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# Revisiting the radical copolymerization of vinylidene fluoride with perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride for proton conducting membranes

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## ABSTRACT

The radical copolymerizations of vinylidene fluoride (VDF) with perfluoro-3,6-dioxa-4-methyl-7-octene sulfonyl fluoride (PFSVE) and hPFSVE (hydrolyzed form of PFSVE) are presented. The resulting poly(VDF-co-PFSVE) random copolymers were hydrolyzed then cast into proton conducting membranes. Another strategy was first to hydrolyze PFSVE under basic conditions, then to copolymerize it with VDF. The radical copolymerization of VDF with PFSVE led to homogeneous copolymers in contrast to that of VDF with hPFSVE, as assessed by <sup>19</sup>F NMR spectroscopy. The thermal and electrochemical properties of all copolymers were determined. As expected, the thermal stability of the poly(VDF-co-PFSVE) copolymers bearing -SO<sub>2</sub>F groups were higher than that of the hydrolyzed copolymers containing -SO<sub>3</sub>H moieties. Membranes processed by casting displayed water uptake of ca. 40%, ion exchange capacity of 1.25 meq.g<sup>-1</sup> and conductivities up to 28 mS cm<sup>-1</sup> at 80 °C and 100% relative humidity.

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## Introduction

Although proton exchange membrane fuel cell (PEMFC) technology is already being implemented in stationary [1] and transport [2–4] applications involving hydrogen as fuel, further research is essential to resolve bottlenecks of materials, manufacturing costs, and durability. Aromatic polymers

[5–7] have been extensively explored as ionomers for low temperature PEMFCs but perfluorinated functional polymers bearing sulfonic acid side groups (perfluorosulfonic acids, PFSAs) generally show exceptional ex situ chemical, hydrolytic, and thermal stabilities [8–15]. However, the corresponding membranes undergo degradation during operation unless mitigation strategies are implemented [16,17]. The Nafion<sup>®</sup>-type [18], so-called long-side-chain ionomer

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membrane, is processed from hydrolyzed poly(TFE-co-PFSVE) copolymers (where, TFE and PFSVE stand for tetrafluoroethylene and perfluoro-3,6-dioxo-4-methyl-7-octene sulfonyl fluoride, respectively). Commercially available polymers with equivalent structure are Flemion® (trademark of Asahi Glass Company), Aciplex® (produced by Asahi Kasei), and Fumion® F (developed by FuMA-Tech). Ionomers with a shorter pendant side chain are referred to as short-side-chain (SSC) ionomers, where the length of the perfluoro vinyl ether side chain varies between 2 and 4 carbons for the two commercially available SSC ionomers (i.e., Aquivion® and 3M™, respectively). In contrast to TFE, vinylidene fluoride (VDF) is not a perfluorinated monomer and induces weaker chemical and thermal stabilities of the resulting copolymers. The radical copolymerization of PFSVE with VDF has been claimed in patents [19–21] and reported by academic labs [21–29], but the evolution of the composition of the poly(VDF-co-PFSVE) copolymers produced along the copolymerization has never been investigated. VDF is less hazardous than TFE (TFE deflagration risk in the presence of oxygen is quite high [28]), which facilitates monitoring of the radical copolymerization with PFSVE. Hence, the objective of this present study aims at revisiting the radical copolymerization of PFSVE (and its hydrolyzed form) with VDF, notably to investigate whether a possible drift of composition occurs while the copolymerization proceeds. Additionally, the resulting copolymers were processed into membranes which physico-chemical and electrochemical properties were studied.

## Experimental

### Materials

Unless described, all reactants were used as received. Vinylidene fluoride (VDF) was kindly provided by Arkema (France), perfluoro-3,6-dioxo-4-methyl-7-octene sulfonyl fluoride (PFSVE) was purchased from Apollo Scientific (France), and tert-butyl peroxyvalate was generously given by Akzo Nobel (Chalons Sur Marne, France). Deuterated acetone (acetone- $d_6$ ) used for Nuclear Magnetic Resonance spectroscopy was purchased from Euroiso-top (Grenoble, France) (purity >99.8%).

### Copolymerization

The radical copolymerization of PFSVE (or hPFSVE) with VDF was carried out in a 50 mL Hastelloy autoclave Parr System, equipped with a rupture disk, a Bourdon-pressure gauge, and inlet and outlet valves. An electronic device controlled and regulated both the heating and the stirring of the autoclave (Fig. S10). The vessel was closed and purged three times with 20 bar of pressure with nitrogen for 2 min and a vacuum 0.10 mbar for 15 min. The initiator, PFSVE or hPFSVE, and the solvent were introduced via a funnel tightly connected to the inlet valve. The autoclave was frozen at  $-90^\circ\text{C}$ . Then, VDF was transferred by double weighing. The autoclave was then heated to the required temperature. During the polymerization, the pressure reached ca. 20 bar and then dropped to ca. 5–10 bar (Table 2). After reaction, the autoclave was cooled down to room temperature and then placed into an ice bath.

After outgassing to remove any unreacted monomers, the autoclave was opened. The solvent was evaporated, the polymer was solubilized in acetone, and precipitated from cold pentane. After filtration and drying under vacuum at  $50^\circ\text{C}$  for 24 h, a white powder was recovered. The yields of the reactions were determined gravimetrically (mass of copolymers obtained/mass of monomers transferred into the autoclave). The polymers were characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopies.

### Hydrolysis of PFSVE and poly(VDF-co-PFSVE) copolymers

The PFSVE monomer or poly(VDF-co-PFSVE) copolymers were placed in a 50 mL flask. A  $2\text{ mol L}^{-1}$  basic solution (NaOH or KOH) with 2 equivalents of base for one  $\text{SO}_2\text{F}$  equivalent was added at room temperature, and the solution was stirred. Excess base was neutralized with HCl, and the solution was filtered to remove the salts. The solvent was then evaporated and the product dried under vacuum at  $50^\circ\text{C}$  for 24 h. The yield was determined gravimetrically (obtained weight/starting weight). The products were characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopies.

#### Characterization of PFSVE monomer

$^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ):  $\delta$  45.3 (s,  $-\text{SO}_2\text{F}$ , 1F), -74.8 (m,  $\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 2F), -75.6 ( $\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 3F), -80.2 ( $\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 2F), -107.7 ( $\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 2F), -108.6 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -117.0 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -132.4 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -140.1 (m,  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_2\text{F}$ , 1F).

The COSY  $^{19}\text{F}$ - $^{19}\text{F}$  NMR spectrum, supplied in Fig. S2, displays the correlations of the signals assigned to the different  $\text{CF}_x$  groups.

IR ATR:  $\text{SO}_2\text{F}$  1460–1470  $\text{cm}^{-1}$  (asymmetric S=O),  $\text{SO}_2$  1200–1220  $\text{cm}^{-1}$  (symmetric S=O), CF 1100–1200  $\text{cm}^{-1}$ , COC 970–980  $\text{cm}^{-1}$ , SF 810–820  $\text{cm}^{-1}$ .

#### Characterization of H4 monomer (hPFSVE)

$^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ):  $\delta$  -79.1 (m,  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ , 5F), -84.4 (m,  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ , 2F), -112.8 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -117 (m,  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ , 2F), -121.3 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -136.6 (m,  $\text{CF}_2=\text{CF}-$ , 1F), -144.3 (m,  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ , 1F).

IR ATR: OH (in  $\text{SO}_3\text{H}$ ) 3300–3500  $\text{cm}^{-1}$  and 1050  $\text{cm}^{-1}$ ,  $\text{SO}_2$  1200–1220  $\text{cm}^{-1}$  (symmetric S=O), CF 1100–1200  $\text{cm}^{-1}$ , COC 970–980  $\text{cm}^{-1}$ .

#### Characterization of PH3 copolymer

$^1\text{H}$  NMR (400 MHz, acetone- $d_6$ ):  $\delta$  0.82 to 1.45  $\text{CH}_3-(\text{CH}_2\text{CF}_2)-$ ,  $(\text{CH}_3)_3\text{C}-(\text{CF}_2\text{CH}_2)-$ ,  $(\text{CH}_3)_3\text{CO}-(\text{CF}_2\text{CH}_2)-$ ,  $(\text{CH}_3)_3\text{C}-(\text{CH}_2\text{CF}_2)-$  and  $(\text{CH}_3)_3\text{CO}-(\text{CH}_2\text{CF}_2)-$ ; 1.80  $\text{CH}_3-(\text{CF}_2\text{CH}_2)-$ , 2.26 to 2.55  $-(\text{CF}_2\text{CH}_2)-(\text{CH}_2\text{CF}_2)-$ ,  $\text{CH}_3-(\text{CH}_2\text{CF}_2)-$ ,  $(\text{CH}_3)_3\text{C}-(\text{CH}_2\text{CF}_2)-$  and  $(\text{CH}_3)_3\text{CO}-(\text{CH}_2\text{CF}_2)-$ ; 2.68 to 3.24  $-(\text{CF}_2\text{CH}_2)-(\text{CF}_2\text{CH}_2)-$ ; 3.24 to 3.51  $-(\text{CF}_2\text{CH}_2)-(\text{PFSVE})-$ ; 6.12 to 6.48  $\text{H}-(\text{CF}_2\text{CH}_2)-$  (H,  $^3J_{\text{HF}} = 48\text{ Hz}$ ,  $^3J_{\text{HH}} = 7\text{ Hz}$ ).

$^{19}\text{F}$  NMR (376 MHz, acetone- $d_6$ ):  $\delta$  -78.91 to -81.81  $-\text{OCF}_2\text{CF}(\text{CF}_3)\text{OCF}_2\text{CF}_2\text{SO}_3\text{H}$ , -91.33 to -93.97  $-\text{CF}_2-\text{CH}_2\text{CF}_2-\text{CH}_2\text{CF}_2-$  (Regular addition HT), -93.98 to -96.54  $-\text{CF}_2\text{CH}_2-$ .

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