymerization of 1,1-difluoroethyl 1,1,2,2-tetrafluoro-2-(trifluoroethenyloxy)ethanesulfonate (20) with TFE

The following procedure is typical. The monomer **20** (20.0 g, 58.5 mmol) and HFC43-10mee ($CF_3CHFCHFCF_2CF_3$) (60.0 g) were charged in a 200 mL 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 to 23 °C. To the autoclave was added 5 wt.% $(C_3F_7CO_2)_2$ solution in HFC43-10mee (1.00 g, 0.12 mmol), and then TFE was added to the pressure of 0.26 MPa. The reaction temperature was kept at 23 °C while the consumed TFE was compensated by the addition of TFE to maintain the pressure of 0.26 MPa. When the desired amount of TFE was consumed, the remaining TFE was vented. The mixture of HFC43-10mee and *n*-hexane was added to the reaction mixture to precipitate a colorless solid. The colorless solid was isolated by centrifugation, washed three times with HFC43-10mee and dried *in vacuo* at room temperature to give the copolymer **21** (4.79 g).

4.5. Preparation of the polymer solution

To a 50 mL autoclave were charged the copolymer **21** (1.0 g) and ethanol–water mixture (1:1, weight ratio) (39.0 g) at room temperature. After the autoclave was purged with N_2 gas, the mixture was stirred at 180 °C for 3.5 h. After cooling to room temperature, the contents of the autoclave were filtered through a PTFE membrane filter (pore size: 0.45 μm) to give the clear polymer solution (34.9 g, ionomer **2** content: 2.3 wt.%).

4.6. Preparation of the solution-cast film (2′)

The mixture of the polymer solution (19.8 g, ionomer **2** content: 2.3 wt.%) and DMF (6.0 g) was poured into a petri dish and raised to 180 °C for 3 h on a hot plate. After cooling to room temperature, deionized water was added to the petri dish, and the formed film was peeled off. The film was immersed in 4N sulfuric acid at 90 °C for 1 h, washed with deionized water until the wash water was neutral, and dried to give the solution-cast film **2′** (thickness: 60 μm).

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