



# Synthesis of difluoroethyl perfluorosulfonate monomer and its application

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## ARTICLE INFO

### Article history:

Received 24 February 2008

Received in revised form 9 April 2008

Accepted 15 April 2008

Available online 24 April 2008

### Keywords:

Perfluorosulfonic acid ionomer  
Difluoroethyl perfluorosulfonate  
Vinylidene fluoride  
Polymer solution

## 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**.

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## 1. Introduction

Perfluorosulfonic acid ionomers such as DuPont's Nafion<sup>®</sup> **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<sub>2</sub>CO<sub>3</sub> [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<sub>3</sub> 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 Tatamoto's method [10]. Namely, the acyl fluoride **5** was added to

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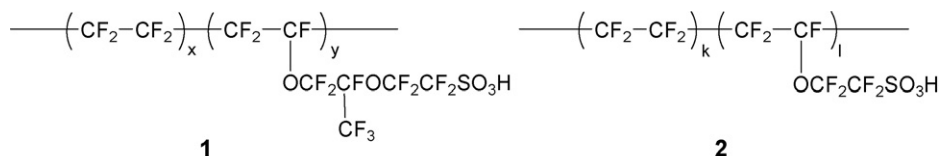
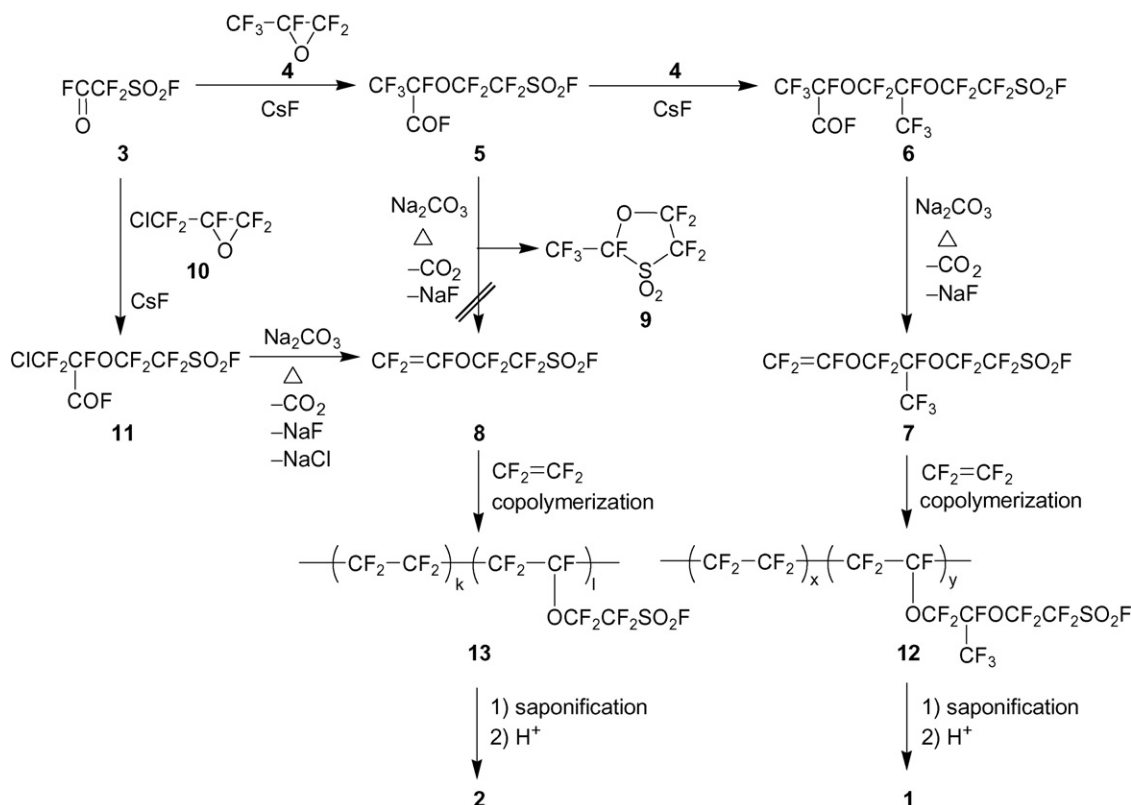


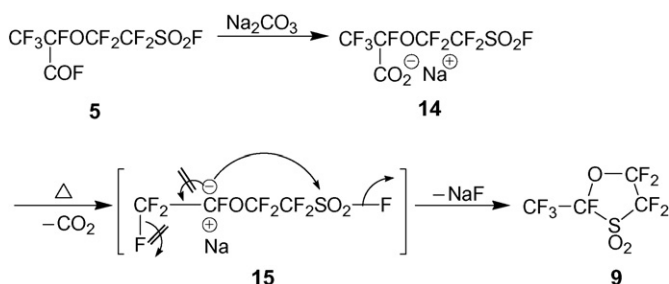
Fig. 1. Perfluorosulfonic acid ionomers.



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  $^{19}\text{F}$  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  $\text{SO}_3^-$  group, because the  $\text{SO}_3^-$  group has a negative charge and suppresses the nucleophilic attack of the carbanion on the  $\text{SO}_3^-$  site. The carbanion abstracts fluoride ion in the  $\text{CF}_3$  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**.  $(\text{Me}_3\text{Si})_2\text{N}^-$  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  $\text{H}_2\text{SO}_4$  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

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