Proton-Conducting Polymer Electrolyte Membranes Based on Fluoropolymers Incorporating Perfluorovinyl Ether Sulfonic Acids and Fluoroalkenes: Synthesis and Characterization[×]

R. Souzy[1], B. Ameduri[1]*, B. Boutevin[1], P. Capron[2], D. Marsacq[2], and G. Gebel[3]

[1] Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France
[2] CEA, DTEN/SCSE/LSME, 17 rue des Martyrs, 38054 Grenoble Cedex, France
[3] CEA, DRFMC/SI3M, 17 rue des Martyrs, 38054 Grenoble Cedex, France

Received May 7, 2004; accepted October 1, 2004

Abstract

This paper presents the synthesis of new polymer electrolyte membranes based on fluoropolymers incorporating aromatic perfluorovinyl ether sulfonic acids. A novel synthetic route describing the preparation of perfluorovinyl ether monomer containing sulfonic functionalities, 4-[(α,β,β-trifluorovinyl)-oxy]benzene sulfonic acid (TFVOBSA), is reported. The radical (co) and terpolymerisation of 4-[(α,β,β-trifluorovinyl)oxy]benzene sulfonyl chloride (TFVOBSC) with 1,1-difluoroethylene (or vinylidene fluoride, VDF), hexafluoropropene (HFP), and perfluoromethyl vinyl ether (PMVE) is described. The terpolymers of TFVOBSC with VDF and HFP, or VDF and PMVE, were hydrolysed and also led to new fluorinated terpolymers bearing sulfonic acid aromatic side-groups. The terpolymers were characterized by ^{1}H and ^{19}F NMR spectroscopies, SEC, DSC, and TGA. Membranes incorporating these functional fluoropolymers were prepared and the electrochemical properties (*IEC*, proton conductivity, swelling rates) were studied and discussed.

Keywords: [(α,β,β-trifluorovinyl)oxy] Benzene Sulfonic Acid, Electrochemical Properties, Fluoro-Membranes, Hexafluoropropene (HFP), Perfluoromethyl Vinyl Ether (PMVE), Proton Exchange Membranes for Fuel Cells, Radical Copolymerisation, Vinylidene Fluoride (VDF)

1 Introduction

Polymeric materials, functionalised by acid groups, have dominated as the ion-exchange component for membranes in proton exchange membrane fuel cells (PEMFC) [1]. Polymers for PEMFCs are divided into two categories.

The first, encompasses non-fluorinated polymers (Table 1), like sulfonated polystyrenes (crosslinked or not) [2], sulfonated polyimides (PI) [3], sulfonated poly(aryl ether sulfones) [4], sulfonated poly(aryl ether ketones) [5], sulfonated phenol formol resins [6], sulfonated poly(phenylene oxide) [7], phosphonic poly(phenylene oxide) [8], sulfonated silicates [9], sulfonated poly(benzimidazole) [9], and sulfonated organic-inorganic hybrids [10].

On the other hand, fluorinated polymers are very interesting materials because of their outstanding properties [11], and are currently used as materials for the preparation of ion exchange resins [12, 13], proton exchange membranes for fuel cells (PEMFC) [14–18], and are commercially available under the Nafion®, Flemion®, Hyflon® or Aciplex® trade names [20–22].

[×] *Article is part of Topical Issue 'Polymer Membranes'*

[*] *Corresponding author, ameduri@cit.enscm.fr*

 DOI: 10.1002/fuce.200400071

Table 1 Non-fluorinated polymers used in the PEMFC.

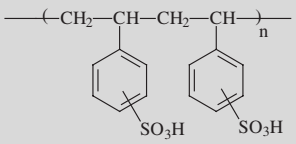
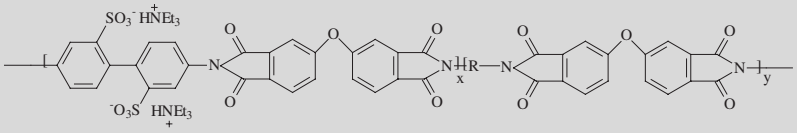
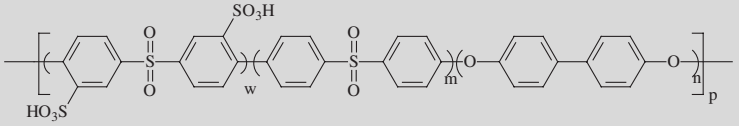
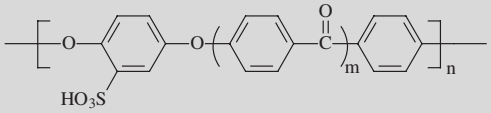
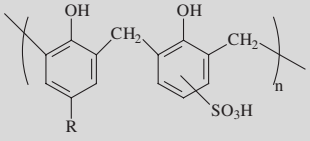
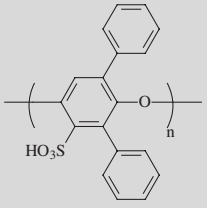
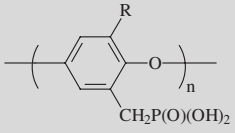
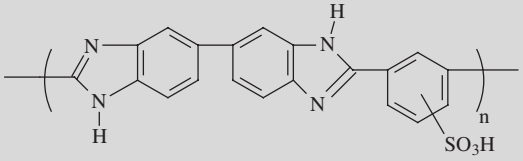
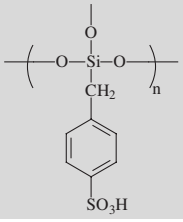
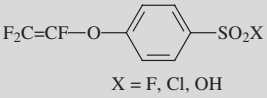
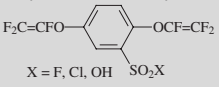
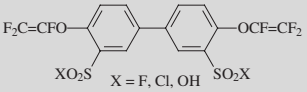
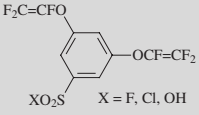
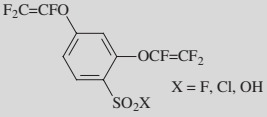
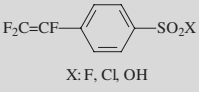
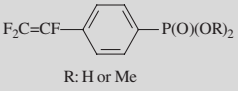
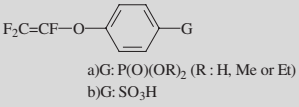
Polymers	Structure	Reference
Sulfonated polystyrenes		[2]
Sulfonated polyimides		[3]
Sulfonated poly(aryl ether sulfones)		[4]
Sulfonated poly(aryl ether ketones)		[5]
Sulfonated phenol formol resins		[6]
Sulfonated poly(phenylene oxide)		[7]
Phosphonic poly(phenylene oxide)	 R : CH_3 or $CH_2P(O)OH)_2$	[8]
Sulfonated poly(benzimidazole)		[9]
Sulfonated silicates		[10]

Table 2 Fluoropolymers used in the PEMFC.

Structure of (co)polymers	Reference	Structure of (co)polymers	Reference
Copolymer of Rf-CF=CF-SO_2F with TFE	[23–25]	F_2C=CF-O-C_3F_6-P(O)$(OEt)_2$ diethyl perfluoro-(3-vinyloxypropyl) phosphonate co- or terpolymerized with TFE and perfluoro (propyl vinyl ether)	[40, 41]
Copolymer of F_2C=CF-$(OCF_2CF(CF_3))_pOCF_2CF_2SO_2F$ with TFE (p: 0 or 1) Nafion®, Flemion®	[26]	F_2C=CFP(O)$(OH)_2$	[42]
Copolymer of F_2C=CF-$OCF_2CF_2SO_2F$ with TFE Dow Chemical Membrane, Hyflon®Ion	[1, 27, 28]	 X = F, Cl, OH	[13]
Copolymer of F_2C=CF-$CF_2OCF_2CF_2SO_2F$ with TFE	[29, 30]	Polymer obtained by thermo-cyclodimerisation 	[13]
Copolymer of F_2C=CF-$OCF_2CF(CF_3)OCF_2CF_2G$ with TFE G: $SO_2NHSO_2CF_3$, $N(Na)SO_2CF_3$ or $N(Na)SO_2C_4F_8SO_2N(Na)SO_2CF_3$	[31]	Polymer obtained by thermo-cyclodimerisation 	[13]
Copolymer of perfluorovinyl ethoxy sulfonyl fluoride with VDF	[32]	Polymer obtained by thermo-cyclodimerisation 	[13]
(Ter)polymer of perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE) with VDF and / or HFP	[33–35]	Polymer obtained by thermo-cyclodimerisation 	[13]
Copolymer of H_2C=$CFCF_2OCF(CF_3)CF_2CO_2CH_3$ with VDF	[36]	Polymer obtained by thermo-cyclodimerisation 	[18, 46]
Copolymer of F_2C=$CFOCF_2CF(CF_3)OC_2F_4R$ with VDF	[37, 38] R : $NHSO_2CF_3$ [33, 39] R :$SO_2CLi(SO_2CF_3)_2$, $SO_2NLiSO_2CF_3$ and SO_2F (PSEPVE) [38]	Homopolymer or copolymer with Trifluorostyrene 	[19]
Copolymer of F_2C=CF-COOH with TFE	[32, 33, 37]	Homopolymer or copolymer with Trifluorostyrene 	[47, 48] [this work]
Copolymer of F_2C=$CFOCF_2CF(CF_3)OCF_2CF_2COOCH_3$ with TFE	[38]	Terpolymer with VDF / HFP or VDF / PMVE	
Copolymer of F_2C=$CFOCF_2CF_2COOCH_3$ with TFE	[39]		

Fluoropolymers for fuel cells can be divided in two groups (Table 2) [23–48]. The first group are polymers that incorporate aliphatic monomers. These monomers can be functionalised by a sulfonic acid or a sulfonyl fluoride function (the corresponding sulfonic acid component was obtained by hydrolysis) like trifluorovinyl sulfonyl fluoride [23–25] or perfluorosulfonyl fluoride ethoxy propyl vinyl ether, monomer produced by Nafion®: (F_2C=CF-($OCF_2CF(CF_3)$)$_p$-$OCF_2CF_2SO_2F$) [26], (F_2C=CF-$OCF_2CF_2SO_2F$) [1, 27–28], or F_2C=$CFCF_2OC_2F_4SO_2F$ [29–30], or F_2C=CF-OCF_2CF-(CF_3)OCF_2CF_2G (G: $SO_2NHSO_2CF_3$, N(Na)SO_2CF_3 or N(Na)-$SO_2C_4F_8SO_2N(Na)SO_2CF_3$ [31]). The comonomer is usually tetrafluoroethylene (TFE) but can be also vinylidene fluoride (VDF or VF_2) with perfluorovinyl ethoxy sulfonyl fluoride [32], perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE) [28–29], functional comonomers such as F_2C= $CFOCF_2CF(CF_3)OC_2F_4R$ [37, 38] where R stands for $NHSO_2CF_3$ [31, 39], $SO_2CLi(SO_2CF_3)_2$, $SO_2NLiSO_2CF_3$, and SO_2F (PSEPVE) [38]. These monomers can also be functionalised by a carboxylic acid group [32, 33, 37], H_2C=$CFCF_2$-$OCF(CF_3)CF_2CO_2CH_3$ [36], F_2C=$CFOCF_2CF(CF_3)OCF_2CF_2$-$COOCH_3$ [38], or F_2C=$CFOCF_2$-CF_2COOCH_3 [39]. Finally, they can be functionalised by phosphonic acid groups [8, 40, 41], like diethyl perfluoro(3-vinyloxypropyl) phosphonate [41], or F_2C=$CFP(O)(OH)_2$ [42]. Furthermore, various functional trifluorovinyl monomers have also been prepared, bearing either a carboxylic acid [43], or a sultone [44] group.

The second group of fluorinated membranes are those which are prepared from (co)polymers incorporating an aromatic fluoromonomer [13, 18, 19, 46] (Table 2). In fact, in recent decades, fluoropolymers incorporating aromatic monomers with sulfonic acid, like perfluorovinyl aryl ether [13], trifluorostyrene [15, 46], or with a phosphonic acid [19, 40, 41, 47, 48], have been of growing interest. In the case of trifluorostyrene (functionalised by a phosphonic acid, or by halogenosulfonyl group post hydrolysable into sulfonic acid), polymers are prepared by their (co)polymerisation with trifluorostyrene (TFS). Concerning perfluorovinyl aryl ether, the materials are synthesised by thermo-cyclodimerisation [2π+2π] [26, 28, 49, 50], giving thermoplastic and thermoset polymers containing perfluorocyclobutane rings (PFCB). Such thermo-cyclopolymerisation is usually observed at temperatures ranging between 150 and 210 °C [49, 50].

To the best of our knowledge, prior to 2004, no fluorinated membrane for the PEMFC, prepared from a (co) or a (ter)polymer obtained by the radical (ter)polymerisation of [(α,β,β-trifluorovinyl)oxy] benzene halogenosulfonyl with fluoroalkenes, had been prepared. Hence, the objective of this paper concerns the synthesis and characterization of a new generation of original membranes, prepared from aromatic fluorinated copolymers [45, 47] incorporating fluoroalkenes, such as VDF, hexafluoropropene (HFP, F_2C=$CFCF_3$), perfluoromethylvinylether (PMVE, F_2C=$CFOCF_3$) and an aromatic fluorinated monomer functionalised by a sulfonic acid. First, the syntheses and the (ter)polymerisations of [(α,β,β-trifluorovinyl)oxy] benzene halogenosulfonyl are presented. The second part concerns the preparation of fuel cell proton exchange membranes. Finally, the physico-chemical and electrochemical characteristics of the materials were investigated.

2 Experimental

2.1 Materials

Vinylidene fluoride (VDF), hexafluoropropene (HFP), and 1,1,1,3,3-pentafluorobutane were generously provided by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium. Perfluoromethylvinyl ether (PMVE, Fluorochem), 1,2-dibromotetrafluoroethane, and 2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90% (Luperox 101®) (Aldrich Chimie, 38299 Saint Quentin-Fallavier, France) were used as supplied. *t*-Butyl lithium (1.7 M in hexane) and sulfonyl dichloride were used as received. Acetonitrile, dimethylsulfoxide, N-methyl pyrolidinone (analytical grade), and diethyl ether (Aldrich Chimie, as above) were distilled over calcium hydride prior to use.

2.2 Analysis

The compositions of the terpolymers (the molar contents of VDF, PMVE or HFP, and TFVOBSA monomeric units in the prepared terpolymer) were determined by ^{19}F NMR spectroscopy. The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or $CFCl_3$) as the reference for ^{1}H (or ^{19}F) nuclei. Coupling constants and chemical shifts are given in Hz and ppm, respectively. The experimental conditions for the ^{1}H (or ^{19}F) NMR spectra were as follows: flip angle 90° (30°), acquisition time 4.5 s (0.7 s), pulse delay 2 s (5 s), number of scans 16 (64), and the pulse width for ^{19}F NMR was 5 μs.

Infrared spectra were recorded from KBr pellets on a Nicolet 510P Fourier Transform spectrometer, the intensities of the absorption bands were denoted as s = strong, m = medium, and w = weak, and given in cm^{-1} (accuracy ± 2 cm^{-1}).

Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer. The apparatus was calibrated with indium and n-decane. After its insertion into the DSC apparatus, the sample was initially cooled to –105 °C for 15 min. Then, the first scan was conducted at a heating rate of 40 °C min^{-1} up to 80 °C, where it remained for 2 min. It was then cooled to –105 °C at a rate of 320 °C min^{-1} and left for 10 min at that temperature before a second scan was started at a heating rate of 20 °C min^{-1}. Finally, another cycle was performed and a third scan at a heating rate of 20 °C min^{-1} was initiated, giving the T_g values reported herein, taken at the half-height of the heat capacity jump of the glass transition.

Thermogravimetric analyses were performed with a Texas Instrument TGA 51-133 apparatus in air, at a heating rate of 10 °C min^{-1} from room temperature up to a maximum of 600 °C.

The synthesised copolymers were characterized by size exclusion chromatography (SEC), carried out in tetrahydrofuran at 30 °C, at a flow rate of 0.8 mL min^{-1}, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer, and a set of four columns connected in series: Styragel (Waters) HR4 5 μ, HR3 analyses 5 μ, PL Gel (Polymer Laboratories) 5 μ 100 Å. Monodispersed poly(styrene) standards were used for calibration. Aliquots were sampled from the reaction medium, diluted with tetrahydrofuran up to a known concentration (ca. 4 wt.%), filtered through a 20 μm PTFE Chromafil Membrane and finally analysed by GPC under the conditions described above.

The high frequency resistance of the membrane was measured by impedance [60–62]. Using a mercury cell, the variation of the membrane resistance, both as a function of its ionic composition and water content, could be monitored.

2.3 Monomer Synthesis

2.3.1 Synthesis of 4-[(α,β,β-Trifluorovinyl)Oxy] Bromo Benzene (TFVOBB)

4-[(α,β,β-trifluorovinyl)oxy]bromobenzene was prepared following a literature method [50]. Under a nitrogen atmosphere, 100.1 g (0.582 mol) of 4-bromophenol, 37.4 g (0.583 mol) of KOH, 320 mL of DMSO, and 80 mL of xylene were introduced into a two-necked round bottom flask, equipped with a Dean-Stark azeotropic distillation assembly, a reflux condenser, and a magnetic stirrer. The mixture was stirred and heated to 100 °C (ca. 200 mmHg) for 48 hours during which time water was removed. The solution was cooled to 30 °C, and 166.5 g (0.641 mol) of 1,2-dibromotetrafluoroethane were added drop-wise over 4 hours, such that the temperature did not exceed 30 °C. The mixture was stirred for 16 hours at 22 °C, and then for 10 hours at 35 °C. The reaction mixture was diluted with H_2O, extracted with methylene chloride, and dried with $MgSO_4$. 4-(2-Bromotetrafluoroethoxy)bromobenzene **(1)** was purified (yield 70%) from the crude oil by distillation (*b.p.* = 110–115 °C, 25 mmHg). Afterwards, 100 g (0.284 mol) of bromo ether **(1)** was slowly added, under nitrogen, to a stirring mixture of 18.6 g (0.284 mol) of zinc turnings in 250 mL of acetonitrile at 80 °C. The mixture was refluxed for 24 hours and then the solvent was evaporated. The crude product was extracted from the salts with hexane, concentrated and distilled (*b.p.* = 65–75 °C, 20 mmHg) giving 57 g (78%) of 4-[(trifluorovinyl)oxy]bromobenzene. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 6.9 (2H, d, $^3J_{HH}$ = 8.8 Hz), 7.4 (2H, d, $^3J_{HH}$ = 8.8 Hz); ^{19}F NMR (250 MHz, $CDCl_3$) δ: -119.8 (dd, *cis*-CF=C$\underline{F}_2$, F_a, $^2J_{FaFb}$ = 96 Hz, $^3J_{FaFc}$ = 58 Hz, 1F), -126.7 (dd, *trans*-CF=C$\underline{F}_2$, F_b, $^2J_{FbFa}$ = 96 Hz, $^3J_{FbFc}$ = 110 Hz, 1F), -134.9 (dd, C$\underline{F}$=CF_2, F_c, $^3J_{FcFa}$ = 58 Hz, $^3J_{FcFb}$ = 110 Hz, 1F).

2.3.2 Synthesis of 4-[(α,β,β-Trifluorovinyl)Oxy] Benzene Sulfonyl Chloride (TFVOBSC)

22.802 g (0.091 mol) of TFVOBB and 50 mL of diethyl ether were introduced, under a nitrogen atmosphere, into a two-necked round bottom flask, containing a septum and a nitrogen purge, and then cooled to –80 °C. 50 mL of 1.7 M *t*-butyl lithium (in hexane) (0.088 mol) were added drop-wise to this mixture over 45 minutes with additional stirring for 2 hours, while maintaining the temperature at –80 °C. The lithium reagent was added drop-wise, using vacuum/nitrogen flow techniques, through a double ended needle into a separate two-necked round bottom flask containing 50 mL of ether and 15 g of SO_2Cl_2 (0.11 mol), also maintained at –80 °C. The reaction mixture was stirred for 30 minutes at –80 °C. Then, 100 mL of deionised water were added to the reaction forming an organic and an aqueous layer. The two layers were separated. TFVOBSA was dried over $MgSO_4$ and purified by vacuum distillation (*b.p.* = 116–121 °C, 0.1 bar) and a 68% yield was obtained (purity 90%). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.1–7.3 (m, ArH, 2H), 7.9–7.1 (m, ArH, 2H); ^{19}F NMR (250 MHz, $CDCl_3$) δ: –117.8 (dd, *cis*-CF=C$\underline{F}_2$, F_a, $^2J_{FaFb}$ = 98 Hz, $^3J_{FaFc}$ = 55 Hz, 1F), –124.7 (dd, *trans*-CF=C$\underline{F}_2$, F_b, $^2J_{FbFa}$ = 98 Hz, $^3J_{FbFc}$ = 117 Hz, 1F), –136.1 (dd, C$\underline{F}$=CF_2, F_c, $^3J_{FcFa}$ = 55 Hz, $^3J_{FcFb}$ = 117 Hz, 1F). FTIR: 1196 (s, C-F stretch), 1381 (s, O=S=O stretch).

2.3.3 Synthesis of 4-[(α,β,β-Trifluorovinyl)Oxy] Benzene Sulfonic Acid (TFVOBSA)

Under a nitrogen atmosphere, 18.005 g (0.070 mol) of *TFVOBSC* were added to a two-necked round bottom flask, equipped with a reflux condenser and a magnetic stirrer. 280 mL of a solution of KOH in methanol (0.5 M) were added drop-wise to the mixture at room temperature over 2 hours. The mixture was allowed to stir for 12 hours. Then, the salts were filtered off and the solvent was evaporated under vacuum. TFVOBSA was extracted (yield 88%) from the crude oil by distillation under vacuum (*b.p.* = 119–125 °C, 5 mmHg). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.4–7.6 (m, ArH, 2H), 8.0–8.2 (m, ArH, 2H); ^{19}F NMR (250 MHz, $CDCl_3$) δ: –115.1 (dd, *cis*-CF=C$\underline{F}_2$, F_a, $^2J_{FaFb}$ = 102 Hz, $^3J_{FaFc}$ = 59 Hz, 1F), –122.2 (dd, *trans*-CF=C$\underline{F}_2$, F_b, $^2J_{FbFa}$ = 102 Hz, $^3J_{FbFc}$ = 109 Hz, 1F), –137.1 (dd, C$\underline{F}$=CF_2, F_c, $^3J_{FcFa}$ = 59 Hz, $^3J_{FcFb}$ = 109 Hz, 1F). FTIR: 3373 and 1029 (s, $S(O)(OH)_2$ stretch), 1000–1300 (s, C-F stretch).

2.4 Terpolymerisation

The batch terpolymerisations of VDF, HFP or PMVE with TFVOBSC were performed in a 160 mL HASTELLOY (HC 276) autoclave, equipped with a manometer, a rupture disk, and an inlet valve. This vessel was left closed for 20 minutes and purged with 20 bar of nitrogen to prevent any leakage, and degassed afterwards. Then, a 20 mmHg vacuum was applied for 15 min and the initiator (2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane, tech, 90%: C_0 = ([2,5-Bis-(*tert*-butylperoxy)-2,5-dimethylhexane] / Σ[Monomers]) = 0.9 mol%), TFVOBSC, and 1,1,1,3,3-pentafluorobutane were introduced, successively, via a funnel tightly connected to the introduction valve. Next, HFP or PMVE, and VDF were introduced by double weighing. The autoclave was then heated

up to 134 °C for 10 hours. After reaction, the vessel was cooled to room temperature and then put in an ice bath. The crude product was analysed by ^{19}F NMR spectroscopy. The solvent was evaporated and the crude product was solubilised in DMF and then precipitated from cold water. The precipitate was filtered off and dried over P_2O_5 at room temperature under a 20 mmHg vacuum for 48 hours.

2.5 Hydrolysis of the Terpolymers Containing TFVOBSC Units

10 g of the terpolymers incorporating VDF, HFP or PMVE, and TFVOBSC were placed in a 50 mL flask and stirred with 25 mL of acetone. At room temperature, a solution of KOH in MeOH (0.5 mol L^{-1}) with a 1.0 equivalent molar ratio was added drop-wise to this solution. After the addition, the solution was allowed to stir for 1 hour. Subsequently, the excess basic solution was neutralized by HCl, since the *pH* goes below 7. The solution was filtered, the solvent was evaporated, and the product precipitated from cold water. The precipitate was filtered off and dried over P_2O_5 at room temperature under a 20 mmHg vacuum for 48 hours.

2.6 Preparation of the Membranes by Casting

The terpolymers, containing VDF, HFP or PMVE, and TFVOBSA (70 wt.%), and a commercial poly(VDF-*co*-HFP) copolymer (3M) (30 wt.%), were placed in a 50 mL flask and stirred with NMP for 1 hour at 45 °C. Afterwards, the mixture was sprayed on a Teflon® substrate, and the solvent was evaporated using a heating table at 40 °C. The cast membranes were removed from the substrates in the presence of water. The average thickness ranged between 60 and 80 μm.

3 Results and Discussion

The development of the membranes was carried out in three steps. The first section seeks to report the synthesis of 4-[(α,β,β-trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC). The second part covers the terpolymerisation of TFVOBSC with fluoroalkenes. The physico-chemical properties of the terpolymers are discussed. The third part is devoted to the hydrolysis of these fluorinated macromolecules and to the proton exchange membranes obtained by casting. Finally, the properties of the membranes are presented.

3.1 Monomer Synthesis

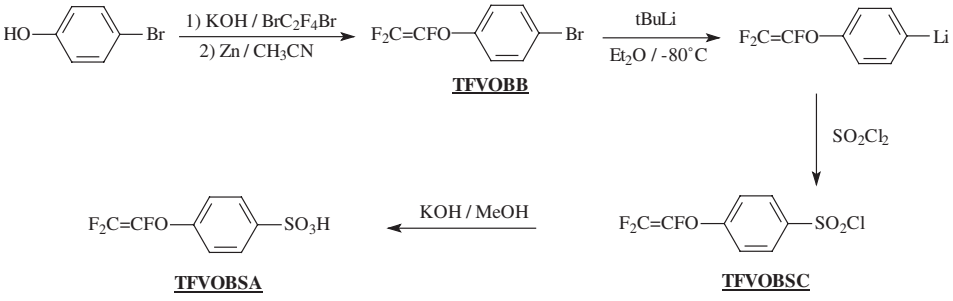
First, the synthesis and characterization of 4-[(α,β,β-trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC) were studied.

In 1996 Smith et al. reported the synthesis of 4-[(α,β,β-trifluorovinyl)oxy] bromo benzene (TFVOBB) [50, 51]. It is based on the nucleophilic substitution of 4-bromophenolate on 1,2-dibromotetrafluoroethane followed by a dehalogenation reaction (Scheme 1).

Subsequently, a novel synthetic route for the preparation of 4-[(α,β,β-trifluorovinyl)oxy] benzene sulfonic acid (TFVOBSA) was focussed on. DesMarteau et al. [13, 52] investigated the synthesis of 4-[(α,β,β-trifluorovinyl)oxy] benzenesulfonyl chloride (TFVOBSC), obtaining a 65% yield, they used sulfonyl chloride fluoride (FSO_2Cl) as one of the reactants. Here, a new method for the synthesis of TFVOBSC is proposed. Interestingly, it was found that the organolithium intermediate of TFVOBB [48, 52–54] reacted with SO_2Cl_2 at –80 °C (Scheme 1) yielding TFVOBSC in a better yield (72%) than that previously reported [52].

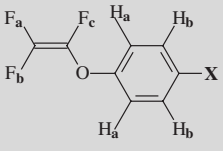
TFVOBSA was obtained, at an 88% yield, from the basic hydrolysis of TFVOBSC in the presence of KOH and methanol (Scheme 1).

TFVOBSC and TFVOBSA were characterized by ^1H, ^{19}F NMR, and IRTF (Table 3). The ^1H NMR spectra of these monomers show multiplets centred between 7.2 and 8.1 ppm, characteristic of the aromatic protons. The ^{19}F NMR spectra exhibit three doublet of doublets, centred at –117.8, –124.7, and –136.1 ppm character-



Scheme 1 Synthesis and hydrolysis of 4-[(α,β,β-trifluorovinyl)oxy] benzene sulfonyl chloride (TFVOBSC).

Table 3 Chemical shifts and IR frequencies of [(α,β,β-trifluorovinyl)oxy] benzene functionalised with halogenosulfonyl or sulfonic acid groups.



X	F_a δ / ppm	F_b δ / ppm	F_c δ / ppm	H_a δ / ppm	H_b δ / ppm	ν (X) / cm^{-1}
Br (TFVOBB)	–119.8	–126.7	–134.9	7.1	7.5	–
SO_2Cl (TFVOBSC)	–117.8	–124.7	–136.1	7.2	8.1	1,381 (O=S=O stretch)
SO_2F (TFVOBSF)	–117.1	–124.1	–136.2	7.4	8.2	1,421 (O=S=O stretch)
SO_3H (TFVOBSA)	–115.1	–122.2	–137.1	7.5	8.1	3,373 (S(O)$(OH)_2$ stretch) 1,029 (S(O)$(OH)_2$ stretch)

istic of the F_a, F_b, and F_c atoms, respectively (Table 3). Note that there was a slight difference in the chemical shifts in the ^1H and ^{19}F NMR spectra for TFVOBSA, induced by the electron-withdrawing nature of the para-group.

3.2 Radical Terpolymerisations of TFVOBSC with Fluoroalkenes

This section covers the synthesis of novel fluorinated terpolymers incorporating TFVOBSC, obtained in radical conditions. The physico-chemical properties of the materials are reported.

Table 4 Determination of the Monomer/Terpolymer composition of VDF/Terolefin/ TFVOBB *vs.* the reaction conditions in the radical terpolymerisation of VDF, Terolefin (HFP or PMVE) with TFVOBB. Terpolymerisation conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [Terolefin]$_0$ + [TFVOBB]$_0$) = 0.9 mol%, 134 °C, 10 hours [47].

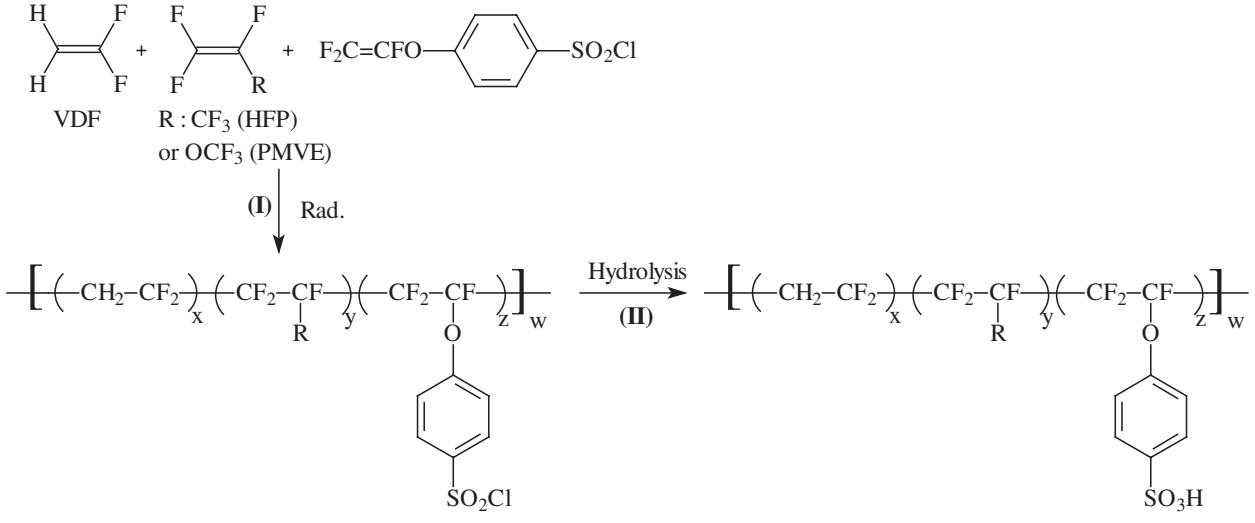
Exp. #	VDF in feed / mol%	Terolefin in feed / mol%	TFVOBB in feed / mol%	VDF in terpolymer / mol%	Terolefin in terpolymer / mol%	TFVOBB in terpolymer / mol%	Massic yields / %
1	83	12 HFP	5	84	10 HFP	6	38
2	79	13 HFP	8	82	8 HFP	10	20
3	80	9 HFP	11	81	5 HFP	14	17
4	70	25 PMVE	5	78	15 PMVE	7	41
5	66	24 PMVE	10	72	13 PMVE	15	17
6	64	22 PMVE	14	71	10 PMVE	19	15

3.2.1 Radical (Co)Polymerisation of Aryl α,β,β-Trifluorovinyl Ether

Previously, a model of radical (co)polymerisation of aryl α,β,β-trifluorovinyl ether was achieved [55]. [(α,β,β-Trifluorovinyl)oxy]bromobenzene (TFVOBB) was used as the model monomer. First, it was shown that aryl α,β,β-trifluorovinyl ether does not homopolymerise under radical initiation but undergoes thermo-cyclodimerisation [2π+2π] [26, 28, 45, 49, 50, 51, 55]. Furthermore, this study showed that copolymerisation with commercially available fluoroalkenes, initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, led to better massic yields. The radical polymerisation was performed in 1,1,1,3,3-pentafluorobutane because of its lower transfer activity on the growing macroradical than that of acetonitrile [56]. In order to enhance the reactivity of VDF, a termonomer, like hexafluoropropene (HFP), or perfluoromethyl vinyl ether (PMVE), was also introduced. A series of terpolymerisations of aryl vinyl ethers with VDF, and HFP (or PMVE) were investigated, and the microstructures of the products (i.e., the molar percentages of each termonomer in the terpolymer) were characterized by ^1H and ^{19}F NMR spectroscopies. It has been demonstrated that the ^{19}F NMR signals centred at –113.5 and –124.5 ppm can be assigned to the difluoromethylene group and the tertiary fluorine of a α,β,β-trifluorovinyl ether, respectively [55]. The results of the level of incorporation of each terolefin are gathered in Table 4. Finally, it appears that the incorporation of α,β,β-trifluorovinyl ether in the terpolymer is enhanced in the VDF/PMVE system, being better than that in the VDF/HFP system.

3.2.2 Radical Terpolymerisation of TFVOBSC

The initial goal was to produce materials incorporating TFVOBSC units. In fact, earlier results, described above, were used, since it can be assumed that the influence of the chlorosulfonyl function (SO_2Cl) is similar to that of the bromine atom. Because of the low incorporation rates obtained in the



Scheme 2 Radical terpolymerisation: (I) of TFVOBSC with VDF and / or HFP and / or PMVE, and (II) hydrolysis of the corresponding terpolymers [47].

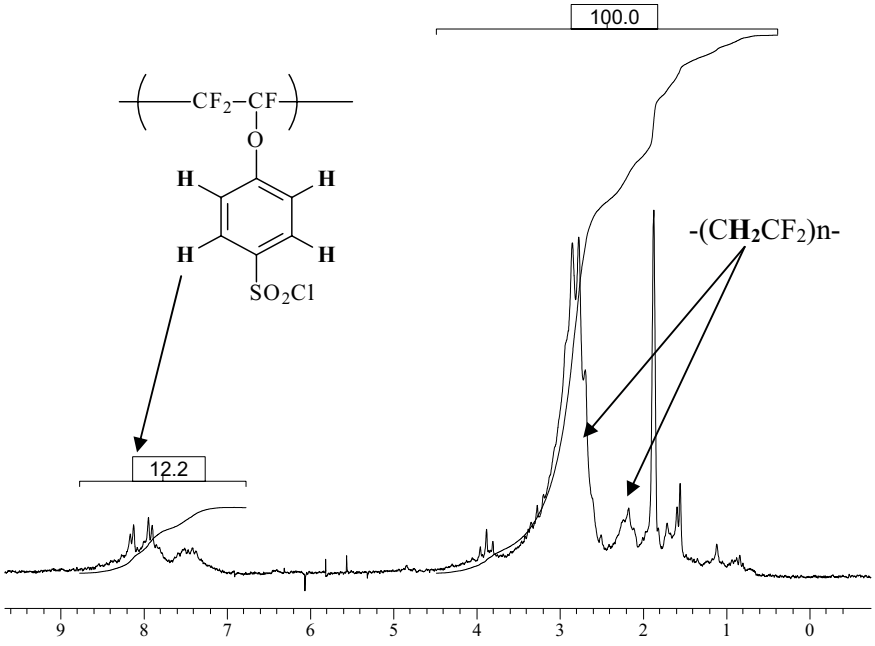


Fig. 1 ^{1}H NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerisation conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$ /([VDF]$_0$ + [HFP]$_0$ + [TFVOBSC]$_0$) = 0.9%, 134 °C, 6 hours and VDF / HFP / TFVOBB initial molar ratio in the feed = 84.9 / 10.3 / 4.8.

study described above, the radical copolymerisation of TFVOBSC with VDF was not attempted. Hence, the radical terpolymerisations of these functional aromatic monomers with VDF and / or HFP and / or PMVE were investigated (Scheme 2).

Using the optimal experimental conditions for the terpolymerisation of TFVOBB with the above fluoroalkenes, it was decided to perform all subsequent experiments in a solution of 1,1,1,3,3-pentafluorobutane initiated by 2,5-bis-(*tert*-butylperoxy)-2,5-dimethylhexane. After reaction, the resulting fluorinated macromolecules were precipitated from cold pentane and the materials were characterized by ^{1}H, ^{19}F NMR, and IR spectroscopies, which enabled the characterisation of the microstructure of the terpolymers and the specific functionalities.

In all cases, statistic terpolymers were obtained in which microblocks of oligo(VDF)s were noted. The level of monomer units in the terpolymers was assessed by ^{19}F NMR. In addition, all ^{1}H NMR spectra exhibited: (i) signals due to the methylene groups of the VDF units, adjacent to difluoromethylene groups in the 3.0–3.4 ppm range (including the "head-to-head" and "head-to-tail addition" in the oligo(VDF) chain) and (ii) signals attributable to aromatic groups at about 7.6 ppm. Interestingly, the absence of a triplet of triplets, centred at 6.1 ppm in the ^{1}H NMR spectra, and that of the multiplet at –114.8 ppm in the ^{19}F NMR spectra, characteristic of –(CH_2CF_2)-$CH_2\underline{CF_2H}$) was noted. Hence, the transfer reaction onto the macroradical can be eliminated.

Terpolymerisation of TFVOBSC with VDF and HFP

^{19}F NMR spectroscopy was chosen as the method for the identification of the corresponding TFVOBSC, VDF, and HFP contents in the terpolymers.

First, the spectrum (Figure 2 and Table 5) shows a signal centred at –91.3 ppm (denoted $L_{91.3}$), assigned to the difluoromethylene groups, characteristic of head-to-tail VDF addition. Furthermore, a series of other signals centred at –95.1 (denoted $L_{95.1}$), –113.7 (denoted $L_{113.7}$), and –115.6 (denoted $L_{115.6}$) ppm are assigned to the CF_2 groups in the (CH_2-CF_2)-(CF_2-CH_2)-(CH_2-$\mathbf{CF_2}$)-(CH_2-CF_2), -(CH_2-CF_2)-($C\mathbf{F_2}$-CH_2)-(CF_2-CH_2)-, and -(CH_2-CF_2)-($C\mathbf{F_2}$-CH_2)-(CH_2-CF_2)- sequences, respectively. They are attributed to head-to-head VDF reverse addition. Furthermore, it was observed that the peaks located at –109.7 ppm (denoted $L_{109.7}$) and –110.2 (denoted $L_{110.2}$) are assigned to the difluoromethylene groups of the VDF unit adjacent to the HFP and TFVOBSC unit, respectively.

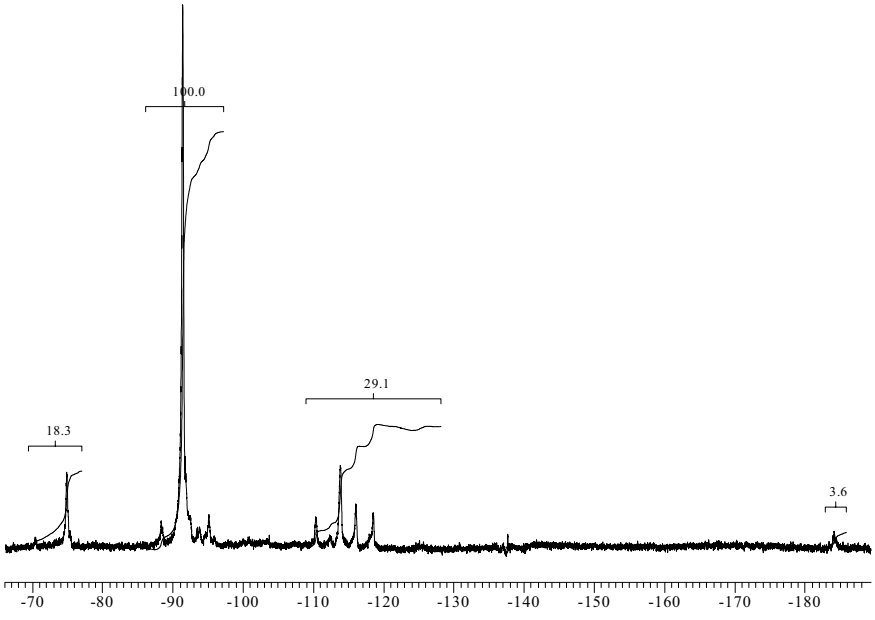


Fig. 2 ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerisation conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [HFP]$_0$ + [TFVOBSC]$_0$) = 0.9%, 134 °C, 6 hours and VDF / HFP / TFVOBSC initial molar ratio in the feed = 87.6 / 9.5 / 2.9 (exp. #7, Table 6).

Table 5 ^{19}F-NMR assignments of fluorinated groups in the poly(VDF-co-HFP-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Chemical shift / ppm	Structure	Integrals in Eq. (1)
–70.9	-$CH_2CF_2CF_2CF(\mathbf{CF_3})$-$CF_2$-$CH_2$-	$L_{-70.9}$
–74.9	-CH_2-CF_2-CF_2-$CF(\mathbf{CF_3})$-CH_2-CF_2-	$L_{-74.9}$
–91.3	-CF_2-CH_2-$\mathbf{CF_2}$-CH_2-CF_2-	$L_{-91.3}$
–95.1	(CH_2-CF_2)-(CF_2-CH_2)-(CH_2-C**F**2)-(CH_2-CF_2)	$L_{-95.1}$
–109.7	-$CH_2\mathbf{CF_2}CF_2CF(CF_3)$-	$L_{-109.7}$
–110.2	-(CH_2-$\mathbf{CF_2}$)-[CF_2-CF(O-Ph- SO_2Cl)]-	$L_{-110.2}$
–113.7	-(CH_2-CF_2)-($\mathbf{CF_2}$-CH_2)-(CF_2-CH_2)-	$L_{-113.7}$
–113.8	-(CH_2-CF_2)-[$\mathbf{CF_2}$-CF(O-Ph- SO_2Cl)]-	$L_{-113.8}$
–115.6	-(CH_2-CF_2)-(C**F**2-CH_2)-(CH_2-CF_2)-	$L_{-115.6}$
–118.7	-$CH_2CF_2\mathbf{CF_2}CF(CF_3)$-	$L_{-118.7}$
–136.3	-(CH_2-CF_2)-[CF_2-C**F**(O-Ph-SO_2Cl)]-	$L_{-136.3}$
–184.1	-$CH_2CF_2CF_2C\mathbf{F}(CF_3)$-	$L_{-184.1}$

In addition, the chemical shifts centred at –70.9 (denoted $L_{-70.9}$) and –74.9 (denoted $L_{-74.9}$) are assigned to the trifluoromethyl side group of HFP in the terpolymer, while those centred at –118.7 (denoted $L_{-118.7}$) and –184.1 (denoted $L_{-184.1}$) ppm are attributed to the difluoromethylene groups and to the tertiary fluorine in HFP, respectively. These expected chemical shifts confirmed previous work [55, 57].

Finally, the multiplet centred at –113.8 ppm (denoted $L_{-113.8}$) is attributed to the difluoromethylene of the TFVOBSC unit in the terpolymer: -($C\mathbf{F_2}$-CF(O-Ph-SO_2Cl))-. The peaks located in the –134.8 to –137.2 ppm region (denoted $L_{-136.3}$) are assigned to the tertiary fluorine atom in the CF group of TFVOBSC, as observed for the copolymers containing TFVOBB [55].

The determination of the molar fractions of VDF, HFP, and TFVOBSC units in the terpolymer was achieved from the ^{19}F NMR spectra and is given by the following equations (Eq. (1)):

$$\textbf{Mol \% of VDF in the terpolymer} = \frac{I_A}{I_A + I_B + I_C} \times 100 \quad (1a)$$

$$\textbf{Mol \% of HFP in the terpolymer} = \frac{I_B}{I_A + I_B + I_C} \times 100 \quad (1b)$$

$$\textbf{Mol \% of TFVOBSC in the terpolymer} = \frac{I_C}{I_A + I_B + I_C} \times 100 \quad (1c)$$

with:

$$I_A = \frac{I_{-91.3} + I_{-95.1} + I_{-109.8} + 2 \times I_{-115.7}}{2}$$

$$I_B = \frac{I_{-70.9} + I_{-74.9}}{3}$$

$$I_C = \frac{I_{-113.8} + I_{-115.7}}{2}$$

The percentage incorporation of each monomer in the terpolymers is listed in Table 6.

Terpolymerisation of TFVOBSC with VDF and PMVE

The ^{19}F NMR spectrum (Figure 3) of the poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) shows the presence of signals characteristic of the difluoromethylene groups of VDF addition and centred at about –91.1, –94.3, –113.1, and –115.8 ppm, denoted $L_{-91.1}$, $L_{-94.3}$, $L_{-113.1}$, and $L_{-115.8}$, respectively, as in the example above. In addition, the signals located in the –110.1 to –110.8 ppm range are assigned to the difluoromethylene groups of the VDF unit adjacent to the PMVE (denoted $L_{-110.1}$) and TFVOBSC (denoted $L_{-110.8}$) unit, respectively. Furthermore, the chemical shifts centred at –48.3 and –52.1ppm (denoted $L_{-48.3}$ and $L_{-52.1}$) are assigned to the trifluoromethyl side group, –120.8 ($L_{-120.8}$) and –122.2 ($L_{-122.2}$) ppm are characteristic of the difluoromethylene groups, and –125.4 ($L_{-125.4}$) and –145.3 ($L_{-145.3}$) ppm are assigned to the tertiary fluorine of PMVE. These expected chemical shifts are in good agreement with those noted for the copolymers of VDF and PMVE [55]. Finally, the peaks centred at –113.4 ($L_{-113.4}$) and –136.3 ($L_{-136.3}$) ppm are attributed to the difluoromethylene group and tertiary fluorine atom of the TFVOBSC unit in the terpolymer, respectively (Table 7).

Hence, the molar percentages of VDF, PMVE, and TFVOBSC in the terpolymers can be assessed from Eq. (2), and the results of incorporation are gathered in Table 6.

$$\textbf{Mol \% of VDF in the terpolymer} = \frac{I_D}{I_D + I_E + I_F} \times 100 \quad (2a)$$

$$\textbf{Mol \% of PMVE in the terpolymer} = \frac{I_E}{I_D + I_E + I_F} \times 100 \quad (2b)$$

Table 6 Determination of the Monomer/Terpolymer composition of VDF / Terolefin / TFVOBSC *vs.* the reaction conditions in the radical terpolymerisation of VDF, Terolefin (HFP or PMVE) with TFVOBSC. Terpolymerisation conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [Terolefin]$_0$ + [TFVOBSC]$_0$) = 0.9 mol%, 134 °C, 10 hours. Average molecular weights, M_n and M_w, assessed from SEC with poly(styrene) standards. T_g values were measured by DSC.

Exp. #	VDF / mol% in feed	HFP or PMVE / mol% in feed	TFVOBSC / mol% in feed	VDF / mol% in terpolymer	HFP or PMVE / mol% in terpolymer	TFVOBSC / mol% in terpolymer	Massic yields / %	T_g / °C	M_n (M_w) / g mol^{-1}	PDI
7	87.6	9.5 HFP	2.9	90.5	5.9 HFP	3.6	17	–27	14,200 (21,300)	1.5
8	84.9	10.3 HFP	4.8	85.6	7.7 HFP	6.7	12	–21	10,900 (17,500)	1.6
9	81.7	10.5 HFP	7.8	94.5	5.5 HFP	0	2	–30	6,200 (11,800)	1.9
10	72.7	22.7 PMVE	4.6	74.1	17.1 PMVE	8.8	20	–31	16,400 (24,500)	1.5
11	79.4	10.4 PMVE	10.2	95.5	4.5 PMVE	0	4	–35	5,800 (10,800)	1.9

T_g stands for glass transition temperature

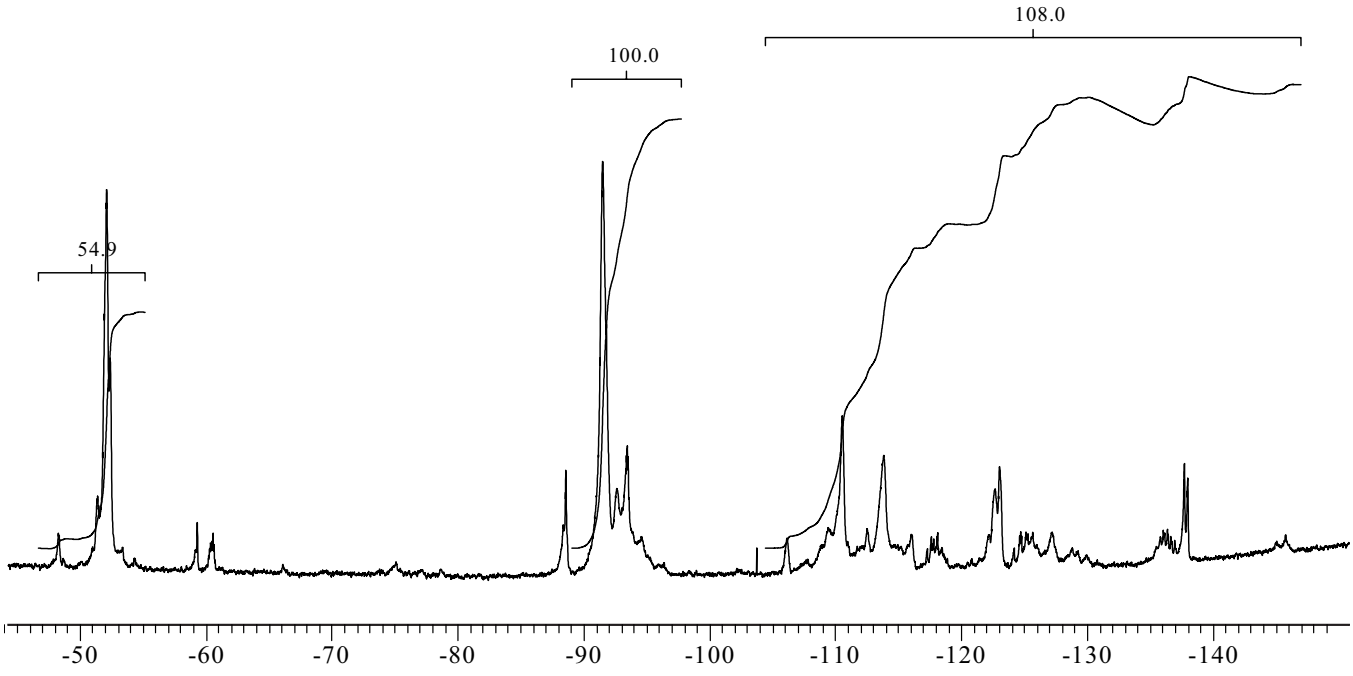


Fig. 3 ^{19}F NMR spectrum of poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) terpolymer, recorded in deuterated acetone. Terpolymerisation conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/([VDF]$_0$ + [PMVE]$_0$ + [TFVOBSC]$_0$) = 0.9%, 134 °C, 6 hours and VDF / PMVE / TFVOBSC initial molar ratio in the feed = 72.7 / 22.7 / 4.6 (exp. #10, Table 6).

$$\textbf{Mol \% of TFVOBSC in the terpolymer} = \frac{\mathbf{I_F}}{\mathbf{I_D}+\mathbf{I_E}+\mathbf{I_F}} \times \mathbf{100} \quad (2c)$$

with:

$$\mathbf{I_D} = \frac{\mathbf{I_{-91.1}}+\mathbf{I_{-94.3}}+\mathbf{I_{-110.1}}+\mathbf{I_{-110.8}}+\mathbf{2}\times\mathbf{I_{-115.8}}}{\mathbf{2}}$$

$$\mathbf{I_E} = \frac{\mathbf{I_{-48.3}}+\mathbf{I_{-52.1}}}{\mathbf{3}}$$

$$\mathbf{I_F} = \frac{\mathbf{I_{-113.4}}+\mathbf{I_{-115.8}}}{\mathbf{2}}$$

Firstly, as expected, the VDF content in the terpolymers is higher than that in the feed. In the VDF/HFP/TFVOBSC terpolymerisation, the results listed in Table 6 show that the presence of the TFVOBSC monomer reduced the mass yield.

Table 7 ^{19}F-NMR assignments of fluorinated groups in the poly(VDF-co-PMVE-co-TFVOBSC) terpolymers recorded in deuterated acetone.

Chemical shift / ppm	Structure	Integrals in Eq. (2)
–52.1	-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-	$L_{52.1}$
–91.1	-CF_2-CH_2-CF_2-CH_2-CF_2-	$L_{91.1}$
–94.3	-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-	$L_{94.3}$
–110.1	-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-	$L_{110.1}$
–110.8	-(CH_2-CF_2)-[CF_2-CF(O-Ph-SO_2Cl)]-	$L_{110.8}$
–113.1	-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-	$L_{113.1}$
–113.4	-(CH_2-CF_2)-[CF_2-CF(O-Ph- SO_2Cl)]-	$L_{113.4}$
–115.8	-CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-	$L_{115.8}$
–120.8	-CF_2-CF(OCF_3)-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-	$L_{120.8}$
–122.2	-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-	$L_{122.2}$
–125.2	-(CH_2-CF_2)-[CF_2-CF(O-Ph- SO_2Cl)]-	$L_{125.2}$
–137.8	-CH_2-CF_2-CF_2-CF(OCF_3)-CH_2-CF_2-	$L_{137.8}$

In the same experimental conditions, starting from TFVOBSC feed molar percentages of 3.4 and 4.8 mol% led to terpolymers containing 3.6 and 6.7 mol%, respectively. Furthermore, above a certain feed concentration of TFVOBSC (> 7 mol%), a drastic decrease in the overall yield was observed. In fact, the higher the level of TFVOBSC in the feed, the lower the mass yield.

Physico-Chemical Properties of Terpolymers Incorporating TFVOBSC

The SEC measurements were not quite accurate due to the lack of standards for poly(VDF-*co*-HFP). Nevertheless, these analyses showed that the value of the molecular weight of the terpolymer synthesised in experiment 7 (2.9 mol% in TFVOBSC feed) was higher than that of experiment 8 (6.1 mol% in TFVOBSC feed). From these results, several hypotheses can be formulated: (i) a strong interaction between the aromatic ring of TFVOBSC and macroradicals, (ii) the low reactivity of the ~TFVOBSC$^\bullet$ macroradical, (iii) the inhibition of the TFVOBSC monomer in the radical terpolymerisation (due to the possible transfer of the chlorine atom on the macroradical, which, as yet, was not observed in the TFVOBB radical terpolymerisation), and (iv) the possible cyclodimerisation of two ~TFVOBSC$^\bullet$ macroradicals. On the basis of these results, two experiments were achieved in the VDF/PMVE/TFVOBSC system. The structure and physico-chemical properties observed (see Table 6) confirmed the last hypothesis.

Furthermore, the glass transition temperatures (T_gs) were assessed by differential scanning calorimetry analyses. Poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers exhibit T_gs val-

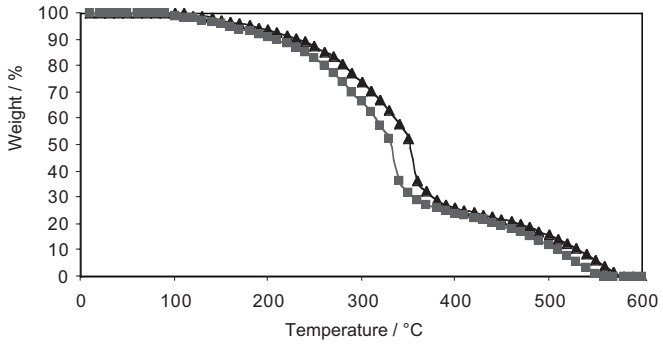


Fig. 4 TGA thermogram under air of poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers: %mol termonomers in the terpolymer 90.5 / 5.9 / 3.6 : VDF / HFP / TFVOBSC: ▲; %mol termonomers in the terpolymer 85.6 / 7.7 / 6.7 : VDF / HFP / TFVOBSC: ■.

ues ranging between –21 and –30 °C, as evidenced by fluoroelastomers. Experiment 9 exhibited the lowest T_g, and is due to the fact that the fluorinated macromolecules prepared incorporated a high level of VDF (T_{gPVDF} = –40 °C). Furthermore, the T_gs values increase with the molar percentage of TFVOBSC in the terpolymer, which confirmed a previous study [55]. The T_gs values for the VDF/PMVE/TFVOBSC system are very low and are characteristics of a (co)polymer incorporating perfluoromethyl vinyl ether [58].

In addition, the thermal analyses (Figure 4) of two poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers (experiments 7 and 8) indicate that the copolymer prepared in experiment 7 is more thermostable than that synthesised in experiment 8, which involved the highest mol% of TFVOBSC in the terpolymer. In fact, the higher the mol% of VDF in the terpolymer the higher its thermostability. Figure 4 illustrates TGA curves that show three steps: (i) the first corresponds to desulfoxidation and the elimination of the O-Ph group ($280 < T < 320$ °C), (ii) the second is attributed to dehydrofluorination ($340 < T < 460$ °C), and (iii) from $T > 500$ °C backbone degradation occurs.

Interestingly, comparing Tables 4 and 6, it can be seen that TFVOBSC is less reactive than TFVOBB in radical terpolymerisation with VDF/HFP or VDF/PMVE. These low incorporation percentages and the yields by mass could be explained by the effect of the aromatic ring, which could undergo side reactions with the growing macroradicals.

3.3 Preparation and Characterization of Proton Exchange Membranes

In this section, the basic hydrolysis of the poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and poly(VDF-*ter*-HFP-*ter*-TFVOBSC) terpolymers and the membrane formulation are discussed. Four main membrane characteristics are presented: (i) the ion exchange capacity, (ii) the thermal stability, (iii) the swelling rates, and (iv) the proton conductivity.

3.3.1 Synthesis of Ionomers Based on the Hydrolysis of Poly(VDF-ter-HFP-ter-TFVOBSC) and Poly(VDF-ter-HFP-ter-TFVOBSC) Terpolymers

The hydrolysis of the terpolymers, prepared above, was required to obtain sulfonic acid groups. TFVOBSC units were then successfully hydrolysed in the corresponding sulfonic acids, using potassium hydroxide in methanol. The overall yields were quantitative. In all cases, the ^{1}H and ^{19}F NMR analysis of the modified terpolymers indicated that the backbone of the macromolecules were not degraded by the basic treatment, especially the VDF units, known to be base sensitive (absence of signals in the 5–6.5 ppm range in ^{1}H NMR spectra). Furthermore, the IR spectra of the hydrolysed materials exhibited absorptions at 3,377 and 1,026 cm^{-1} due to the $S(O)(OH)_2$ stretching vibrations of the sulfonic acid groups. In fact, the absorption signals, centred at 1,381 cm^{-1}, characteristic of the O=S=O stretching vibration of the chlorosulfonyl groups were absent.

At the end of the study, the synthesis and characterization of a PEMFC based on hydrolysed terpolymers, arising from experiments 7, 8, and 10 (denoted ionomers A, B, and C, respectively), were investigated. Furthermore, the SEC chromatograms showed that the average molecular weights in number of the terpolymers, were slightly modified by the hydrolysis, and differential scanning calorimetry also demonstrated that the hydrolysis of sulfonyl chloride end groups enabled the T_g values of the terpolymers to be slightly increased (–15, –7, and –19 °C for ionomers A, B, and C, respectively). The TGA thermograms showed a similar thermostability to that observed for the non hydrolysed terpolymers prepared above, and also confirmed the presence of sulfonic acids by the presence of a degradation step at 330 °C characteristic of the desulfoxidation of sulfonic acids [59].

3.3.2 Fuel Cell Membranes from Ionomers A, B, and C: Synthesis and Characterization

Choice of Solvent for Casting Membranes

This part deals with the preparation of membranes from the ionomers synthesised above. Two main factors were studied in formulating the above fluoropolymers into membranes by casting: the nature and the amount of solvent and the ionomer / commercially available fluoropolymer ratio.

The first factor deals with the nature of the solvent. Solvents are used in membrane formulation to thin the film, to affect application, flow, and final uniformity of the membrane on the substrate. Despite this relatively simple statement, selecting solvents is, in reality, very complex. It is unusual for one solvent to successfully provide all the desirable properties. The solvent must be compatible with the ionomer and must have chemical properties that will not adversely affect the film or harm the substrate. Solvents for the formation of

fluoropolymer films can be divided into three different classes: (i) active solvents, which may totally dissolve or partially dissolve fluoro-ionomers at room temperature; (ii) latent or intermediate solvents that do not dissolve or swell materials at room temperature (working at elevated temperatures is necessary); and (iii) the non-solvent, which does not dissolve fluoropolymers up to their boiling points.

In this study, experiments were conducted using acetone, N-methylpyrrolidinone (NMP), dimethylacetamide (DMAC), and dimethyl formamide (DMF), which are active solvents.

The second factor is the ratio between the ionomer/commercially available fluoropolymer used in the membrane. A series of formulations were investigated with an ionomer/commercially available poly(VDF-co-HFP) copolymer, the mass ratio ranging between 95/5 and 10/90.

From this study, it has been shown that membranes from ionomers formulated in NMP, with a ratio by mass of 70/30 (ionomer/commercially poly(VDF-co-HFP)), had the best film forming properties (in terms of homogeneity, colour, and texture). Furthermore, DSC analysis of these membranes showed only one glass transition temperature, which is characteristic of a good miscibility between the ionomer and the commercial copolymer.

Properties of the Membranes

This section reports the characterization of the membranes prepared above and of incorporating ionomers A, B, and C. Various properties were investigated, such as the ionic exchange capacity (*IEC*), the thermal stability, the swelling rates, and the proton conductivity.

a) Ionic exchange capacity

The *IEC*s (mEq H^+ / g) of the membranes, representing the number of protonic groups for 1 g of terpolymer, were determined. The required molar ratio of each termonomer (VDF, HFP or PMVE, and TFVOBSA) was calculated from ^{19}F NMR (see Eqs. (1) and (2)). Hence, the ionic exchange capacity can be assessed from Eq. (3), and the results are gathered in Table 8 (knowing that the molecular weights of VDF, HFP, PMVE, and TFVOBSA are 64, 150, 166, and 254 g mol^{-1}, respectively).

$$\mathbf{x}\ (\textbf{from scheme 2}) = \frac{\textbf{Mol \% of VDF in the terpolymer}}{\textbf{100}} \quad \text{(see Eq. (1a) or (2a))}$$

$$\mathbf{y}\ (\textbf{from scheme 2}) = \frac{\textbf{Mol \% of HFP or PMVE in the terpolymer}}{\textbf{100}} \quad \text{(see Eq. (1b) (HFP) or (2b) (PMVE))}$$

$$\mathbf{z}\ (\textbf{from scheme 2}) = \frac{\textbf{Mol \% of TFVOBSA in the terpolymer}}{\textbf{100}} \quad \text{(see Eq. (1c) or (2c))}$$

For a poly(VDF-*ter*-HFP-*ter*-TFVOBSA) terpolymer:

$$\mathbf{IEC}\ (\mathbf{Eq/g}) = \frac{\mathbf{1}}{\frac{\mathbf{x}}{\mathbf{z}}\times\mathbf{64}+\frac{\mathbf{y}}{\mathbf{z}}\times\mathbf{150}+\mathbf{254}} \tag{3a}$$

For a poly(VDF-*ter*-PMVE-*ter*-TFVOBSA) terpolymer:

$$\mathbf{IEC}\ (\mathbf{Eq/g}) = \frac{\mathbf{1}}{\frac{\mathbf{x}}{\mathbf{z}}\times\mathbf{64}+\frac{\mathbf{y}}{\mathbf{z}}\times\mathbf{166}+\mathbf{254}} \tag{3b}$$

The *IEC* results (Table 8) ranged between 0.4 and 0.6 mEq H^+ g^{-1}, and as expected, the higher the mol percentage of the sulfonic function in the terpolymer, the higher the *IEC*. However, the values are lower than that for Nafion® 117 (0.9 mEq H^+ g^{-1}) [59].

b) Thermal stability

Furthermore, the thermal properties (T_gs and T_{dec}) of these membranes were studied. Surprisingly, the T_g values were still negative in spite of the presence of sulfonic acids (ranging between –25 and –14 °C). This can be explained by the fact that the membranes were co-formulated with a very low T_g commercially available poly(VDF-co-HFP) fluoropolymer. In fact, the resultant T_g was in the low temperature range. Furthermore, the characterization of the decomposition temperature (*Td*), by TGA under air, showed that the membranes, prepared from ionomers A, B, and C, exhibited a good thermal stability (up to 300 °C, in all cases). Interestingly, thermograms indicated four different thermal degradation steps: the first was attributed to the loss of water (T < 120 °C) because of the good affinity of these terpolymers containing sulfonic acid and water, the second was observed in the 300 °C range and corresponded to desulfoxidation, the third was characteristic of the dehydrofluorination (400 °C), and the last step was in the 500 °C range characteristic of the degradation of the backbone.

Table 8 Membrane characteristics prepared from ionomers A, B, and C (room temperature, 20 %RH).

Membranes based on ionomer	VDF / mol% in ionomer	HFP or PMVE / mol% in ionomer	TFVOBSA / mol% in ionomer	IEC / mEq H^+ g^{-1}	EW / g mol^{-1}	Proton conductivity σ / mS cm^{-1}	Swelling rates / %	T_g / °C	T_d / °C at 10% under air
A	90.5	5.9 HFP	3.6	0.4	2500	0.037	44	–21	238
B	85.6	7.7 HFP	6.7	0.5	2000	0.059	57	–14	231
C	74.1	17.1 PMVE	8.8	0.6	1660	0.082	88	–25	225

T_g stands for glass transition temperature, T_d stands for decomposition temperature

c) Swelling rates (or water uptake)

In addition, the swelling rates (or water uptake) of the ionomer membranes were also calculated (see Eq. (4)) after immersing the membranes in water for 16 hours. The values of the swelling rates, listed in Table 8, ranged between 40 and 90%, and confirmed the presence of sulfonic acids in the material. As expected, the higher the *IEC*, the higher the calculated swelling rate.

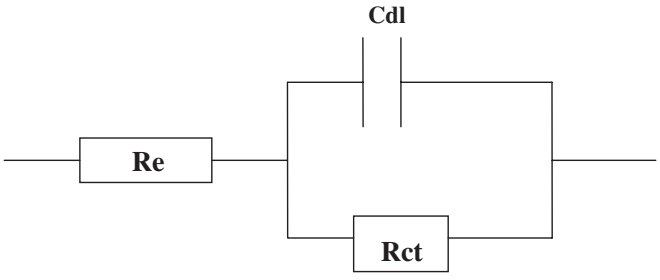
$$\textbf{Swelling rates}\ (\%) = \frac{\mathbf{M_1 - M_0}}{\mathbf{M_0}} \times \mathbf{100} \qquad (4)$$

M_0: weight of the membrane dried for 16 hours at 60 °C

M_1: weight of the membrane after immersing in water for 24 hours

d) Proton conductivity

The next goal was to assess the corresponding proton conductivity values. An Electrode / Membrane / Electrode can be represented by an electrical circuit as follows:



Re: electrolyte resistance
Rct: charge transfer resistance
Cdl: double layer capacity

The complex impedance [60–62], *Z*, of the electrical circuit is given by the following equations (Eq. (5)):

$Z = Z' + jZ''$ (Z': real part; Z'': imaginary part)

$$\mathbf{Z} = \frac{\mathbf{R_e + R_{ct}}}{\mathbf{1 + jR_{ct}C_{dl}}\varpi} \qquad (5)$$

The impedance results are illustrated by plots of the imaginary part of the membrane impedance, Z'', *vs.* the real part Z' (Nyquist diagram) [62]. The value of *Re* was measured when $Z'' = 0$.

The values of the membrane resistance deduced from the Nyquist diagram enabled the calculation of the proton conductivity of the membrane, σ (S cm^{-1}), from the relationship:

$$\sigma = \frac{\mathbf{1}}{\mathbf{Re}} \times \frac{\mathbf{e}}{\mathbf{S}} \qquad (6)$$

Re: electrolyte resistance
e: thickness
S: electrode / membrane – surface

The values of σ, assembled in Table 8, and ranging between 0.01 and 0.1 mS cm^{-1}, increase with increases in the *IEC* values. Although the conductivities are low, these encouraging values need to be optimised (compared to Nafion® (DuPont) (≈ 100 mS cm^{-1})). This may be possible by increasing the *IEC* (i.e., the percentage incorporation of TFVOBSC in the ionomers and increasing the ionomer content in the fluoropolymer blend) or by making polymers with higher molecular weights than those prepared above. In effect, a PEMFC without poly(VDF-*co*-HFP) is possible.

4 Conclusion

The goal of this study was to prepare novel aromatic PEMFC [47] membranes incorporating fluoroalkenes such as VDF, HFP, and PMVE with functional aromatic perfluoro vinyl ether. First, TFVOBSC was synthesised with a 72% overall yield, via a new synthetic route using reactants, which were not used in previous studies [13, 52]. This monomer exhibits a sulfonyl chloride function, quantitatively hydrolysed to the corresponding sulfonic acid. Novel fluorinated aromatic copolymers, bearing sulfonic acid side groups, were obtained using optimised conditions of terpolymerisation in solution. It was shown that the incorporation of TFVOBSC was not as good as that of the brominated homologue (TFVOBB). The pKa of the sulfonic acids was lowered using an aromatic monomer. The poor reactivity of TFVOBSC in radical terpolymerisation is still not well understood and further experiments are required. It is possible that the aromatic ring may have reacted with macroradicals, inducing low rates of incorporation of the functional monomers. Poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and Poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) were hydrolysed by treatment with base, without changing the content of fluoromonomer in the terpolymers. Moreover, casting was used to formulate membranes with a commercially available fluoropolymer, which led to good film-forming properties. The *IEC* values ranged between 0.4 and 0.6 mEq g^{-1}, the corresponding proton conductivities and swelling rates were characterized and the thermal properties studied, indicating that the materials incorporated sulfonic acids, even though the conductivity values were still low. Nevertheless, the properties of these membranes require improvement if they are to be used in PEMCF applications. In order to improve the electrochemical properties, these novel membranes could be formulated without any commercially available fluoropolymer. It would be necessary to prepare higher molecular weight terpolymers, obtained through other polymerisation processes (emulsion, suspension, supercritical CO_2). Nevertheless, these results seem encouraging in the search for new materials for the PEMFC.

Acknowledgements

The authors acknowledge the Centre National de la Recherche Scientifique, the French consortium GDR PACEM 2479, and the Commissariat à l'Energie Atomique for PhD financial support (to R.S.). The authors thank Solvay Solexis S.A. (Tavaux, France and Brussels, Belgium) for their

generous donation of vinylidene fluoride, hexafluoropropene, and 1,1,1,3,3-pentafluorobutane.

References

[1] O. Savadogo, *J. New Mat. Electrochem. Systems* **1998**, *1*, 47.
[2] K. Prater, *J. Power Sources* **1990**, *29*, 239.
[3] S. Faure, R. Mercier, P. Aldebert, M. Pineri, B. Sillion, *FR Patent 9,605,707*, **1996**.
[4] R. Nolte, K. Ledjeff, M. Bauer, R. Mulhaupt, *J. Membrane Sci.* **1993**, *83*, 211.
[5] F. Helmer-Metzman, F. Osan, A. Schneller, H. Ritter, K. Ledjeff, R. Nolte, R. Thorwirth, *European Patent 574,791,A2*, **1993**.
[6] B. Adams, E. Holmes, *J. Soc. Chem. Ind.* **1935**, *54*, 17.
[7] R. B. Hodgdon, A. S. Hay, *US Patent 3,528,858*, **1970**.
[8] I. Xiao, I. Cabasso, *Polym. Mater. Sci. Eng. (Am. Chem. Soc., Div. PMSE)* **1993**, *68*, 55.
[9] J. Roziere, D. Jones, *J. Annu. Rev. Mater. Res.* **2003**, *33*, 503.
[10] J. Roziere, D. Jones, *Handbook of Fuel Cells- Fundamentals, Technology and Applications*, *Vol. 3* (Eds. W. Vielstich, H. A. Gasteiger, A. Lamm), John Wiley & Sons Ltd., Chichester, England, **2003**, pp. 447.
[11] B. Ameduri, B. Boutevin, *Well-Architectured Fluoropolymers: Synthesis, Properties and Applications*, Elsevier, Amsterdam, **2004**.
[12] W. G. Grot, C. J. Molnar, P. R. Resnick, *AU 544027*, assigned to DuPont de Nemours, **1985**.
[13] D. D. DesMarteau, C. W. Martin, L. A. Ford, X. Xie, *US Patent 6,268,532*, assigned to 3M Innovative Properties company, **2001**.
[14] C. W. Martin, P. J. Nandapurkar, S. S. Katti in *Polymeric Materials Encyclopaedia*, CRC Press Inc., Boca Raton, FL, **1995**.
[15] A. E. Feiring, E. R. Wonchoba, *J. Fluorine Chem.* **2000**, *105*, 129.
[16] A. E. Feiring, S. K. Choi, M. Doyle, E. R. Wonchoba, *Macromolecules* **2000**, *33*, 9262.
[17] Z.-Y. Yang, L. Wang, N. E. Drysdale, M. Doyle, *Macromolecules* **2003**, *36 (22)*, 8205.
[18] C. Stone, A. E. Steck, R. D. Lousenberg, *US 5,602,185*, assigned to Ballard Power Systems Inc., **1997**.
[19] C. Stone, T. S. Daynard, L. Q. Hu, C. Mah, A. E. Steck, *J. New Mater. Electrochem. Syst.* **2000**, *3 (1)*, 43.
[20] V. Arcella, A. Ghielmi, G. Tommasi, *Ann. N.Y. Acad. Sci.* **2003**, *984*, 226.
[21] M. Doyle, G. Rajendran in *Handbook of Fuel Cells- Fundamentals, Technology and Applications*, *Vol. 3* (Eds. W. Vielstich, H. A. Gasteiger, A. Lamm), John Wiley & Sons Ltd., Chichester, England, **2003**, pp. 351.
[22] Q. Li, R. He, J. Oluf Jensen, N. J. Bjerrum, *Chem. Mater.* **2003**, *15*, 4896.
[23] H. H. Gibbs, V. W. Vienna, R. N. Griffin, *US Patent 3,041,317*, assigned to Du Pont de Nemours, **1962**.
[24] R. E. Banks, G. M. Haslam, R. N. Haszeldine, A. J. Peppin, *J. Chem. Soc.* **1966**, *C*, 1171.
[25] W. Navarrini, D. D. DesMarteau, *US Patent 5,103,049*, assigned to Ausimont S.p.A. **1992**.
[26] R. Beckerbauer, *US Patent 3,397,191*, assigned to DuPont de Nemours, **1968**.
[27] B. R. Ezzel, W. P. Carl, *US Patent 4,940,525*, assigned to Dow Chemical Co., **1990**.
[28] D. A. Babb, K. S. Clement, B. R. Ezzel, *US Patent 5,159,038*, assigned to Dow Chemical Co., **1992**.
[29] C. G. Krespan, D. C. England, *J. Amer. Chem. Soc.* **1981**, *103*, 5598.
[30] G. Kostov, S. Kotov, G. D. Ivanov, D. Todorova, *J. Appl. Polym. Sc.* **1993**, *47*, 735.
[31] D. D. DesMarteau, *US Patent 5,463,005*, assigned to Gas Research Institute, **1995**.
[32] B. R. Ezzel, W. P. Carl, *Eu. Patent EP 289,869*, assigned to Dow Chemical Co, **1988**.
[33] D. J. Connolly, W. F. Gresham, *US Patent 3,282,875*, assigned to DuPont, **1966**.
[34] B. Ameduri, M. Armand, M. Boucher, A. Manseri, *WO 01/49757*, assigned to Hydro-Quebec, **2001**.
[35] B. Ameduri, B. Boutevin, M. Armand, M. Boucher, *WO 01/49758*, assigned to Hydro-Quebec, **2001**.
[36] G. Bauduin, B. Ameduri, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 3109.
[37] A. E. Feiring, C. M. Doyle, M. G. Roelofs, W. B. Farnham, P. G. Bekiaran, H. A. K. Blair, *Patent PCT WO 99/45048*, assigned to Du Pont, **1999**.
[38] P. G. Bekiarian, C. M. Doyle, W. B. Farnham, A. E. Feiring, P. Morken, M. G. Roelofs, W. J. Marshall, *J. Fluorine Chem.* **2004**, *125*, 1187.
[39] X. Xue, *PhD dissertation*, Clemson University, **1996**.
[40] I. Cabasso, J. Jagur-Grodzinski, D. Vofsi, *US Patent 4,073,754*, **1978**.
[41] S. V. Kotov, S. D. Pedersen, W. Qiu, Z. M. Qiu, D. J. Burton, *J. Fluorine Chem.* **1996**, *82*, 13.
[42] H. Ukihashi, M. Yamabe, H. Mikaye, *Progr. Polym. Sci.* **1986**, *12*, 229.
[43] W. R. Dolbier Jr, M. D. Rong, H. Barberger, B. E. Koroniak, B. E. Smart, *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 219.
[44] J. Mohtasham, D. G. Cox, D. J. Burton, G. L. Gard, *J. Fluorine Chem.* **1989**, *42*, 119.
[45] R. Souzy, B. Ameduri, B. Boutevin, *Prog. Polym. Sci.* **2004**, *29 (2)*, 75.
[46] P. L. Heinze, D. J. Burton, *J. Org. Chem.* **1988**, *53 (12)*, 2714.
[47] D. Marsacq, M. Pineri, B. Ameduri, R. Souzy, *FR Patent 2,843,398*, assigned to CEA, **2004**.
[48] R. Souzy, B. Ameduri, B. Boutevin, D. Virieux, *J. Fluorine Chem.* **2004**, *125*, 1317.
[49] D. A. Babb, N. G. Rondan, D. W. Smith Jr., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36 (1)*, 721.

[50] D. W. Smith Jr., D. A. Babb, *Macromolecules* **1996**, *29*, 852.
[51] S. C. Ligon Jr., M. Krawieck, A. Kitaygorodskiy, D. W. Smith Jr., *J. Fluorine Chem.* **2003**, *123 (1)*, 139.
[52] L. A. Ford, D. W. Smith Jr., D. D. DesMarteau, *Polym. Mater. Sci. Eng. (Am. Chem. Soc., Div. PMSE)* **2000**, *83*, 10.
[53] J. Ji, S. Narayan-Sarathy, R. H. Neilson, J. D. Oxley, D. A. Babb, N. G. Rondan, D. W. Smith Jr., *Organometallics* **1998**, *17 (5)*, 783.
[54] S. Narayan-Sarathy, R. H. Neilson, D. W. Smith Jr., *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1998**, *39 (1)*, 609.
[55] R. Souzy, B. Ameduri, B. Boutevin, *J. Polym. Sci. Part A Polym. Chem* **2004**, *42*, 5077.
[56] J. Guiot, B. Ameduri, B. Boutevin, *Macromolecules* **2002**, *35*, 8694.
[57] M. P. Gelin, B. Ameduri, *J. Polym. Sci. Part A, Polym. Chem* **2003**, *41*, 160.
[58] B. Ameduri, B. Boutevin, G. Kostov, *Prog. Polym. Sci.* **2001**, *26*, 105.
[59] A. Balland-Longeau, F. Pereira, P. Capron, R. Mercier, *Fr Patent 0,210,008*, assigned to CEA, **2002**.
[60] V. Subrahmanian, N. Lakshminarayanaiah, *J. Phys. Chem.* **1968**, *72*, 4314.
[61] C. Gavach, G. Pomboutzoglou, M. Nedyalkov, G. Pourcelly, *J. Membrane Sci.* **1989**, *45*, 37.
[62] G. Pourcelly, P. Sistat, A. Chapotot, C. Gavach, V. Nikonenko, *J. Membrane Sci.* **1996**, *110*, 69.