

Synthesis and Characterization of a Novel Perfluorinated Ionomer Polymer Containing Sulfonimide Functionality[†]

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The novel perfluorinated vinyl ether containing sulfonimide functionality $\text{CF}_2 = \text{CFOR}_f\text{SO}_2\text{NHSO}_2\text{CF}_3$ was synthesized by multiple reaction steps. It could be copolymerized with tetrafluoroethylene by radox initiator to give a novel perfluorinated ionomer polymer. Its physical and chemical properties were studied.

Keywords perfluorinated vinyl ether, sulfonimide, copolymerization, ionomer, resin

Introduction

Most perfluorinated polymers have unusual and outstanding properties such as high thermal stability, low dielectric constant, inertness to the chemical reaction and low coefficient friction *etc.*¹ Properties of polymers are changed dramatically when an ionic functional group was introduced into the polymers. Since the ionomer polymer was developed in 1960s, considerable research works have been focused on the topic of the ionomer polymers.² The perfluorinated ionomer polymers are of interest to us due to their special properties and applications.

Nafion³ is a perfluorinated ionomer polymer containing sulfonic acid group at the end of the pendent side chain. Due to its high acidity together with the chemical and thermal stability Nafion has many applications such as a membrane in full cell and as catalysts in organic synthesis, and in the field of chemical industry.

During our continually studies on the super nitrogen acid and carbon acid,⁴ $(\text{R}_f\text{SO}_2)_2\text{NH}$ and $(\text{R}_f\text{SO}_2)_3\text{CH}$ *etc.* have been successfully prepared. The pH value of the bis(fluoroalkylsulfonyl) imide in anhydrous acetic acid is 7.8, which is more stronger than the nitric acid under the same conditions. The gas phase acidities of these fluorides containing nitrogen and carbon acids have also been measured.^{4b} Their fundamental electrochemical studies have shown favorable properties.⁵ These results gave us a new super acid concept. Recently our group further prepared

the perfluorinated vinyl ether containing the acidic sulfonimide group $\text{CF}_2 = \text{CFOR}_f\text{SO}_2\text{NHSO}_2\text{CF}_3$ and $\text{CF}_2 = \text{CFOR}_f\text{SO}_2\text{NHR}_f\text{P}(\text{O})(\text{OH})_2$.⁶

They are very strong acids and exhibit a high degree of stability in aqueous solution at an elevated temperature. These properties make them as the attractive monomer for preparation of the ionomer polymer with tetrafluoroethylene (TFE), which could be posses special property as Nafion.

In this paper, the preparations of the novel monomer $\text{CF}_2 = \text{CFOR}_f\text{SO}_2\text{NHSO}_2\text{CF}_3$ and its copolymer with TFE were described.

Results and discussion

As reported recently, our group has successfully prepared the compound of $\text{CF}_3\text{SO}_2\text{N}(\text{Na})\text{SO}_2(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{I}$ by the reaction of $\text{CF}_3\text{SO}_2\text{N}(\text{Na})\text{SiMe}_3$ (**3**) with $\text{I}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_2\text{F}$.⁶ However, the monomer $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{NHSO}_2\text{CF}_3$ (**6**) could not be synthesized directly from the reaction of $\text{CF}_3\text{SO}_2\text{N}(\text{Na})\text{SiMe}_3$ (**3**) with $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**1**). Due to the carbon-carbon double bond of the highly electrophilic perfluoroolefin **1** is easily attacked by compound **3**, which leads to lose the double bond, compound **1** should be protected first. Thus, **1** was treated with bromine at room temperature to give the protected product $\text{BrCF}_2\text{CF}(\text{Br})\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**2**) in quantitative yield. The reaction of **2** with **3** was carried out in CH_3CN . After stirring the mixture for 48 h at 80 °C, the solvent was evaporated. The product $\text{BrCF}_2\text{CFBrOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ (**4**) was formed in 78% yield. Debromination was accomplished by the treatment of **4** with zinc dust in Ac_2O to give $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ (**5**). Other solvents such THF, dioxane, methanol are also usable, however, the use of Ac_2O as the solvent gave the best results (>90%).

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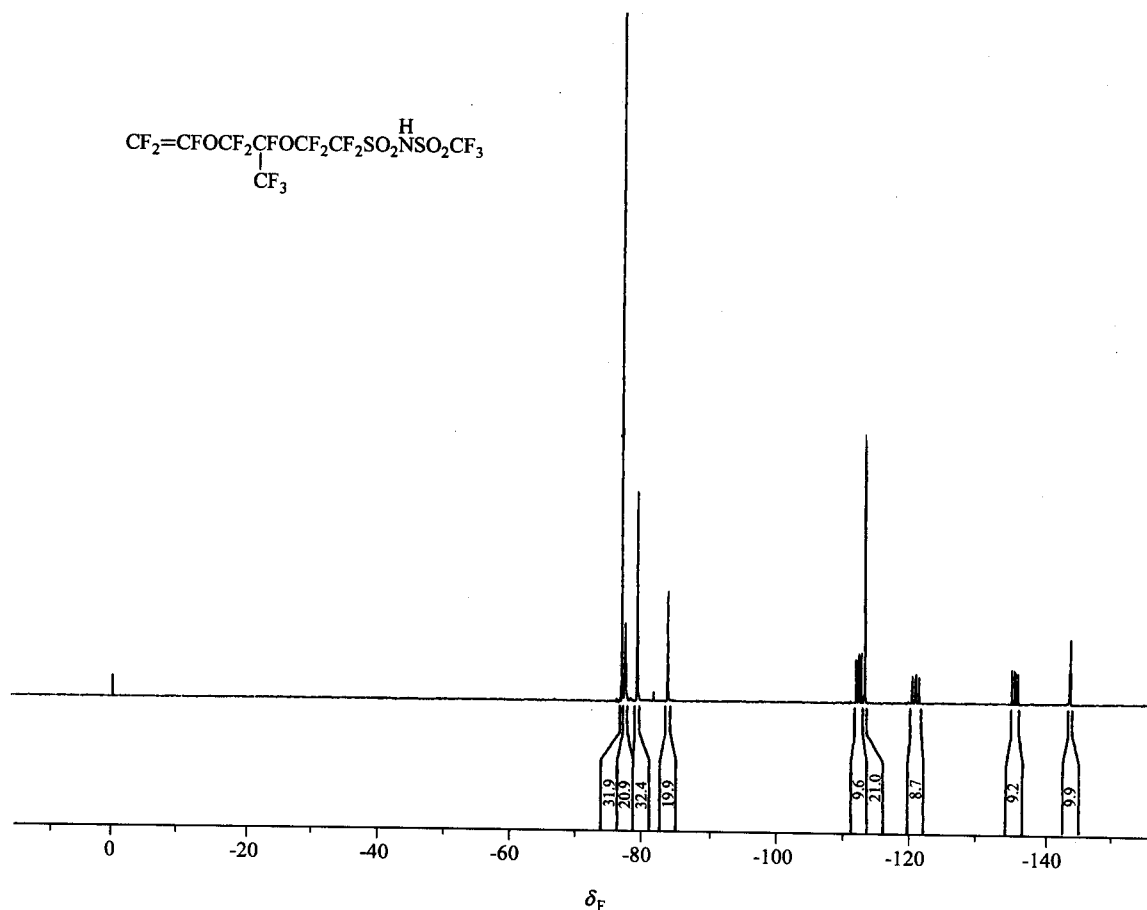


Fig. 2 ^{19}F NMR of compound 6.

The average number (n) of C_2F_4 in the ionomer is $(1333 - 575)/100 = 7.6$ (the molecular weight of the functional monomer and TFE are 575 and 100 respectively). This result is basically confirmed by the element analysis of the ionomer 7. The contents of sulfur and nitrogen in the ionomer are 4.90% and 1.05% respectively.

The property of copolymer 7 also was characterized by DSC and TGA. The spectra are shown in Figs. 3 and 4. It is obvious that the copolymer is uniform (only one

peak T_m 178.9 $^{\circ}\text{C}$) without peak of homopolymer PTEF ($T_m = 327$ $^{\circ}\text{C}$) from DSC spectrum. The thermal stability of 7 was excellent, and its initial decompose temperature was at 391.8 $^{\circ}\text{C}$.

At present, proton exchange membrane (PEM) fuel cells usually use Nafion and the operation is at 80 $^{\circ}\text{C}$. The methanol PEM fuel cell suffers from catalyst poisoning by CO at anode. Operation at higher temperature (200 $^{\circ}\text{C}$) should solve the problem of catalyst poisoning, but it results in dehydration of Nafion and loss of ionic conductivity.^{5b} The high thermal stability of the ionomer polymer 7 may be a good alternative of Nafion. The further work is in progress.

In summary a novel perfluorinated vinyl ether bearing sulfonimide group was synthesized. It was copolymerized with TFE by radox initiator to give the ionomer polymer. The chemical and physical properties of the ionomer polymer were studied. The strong acidity together with the high thermal stability of the ionomer makes it as an attractive candidate for PEM in the fuel cell. Its electrochemical behavior and application as super acid catalysts are now under investigation.

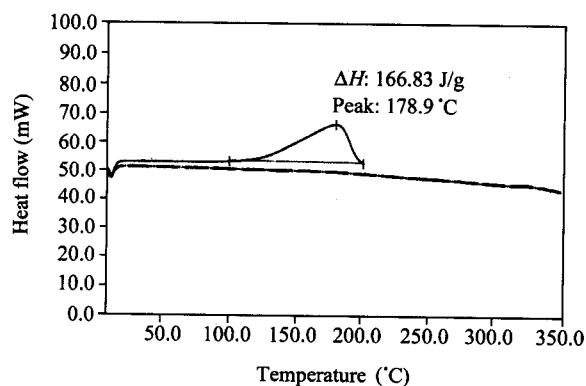


Fig. 3 DSC spectrum of compound 7.

Experimental

IR spectra were obtained using a Perking-Elmer 1430 ratio recording instrument or a Perking-Elmer 1600FT-IR instrument. ^{19}F NMR and ^1H NMR were recorded on an IBM NR 200AF spectrometer using CFCl_3 and TMS as internal standards, and CD_3CN or CD_3COCD_3 as solvent. ^{19}F NMR chemical shift is positive when found at a lower field than that of CFCl_3 . DSC and TGA spectra were carried out by Perkin-Elmer Instruments. Elemental analyses were performed by Shanghai Institute of Organic Chemistry. The boiling points are uncorrected.

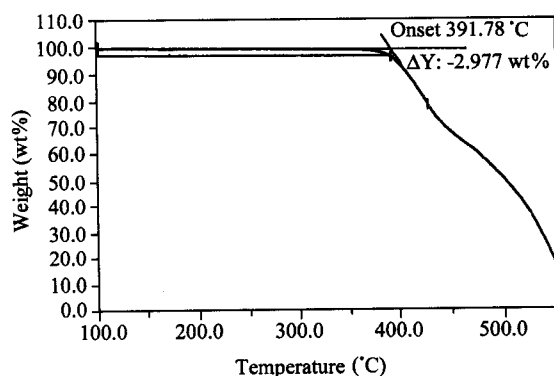


Fig. 4 TGA spectrum of compound 7.

Preparation of the monomer $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{-CF}_2\text{SO}_2\text{NHSO}_2\text{CF}_3$ (**6**)

At room temperature, Br_2 (8.8 g, 55 mmol) was added dropwise into a 50-mL flask containing $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**1**) (22.3 g, 50 mmol) which was prepared from tetrafluorosulfon and hexafluoropropene oxide (HFPO) according to the reported method.⁷ After addition (about 3 h), the reaction mixture was continually stirred for another 3 h, then washed twice with ice water, the oil layer was separated and dried over Na_2SO_4 to give quantitative product $\text{BrCF}_2\text{CFBrOCF}_2\text{CF}(\text{CF}_3)\text{-OCF}_2\text{CF}_2\text{SO}_2\text{F}$ (**2**) (30.2 g). ^{19}F NMR (CD_3COCD_3) δ : -63.9 (s, BrCF_2), -72.3 (s, BrCF), -79.6, -80.0 (s, CF_3), -81.6—-86.8 (m, OCF_2), -112.7 (s, SCF_2), -145.7 (t, $J = 20$ Hz, CFCF_3), 44.9 (s, SO_2F); IR (KBr) ν : 1460 (s), 1276—1036 (vs), 720 (m) cm^{-1} ; MS m/z (%): 525/527 ($\text{M}^+ - \text{Br}$, 100/97.8), 521/523/525 ($\text{M}^+ - \text{SO}_2\text{F}$, 7.6/15.3/7.2), 129/131 (BrCF_2^+ , 85.7/83.0).

Compound **2** (12 g, 20 mmol) was added into a 100-mL flask containing a solution of dry CH_3CN (50 mL) and **3** (4.9 g, 20 mmol) which was prepared according to the reported method.⁸ The reaction mixture was refluxed and stirred for 48 h. The solvent was then evaporated under vacuum. The obtained solid **4** was dried under vacuum at 70 °C for 24 h and then transformed into a 50-mL one neck flask containing activated zinc dust (5.2 g, 80 mmol) and acetic anhydride (20 mL) under nitrogen gas atmosphere.

This mixture was stirred at 80 °C for 4 h. After evaporating the Ac_2O , the residue was dissolved in hot CH_3CN (50 mL), the inorganic salt was filtered out. The filtrate was evaporated under vacuum to give the product **5** (10.8 g) as white solid, which was mixed with concentrated sulfuric acid (4 mL, 98%) and stirred at 70 °C for 2 h. Vacuum distillation gave colorless liquid **6** (8.1 g) (Fig. 5), b.p. 82—84 °C/29.8 Pa, ^1H NMR (CD_3CN) δ : 10.7 (s), ^{19}F NMR (CD_3CN) δ : -76.8 (s, F_a), -79.3 (s, F_b), -77.6 (m, F_c), -83.9 (m, F_d), -113.4 (s, F_e), -144.1 (t, $J = 20$ Hz, F_f), -135.9 (dd, $J = 114$, 65 Hz, F_g), -121.0 (dd, $J = 114$, 90 Hz, F_h), -112.5 (dd, $J = 90$, 65 Hz, F_i); IR (film, AgCl) ν : 3510 (m), 1780 (m), 1390 (s), 1270—1020 (vs) cm^{-1} . Anal. calcd for $\text{C}_8\text{HF}_{16}\text{NO}_6\text{S}_2$: C 16.70, F 52.87, N 2.43; found C 16.76, F 52.69, N 2.38.

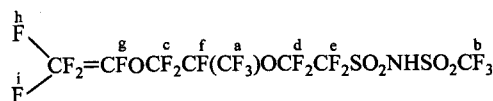


Fig. 5 Formula of compound 6.

Copolymerization of $\text{CF}_2 = \text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{-NHSO}_2\text{CF}_3$ (**6**) with TFE

The acidic monomer **6** (5.25 g, 10 mmol) was neutralized with a solution of NaHCO_3 (0.84 g) in distilled water (15 mL) in a 25-mL beaker. Nitrogen gas was bubbled into the solution for 10 min to remove the dissolved oxygen. A solution of $\text{K}_2\text{S}_2\text{O}_8$ (0.3 g), KHSO_3 (0.3 g), $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 g), $\text{C}_7\text{F}_{15}\text{CONa}$ (0.5 g) and distilled water (30 mL) was prepared in another 50-mL beaker. This solution and the monomer solution were transferred into a 100-mL vacuumed autoclave by suction. Tetrafluoroethylene was introduced to autoclave and the pressure was maintained at 6.7×10^5 Pa. The reaction mixture was stirred at 450 r/min at 23 °C, the pressure was kept between $(6.2\text{--}6.7) \times 10^5$ Pa by periodic addition of the C_2F_4 until 7×10^5 Pa of C_2F_4 was consumed (about 7 h). The copolymerization was stopped. After the excess C_2F_4 was vented out, the autoclave was opened, and the solution was poured into a 250-mL beaker. concentrated hydrochloric acid (35%, 30 mL) was added. The mixture was stirred for 2 h and allowed to stand up overnight. The precipitated copolymer was filtered out and washed with diethyl ether and deionized water until the washed water was neutral. The copolymer was then dried under high vacuum at 100 °C for 24 h, and cooled by liquid nitrogen. The obtained solid then was ground to give light yellowish powder **7** (5.6 g) (Fig. 6). ^{19}F NMR (DMF, aceton- d_6) δ : -124 (broad, F_a), -110 (broad, F_a'), -182.8 (s, F_b), -75.0 (s, F_c), -81.4 (s, F_c'), -117.5 (s, F_d), -144.8 (s, F_e), -71.2 (s, F_f); IR (film, AgCl) ν : 3445—3200 (m), 1365 (m), 1250—1020 (vs) cm^{-1} ; found C 20.81, F

64.40, N 1.05, S 4.90.

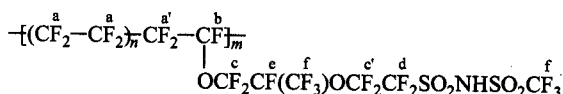


Fig. 6 Formula of compound 7.

Titration of the copolymer

Copolymer 7 (0.5 g) was added into a 200-mL break containing deionized water (20 mL) and ethanol (15 mL). This mixture was stirred for 2 h at 80 °C and then titrated with 0.01 mol/L NaOH aqueous solution using 0.3 mL of 0.5% phenolphthalein methanol solution as indicator. The titration was finished at the end point, which was chosen at the drop of NaOH solution to turn the aqueous polymer solution red and could not be decolorized at 80 °C for 10 min. The consumed NaOH solution was 37.5 mL. The ion-exchange capacity (C_{IEC}) was calculated according to following equation.

$$C_{\text{IEC}} = \frac{0.01 \text{ mol/L} \times V}{W} = \frac{0.01 \times 3.75}{0.5} = 0.75$$

V (consumed NaOH in mL), W (the weight of the copolymer), W_{E} (the equivalent weight) of the copolymer is about 1335, and the average number of C_2F_4 perfunctionalized monomer in the copolymer (n) is 7.3. These values are confirmed the results of elemental analysis of the copolymer 7.

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