



# Functional fluoropolymers for fuel cell membranes

Renaud Souzy, Bruno Ameduri\*

Laboratory of Macromolecular Chemistry, UMR (CNRS) 5076, Ecole Nationale Supérieure de Chimie de Montpellier,  
8 Rue Ecole Normale, 34296 Montpellier Cedex 5, France

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## Abstract

Various routes to synthesize functional fluoropolymers used in membranes for fuel cell applications are presented. They can be separated into three main families of alternatives. The first concerns the direct radical copolymerization of fluoroalkenes with fluorinated functional monomers. The latter are either fluorinated vinyl ethers,  $\alpha,\beta,\beta$ -trifluorostyrenes or trifluorovinyl oxy aromatic monomers bearing sulfonic or phosphonic acids. The resulting membranes are well-known: Nafion<sup>®</sup>, Flemion<sup>®</sup>, Hyflon<sup>®</sup>, Dow<sup>®</sup>, Aciplex<sup>®</sup> or BAM3G<sup>®</sup>. The second route deals with the chemical modification of hydrogenated polymers (e.g. polyparaphenylenes) with fluorinated sulfonic acid synthons. The third alternative concerns the synthesis of FP-g-poly(M) graft copolymers where FP and M stand for fluoropolymer and monomer, respectively, obtained by activation (e.g. irradiation arising from electrons,  $\gamma$ -rays, or ozone) of FP polymers followed by grafting of M monomers. The most used M monomer is styrene, and a further step of sulfonation on FP-g-PS leads to FP-g-PS sulfonic acid graft copolymers. Other processes such as multilayer membranes or the introduction of fillers to prepare organic/inorganic or 'composite membranes' are reported. The electrochemical properties (ionic exchange capacity, conductivity, swelling-rate or water uptake) of membranes produced from fluoropolymers bearing sulfonic, carboxylic or phosphonic acid are presented and discussed.

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**Keywords:** Fluoropolymers; Perfluorinated sulfonic acid membrane; Direct methanol fuel cell; Copolymerization; Chemical modification; Conductivity; Membranes; PEMFC

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\* Corresponding author. Tel.: +33 4 6714 4368; fax: +33 4 6714 7220.

E-mail address: [bruno.ameduri@enscm.fr](mailto:bruno.ameduri@enscm.fr) (B. Ameduri).

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## 1. Introduction

Nowadays, much of the production of energy is mainly linked to nuclear generation or the combustion of fossil fuels. These sources are, however, not environmental friendly, since they produce nuclear wastes or carbon monoxide and carbon dioxide. Among cleaner sources of energy arising, for instance, from wind, water, sun and others, a growing interest comes from fuel cells. This process utilizes an electrochemical device, which efficiently converts the chemical energy of a fuel (hydrogen, methanol, ethanol, ethylene glycol, natural gas, etc.) in a reaction with oxygen (from air for example) into electricity, heat and water. It operates like batteries, and is similar in characteristics and components. Several types of fuel cells exist [1–4], normally classified according to the type of electrolyte used, e.g. Solid Oxide Fuel Cell (SOFC), Molten Carbonate Fuel Cell (MCFC), Phosphoric Acid Fuel Cells (PAFC) and the Proton Exchangeable Membrane Fuel Cell (PEMFC). The operating temperature of the fuel cells is connected to the electrolyte used [1].

The development of PEMFC, also called solid polymer fuel cell, has been strongly related to improvements in performance of the polymer electrolyte membrane. The use of an ion-exchange membrane as electrolyte was first suggested by

Grubb in 1957, and the first fuel cell system based on a sulfonated polystyrene electrolyte was developed by General Electrical in the 1960s for NASA for application as an on-board power source in the Gemini space program. It was successfully developed using a great amount of noble metal loading per cm<sup>2</sup> of electrode, although the polystyrene sulfonate membrane was not electrochemically stable and the cell exhibited limited power density (less than 50 mW/cm<sup>2</sup>).

Fuel cells [1–4] have been involved in the production of stationary electrical energy and as energy sources in fields such as transportation, space, telecommunications, micro combined heat and power (CHP) generators or portable electronic systems (portables, cellular phones), domotics (coproduction of electrical energy and heat, auxiliaries of power (APU) for automobiles (board-computer, electrical commands, air conditioning), and computer security. For application in these systems, it is essential that fuel cells exhibit similar performance and comparable cost to thermal engines.

Basically, a polymer electrolyte membrane fuel cell converts hydrogen and oxygen electrochemically into electrical power, heat and water. The electrochemical reaction takes place in the MEA. It typically consists of an ion-conducting polymer membrane sandwiched between the anode and cathode, each

### Nomenclature

AAc	acrylic acid	PFCB	perfluorocyclobutane
AEM	anion-exchange membrane	PMVE	perfluoromethylvinyl ether
AIBN	azobisisobutyronitrile	PSEPVE	perfluorosulfonyl fluoride ethoxy propyl vinyl ether [or perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride]
CTFE	chlorotrifluoroethylene	PSSA	poly(styrene sulfonic acid)
DMF	dimethylformamide	PTFE	polytetrafluoroethylene
DVB	divinyl benzene	PVDF	polyvinylidene fluoride
$DP_n$	number average degree of polymerization	RT	room temperature
DSC	differential scanning calorimetry	S	styrene
DMFC	direct methanol fuel cell	SFT	swollen film thickness
d.o.g.	degree of grafting	TFE	tetrafluoroethylene
ETFE	poly(ethylene-alt-tetrafluoroethylene) copolymer	TFS	trifluorostyrene
FEP	poly(tetrafluoroethylene-co-hexafluoropropylene) copolymer	$T_d$	decomposition temperature
HFP	hexafluoropropylene	$T_g$	glass transition temperature
HFPO	hexafluoropropylene oxide	TGA	thermal gravimetric analysis
IEC	ion-exchange membrane	TFVOB	$\alpha,\beta,\beta$ -trifluoroethenyl oxy benzene
$M_n$	number average molecular weight	VBC	vinyl benzyl chloride (or chloromethyl styrene)
$M_w$	weight average molecular weight	VDF	vinylidene fluoride
PEMFC	proton exchange membrane fuel cell (or polymer electrolyte membrane fuel cell)	UV	ultra violet
PFA	poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) copolymer	4-VP	4-vinyl pyridine

containing a macroporous diffusion backing and an active catalyst layer.

In fact, hydrogen is split into protons and electrons at the anode (negative electrode). The proton exchange membrane placed in the centre allows protons to pass from the anode to the cathode (positive electrode), while the electrons induce a current through an external circuit to the cathode. At the cathode, the electrons recombine with the protons that have crossed the membrane and with oxygen from the air, according to the reactions shown in Fig. 1. The rate at which that reaction happens is proportional to the area of the electrode. The performance is thus often quoted in terms of current density (current per  $\text{cm}^2$ ).

As long as fuel is supplied to the cell along with an oxidant (typically air), the fuel cell continues to produce electrical energy and heat. The only by-product when fueled with hydrogen is water. A single PEM cell in operation, delivers a voltage lower than 1 V. Therefore, to obtain sufficiently high voltage levels for a specific

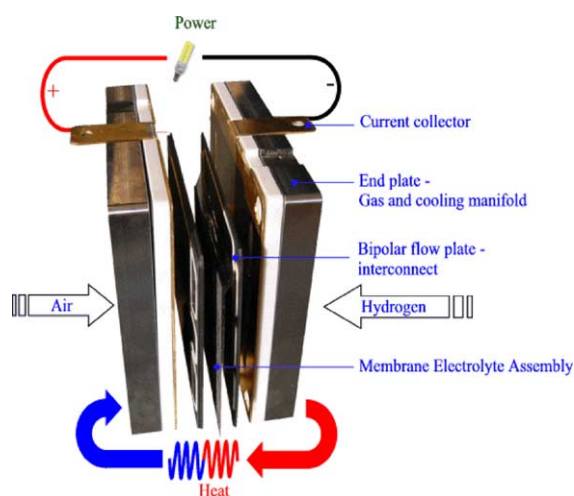


Fig. 1. Schematic representation of a fuel cell.

application, the fuel cells are stacked in series, in which bipolar flow-plates supply fuels to the MEA of each cell. The flow-plates also serve as electrical interconnects between the cells in the stack. The role of a polymer electrolyte is to provide ionic conductivity, to prevent the flow of electrons, to act as a barrier to the reactants, and to maintain chemical and mechanical stabilities. In the operating fuel cell, any gas or fuel permeation through the membrane, often quoted as fuel crossover, is equivalent to an internal current (short) reducing the cell voltage. A reasonable mechanical strength and moderate dimensional changes are required when the electrolyte membrane is used to make the MEA, incorporating the MEA into a stack and during fuel cell operation.

Many investigations have been carried out on fuel cells in term of various characteristics of the PEMFC, including:

1. the synthesis of membranes (the objective is to develop membranes with low cost and endowed with good performances), and to enhance properties such as conductivity and both thermal and mechanical stabilities;
2. the choice of the fuel and its storage, e.g. the use of methanol derived from biomass or other renewable energy sources in Direct Methanol Fuel Cells (DMFC) technology gives the same advantages as PEMFC technology, such as high energy efficiency and low or zero emission, but the low permeability to methanol (or methanol crossover) has to be reduced or suppressed;
3. reduction of the overvoltage of involved electrochemical reactions, such as the oxidation of hydrogen (or other fuels including methanol or ethanol), and the reduction of oxygen;
4. optimization the transportation of reactants and the evacuation of heat at the membrane–electrode-assembly (MEA) system regarded as the heart of the fuel cell;
5. the electrodes, catalysts (or electrocatalysis);
6. the diffusion layer and active layer;
7. process engineering;
8. tests in the heart of the cell;
9. bipolar plates;
10. stack.

Many investigations have been developed on those items, and the number of patents and publications has greatly increased since 2000.

The objective of this review concerns the synthesis and the properties of organic polymers involved in the elaboration of a membrane for fuel cell application. PEMFC membranes can be prepared from both aliphatic and aromatic polymers, but severe requirements are imposed on membranes: they must show good thermo-stability (up to 80–100 °C for 5000 h); high ionic conductivities, mainly under high-humidity conditions; good mechanical strength; good chemical stability (especially the oxidative stability); and low methanol crossover. After a brief summary on various hydrogenated polymers, this review focuses on the strategies of synthesis and uses of fluorinated functional polymers acting as fuel cell membranes, and their properties.

## 2. PEMFC based on non-fluorinated polymers [1–4]

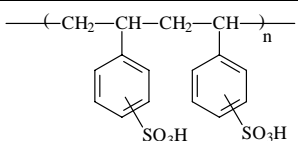
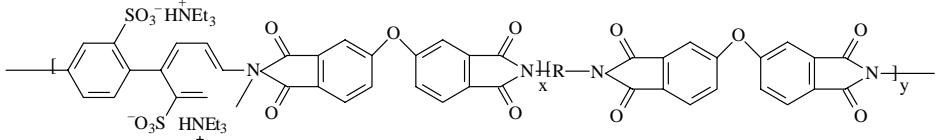
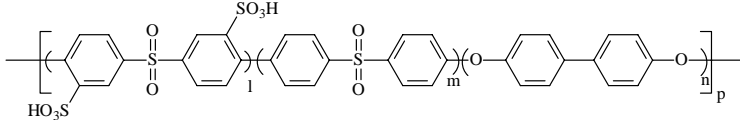
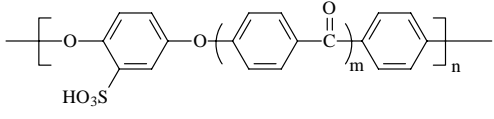
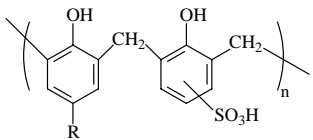
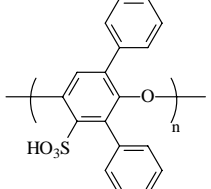
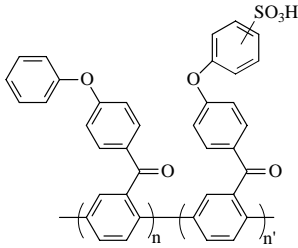
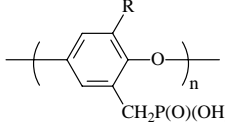
Many hydrogenated polymers [5–26] have already been used as PEMFC; a non-exhaustive list is presented in Table 1, although their performances in fuel cells have already been reviewed [5–11].

The aromatic or heterocyclic polymers can be sulfonated polystyrenes (crosslinked or not) [1e,12–14], sulfonated polyimides (PI) [1e,15], sulfonated poly(aryl ether sulfone)s [1e,16,17], sulfonated poly(aryl ether ketone)s [1e,18], sulfonated phenol formol resins [19], sulfonated poly(phenylene oxide)s [20,21], sulfonated poly(*p*-phenoxybenzoyl-1,4-phenylene)s [22,23], phosphonic poly(phenylene oxide)s [24], sulfonated silicates [25], sulfonated poly(benzimidazole)s [25], sulfonated organic–inorganic hybrids [26] and polyphosphazenes [27]. Nevertheless, most of these non-fluorinated ionomer membranes, although of attractive price, are characterized by a poor resistance to oxidation and to thermal degradation.

## 3. Synthesis of fluoropolymers for PEMFC membranes

In contrast to hydrogenated polymers, fluorinated polymers, regarded as high value-added materials, are potential candidates due to their outstanding

Table 1  
Non-fluorinated polymers used in PEMFC

Polymers	Structure	Reference
Sulfonated poly-styrenes		[12–14]
Sulfonated poly-imides		[15]
Sulfonated poly(aryl ether sulfones)		[4,16,17]
Sulfonated poly(aryl ether ketones) SPEEK		[18]
Sulfonated phenol formol resins		[19]
Sulfonated poly(phenylene oxide)		[20,21]
Sulfonated poly(p-phenoxy-benzoyl-1,4-phenylene)		[22,23]
Phosphonic poly(phenylene oxide)		[24]

R : CH<sub>3</sub> or CH<sub>2</sub>P(O)(OH)<sub>2</sub>

(continued on next page)

Table 1 (continued)

Polymers	Structure	Reference
Sulfonated poly(benzimidazole)		[25]
Sulfonated silicates		[3b,26]
Polyphosphazenes		[27]

properties which opens various applications [28–31]. The small size and the high electronegativity of the fluorine atom confers a strong C–F bond and a low polarizability. Such polymers show low intramolecular and intermolecular interactions, which leads to low cohesive energy, and therefore, to low surface energy. They also exhibit high thermostability and chemical inertness, low refractive index and friction coefficient, good hydrophobicity and lipophobicity, valuable electrical properties, and low relative permittivity. In addition, they are non-sticky and resistant to UV, to ageing and to concentrated mineral acids and alkalis.

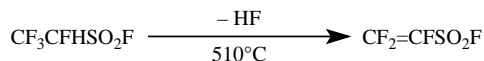
The great value of the unique characteristics of fluorinated polymers in the development of modern industries has insured an increasing technological interest since the discovery of the first fluoropolymer, poly(chlorotrifluoroethylene) in 1934. Hence, their fields of applications are numerous: paints and coatings [32] (for metals [33], wood [34], leather [35], stone [36], optical fibers [37], antifouling [38]), textile finishings [39], novel elastomers [31], high performance resins, membranes [40], surfactants and fire fighting agents [41], functional materials (for photoresists or microlithography [42], optical fibers, and conductive polymers [43]), biomaterials, and thermostable polymers for aerospace [27–31]. Moreover, their thermostability, chemical inertness and the enhanced acidity of sulfonic acid group in  $-\text{CF}_2\text{SO}_3\text{H}$ , various fluorinated polymers have been utilized in

chloroalkali process and as proton exchange membranes for fuel cell applications.

This review focuses on the syntheses of fluoropolymers useful as PEMFC, and is divided into two major parts, each presenting a synthetic method and the properties of the resulting fluoropolymers for membranes applications: the first concerns the direct copolymerization of fluorinated functional (especially acid function) monomers with commercially available monomers (and also fluoroalkenes). The second deals with chemical modification of oligomers or polymers. This modification may be carried out by direct reaction of an oligomeric species onto a reactive group, or through irradiation of fluoropolymers, followed by grafting. Other alternatives have also been mentioned, such as the reinforcement of polymeric membranes, the composites and the preparation of hybrid membranes. The two principal strategies developed for the synthesis of functional fluoropolymers for fuel cell membranes are discussed in the following sections.

### 3.1. Fluorocopolymers from direct copolymerization of functional fluorinated monomers with fluoroalkenes

Fluorinated (co)polymers bearing acidic side groups are particularly interesting materials for the preparation of membranes because of their efficient protonic conduction and their chemical, thermal stabilities and their resistance to ageing [30,40,



Scheme 1. Synthesis of trifluorovinyl-1-sulfonyl fluoride [46].

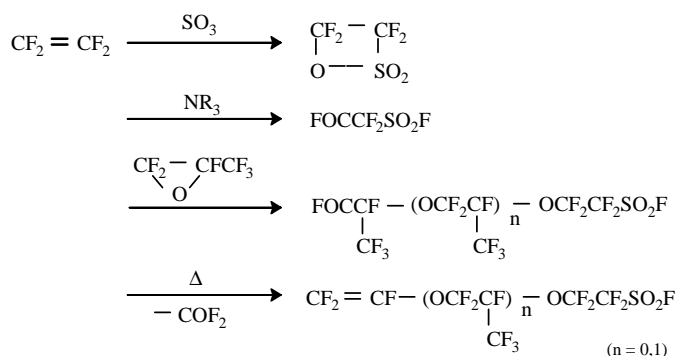
44,45]. Three main groups are distinguished by the acidic function: sulfonic, carboxylic or phosphonic. The syntheses of the corresponding monomers are presented, for aliphatic and aromatic monomers, in that order.

### 3.1.1. From fluorinated aliphatic monomers

#### 3.1.1.1. Strategies of synthesis of functional fluorinated aliphatic monomers.

3.1.1.1.1. Monomers bearing sulfonic acid function. The most pertinent studies were achieved by the DuPont de Nemours Company as early as 1962. This company reported the synthesis of trifluorovinylsulfonyl fluoride by pyrolytic dehydrofluorination of 1,2,2,2-tetrafluoroethane sulfonyl fluoride [46,47] (Scheme 1).

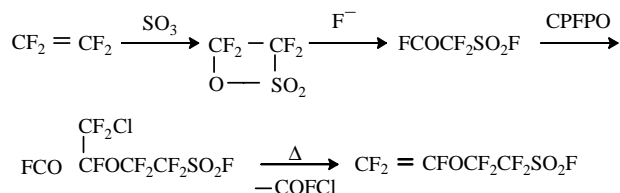
This process was extended to the synthesis of  $\text{R}_F\text{CF}=\text{CF}-\text{SO}_2\text{F}$  from  $\text{R}_F\text{CF}_2\text{CFHSO}_2\text{F}$  [46,47]. Copolymers based on both TFE and these monomers led to original PTFEs bearing sulfonyl fluoride side functions [46,47]. Trifluorovinyl ether monomers of higher molar masses bearing a  $\text{SO}_2\text{F}$  end-group have been patented by DuPont [46,47], Dow Chemical [48], and more recently by Solvay-Solexis [45]. These processes involve a sultone as the key-reactant while the last step consists of a pyrolysis, as depicted the following.



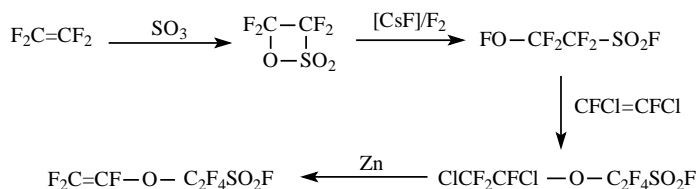
Scheme 2. Synthesis of aliphatic perfluorovinyl ether sulfonyl fluoride according to DuPont [47].

- (a) In the DuPont Technology, the sultone facilitates the introduction of a sulfonyl fluoride end-group and an acid fluoride. The latter reacts to hexafluoropropylene oxide HFPO and, after pyrolysis leads to the sulfonyl fluoride perfluorovinyl ether, as depicted in Scheme 2 [46,47]. This trifluorovinyl ether monomer easily reacts with tetrafluoroethylene (TFE) and leads to Nafion<sup>®</sup> membrane after hydrolysis, initially well-used in the chloroalkali process, because of good stability toward oxidation, reduction and corrosion. Lifetimes of over 50,000 h for Nafion<sup>®</sup> and over 10,000 h for Dow<sup>®</sup> membrane have been shown. Today, Nafion<sup>®</sup> is one of the most advanced commercially available proton conducting polymer material, and has been the preferred electrolyte material for both hydrogen (H<sub>2</sub>-PEMFC) and direct methanol fuel cells (DMFC) [49], although its high cost, medium thermal stability in fuel cell conditions [and hence poor performances under low humidification and at elevated temperatures (above 90 °C) because of water loss], and methanol crossover are limitations.
- (b) The Dow Chemical Company uses chloropentafluoropropylene oxide (CPFPO) instead of HFPO to promote easier formation of the  $\text{F}_2\text{C}=\text{CFO}$  end-group [48], compared to the previous monomers. It is also noted for the presence of a shorter spacer between the trifluorovinyl ether and the sulfonyl end-group (Scheme 3). The radical copolymerization of this fluorinated monomer bearing a sulfonyl fluoride function with TFE was successfully achieved, and although this led to several patents [48], neither industrial





Scheme 3. Synthesis of aliphatic perfluorovinyl ether sulfonyl fluoride according to Dow Chemical Technology [48].



Scheme 4. Synthesis of aliphatic perfluorovinyl ether sulfonyl fluoride according to Solvay Solexis [45].

development nor commercialization of these promising experimental membranes has been achieved.

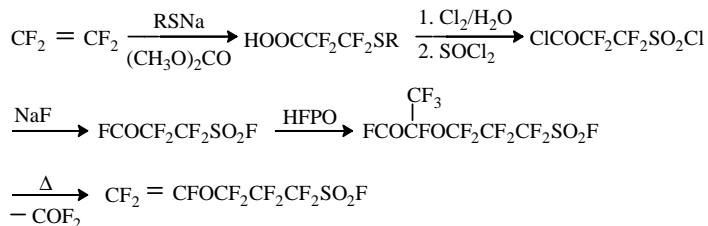
- (c) The Solvay-Solexis Company has recently revisited such potential membranes, and has proposed an alternative synthesis, especially of the monomer described in the preceding paragraph. Their process requires the addition of a hypofluorite to 1,2-difluoro-1,2-dichloroethylene at low temperature, the last step consisting in a simple dehalogenation [45] (Scheme 4).
- (d) The Asahi Glass Company developed two ways to synthesize fluorofunctional monomers involved in the copolymerization of TFE for fuel cell membranes. First, the electrochemical fluorination of a hydrogenated cyclic sulfone led to

$\text{FOC}(\text{CF}_2)_2\text{SO}_2\text{F}$  (in high yields), which reacted with HFPO and underwent a pyrolysis to yield  $\text{F}_2\text{C}=\text{CFO}(\text{CF}_2)_3\text{SO}_2\text{F}$  [50]. The second procedure generates a fluorinated thioether as the intermediate, which can then be oxidized as in Scheme 5.

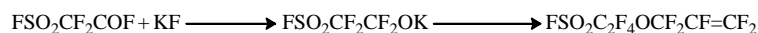
- (e) Several other synthetic methods have been achieved on a research scale.

Krespan and England [51] synthesized perfluoroallyl fluorosulfate from HFP and sulfur trioxide catalyzed by  $\text{BF}_3$  and then isolated  $\text{F}_2\text{C}=\text{CFCF}_2\text{OC}_2\text{F}_4\text{SO}_2\text{F}$  according to the process depicted in Scheme 6.

In addition, Kostov et al. [52] prepared  $\text{FOCCF}_2\text{SO}_2\text{F}$  (from the isomerisation of the tetrafluoroethane- $\beta$ -sultone) that was reacted with  $\text{F}_2\text{C}=\text{CFCF}_2\text{SO}_2\text{F}$

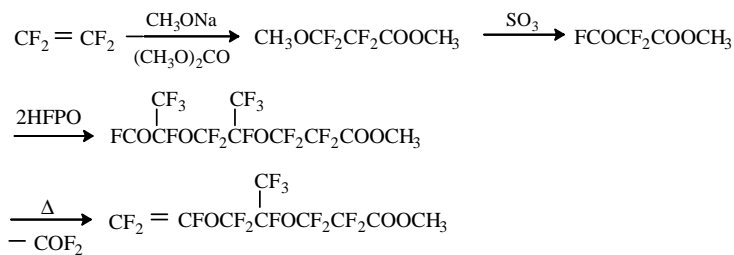


Scheme 5. Strategy of synthesis of aliphatic perfluorovinyl ether sulfonyl fluoride according to Asahi Glass Technology [50].



Scheme 6. Synthesis of perfluoro(3-oxa-hex-5-ene-1-sulfonyl fluoride) [51].





Scheme 7. Strategy of synthesis of methyl perfluoro(5-methyl-4,7-dioxa-non-8-eneoic ester) according to DuPont Technology [60].

(prepared from the addition of HFP onto  $\text{SO}_3$ , catalyzed by  $\text{B}(\text{OCH}_3)_3$  as the catalytic complex) leading to  $\text{F}_2\text{C}=\text{CFCF}_2\text{OC}_2\text{F}_4\text{SO}_2\text{F}$ . Nguyen and Wakselman [53] used another synthesis to introduce various HFPO units.

More recently, DesMarteau [54] achieved the synthesis of an original  $\text{F}_2\text{C}=\text{CFOCF}_2\text{CF}(\text{CF}_3)\text{OC}_2\text{F}_4\text{-G}$ , where G represents  $\text{SO}_2\text{NHSO}_2\text{CF}_3$ ,  $\text{N}(\text{Na})\text{SO}_2\text{CF}_3$  or  $\text{N}(\text{Na})\text{SO}_2\text{C}_4\text{F}_8\text{SO}_2\text{N}(\text{Na})\text{SO}_2\text{CF}_3$ . Additional fluorinated monomers were also described, such as  $\text{R}_\text{F}-\text{CF}=\text{CF}-\text{SO}_2\text{F}$ , where  $\text{R}_\text{F}$  stands for F [47,55] or  $\text{C}_n\text{F}_{2n+1}$  [56], and  $\text{H}_2\text{C}=\text{CH}-\text{R}_\text{F}'-\text{SO}_2\text{F}$ , where  $\text{R}_\text{F}'$  represents  $(\text{CF}_2)_n$ ,  $n=4, 6$  or  $\text{CF}_2\text{CF}(\text{CF}_3)\text{OC}_2\text{F}_4$  [57].

**3.1.1.1.2. Carboxylic perfluoroalkoxyvinyl monomers.** The simple key monomer  $\text{F}_2\text{C}=\text{CFCO}_2\text{H}$  can be prepared by several routes [58,59]. In contrast to the preparation of sulfonated perfluorovinyl ethers, the synthesis of carboxylated perfluorovinyl ether is difficult. The three companies above also share the market of these monomers.

The difluorination step represents the only difference in the methods of the DuPont and Dow Chemical Companies, whereas the Asahi Glass Company presents a different approach:

- (a) In the DuPont Technology, the reaction first led to methyl-3-methoxy tetrafluoroethylene (yield = 74%) but the yield of the third step is low (8–15%). However, improvements were achieved by

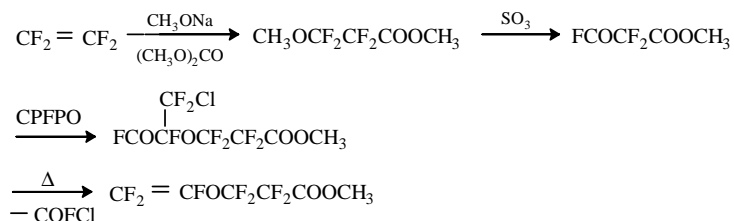
the use of different aprotic solvents producing the perfluoroacid fluoride in 30–40% (Scheme 7) [60].

- (b) In the Dow Chemical process, the first two steps are similar as those above, but CPFPO is used instead of HFPO, as in Scheme 8 [61].
- (c) Interestingly, for Asahi Glass, the telomerization of TFE with iodine followed by a sulfonation brings an originality of synthesis, as depicted in Scheme 9. Such a novel process enables this company to produce Flemion<sup>®</sup> membrane on an industrial scale [68]. The cyclic lactone is obtained in high yields (70–80%) and the controlled addition of methanol to that lactone generated 3-methoxycarbonyl perfluoropropionyl fluoride selectively, to which HFPO was added [63].

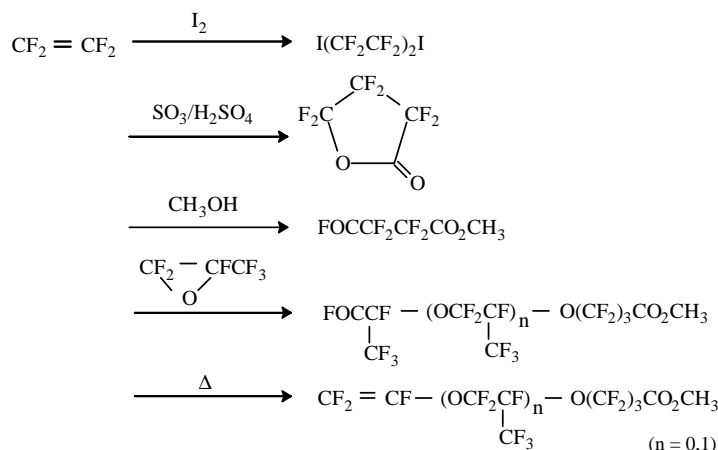
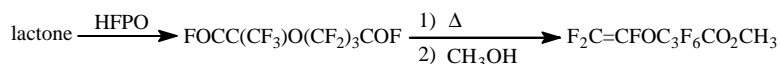
An alternative way from the lactone to the vinyl ether was proposed to improve the yield [63]. The addition of one mole of HFPO to the lactone occurred almost quantitatively and pyrolysis of the asymmetric diacid fluoride led to the perfluorovinyl ether in ca. 70% yield (Scheme 10).

A research-scale route involving an original final step of deiodofluorination was reported in the same review [63], as in Scheme 11.

**3.1.1.1.3. Phosphonic acid perfluoroalkoxyvinyl monomers.** Beside the important carboxylic and sulfonic groups, novel perfluorovinyl ethers bearing



Scheme 8. Strategy of synthesis of perfluoro(4-oxa-hex-5-eneoic acid) according to Dow Chemical [61].

Scheme 9. Strategy of synthesis of perfluoroalkenoic acid according to Asahi Glass Technology [68] for Flemion<sup>®</sup> membranes.

Scheme 10. Synthesis of methyl perfluoro(5-oxa-heptanoic-6-ene ester) [63].

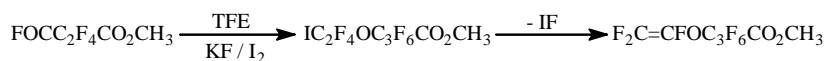
an  $\omega$ -phosphonic acid group have been synthesized. The first was achieved by the chemical modification of carboxylic acid into the phosphonic acid function involving an iodinated intermediate, as in Scheme 12 [62,64].

Then, the synthesis of dimethyl perfluoro(3-vinylxypropyl) phosphonate was achieved and co- or terpolymerized with TFE and perfluoro (propyl vinyl ether) [64]. In an alternative proposed by Petersen et al. [65,66], conversion of the iodides into the corresponding phosphonites used a photo-reaction in the presence of tetraethyl pyrophosphite, followed by an oxidation with hydrogen peroxide to prepare the desired diethyl phosphonate esters.

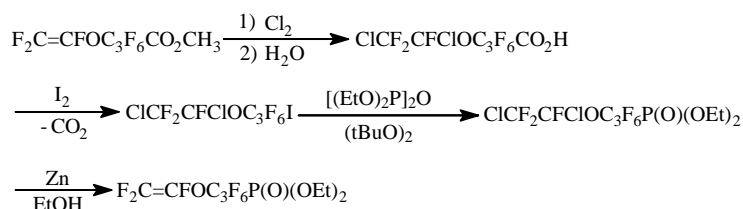
Other exotic functional perfluorovinyl ethers were reported in a very interesting review published by Ukihashi and Yamabe [63]. Tatemoto and Nakamura [67] achieved the preparation of  $\text{F}_2\text{C}=\text{CFP}(\text{O})(\text{OH})_2$  according to Scheme 13.

In fact, most applications [68–70] have involved copolymers containing TFE and perfluorinated vinyl oxy- $\omega$ -sulfonyl fluoride or  $\omega$ -carboxy (or derivatives): membranes for chloroalkali electrolysis, perfluorinated ion exchange materials, solid polymer electrolyte fuel cells or applications in space, ground (for vehicles) and undersea power sources.

3.1.1.2. Aliphatic fluorofunctional copolymers for fuel cell membranes. An interesting example (that has



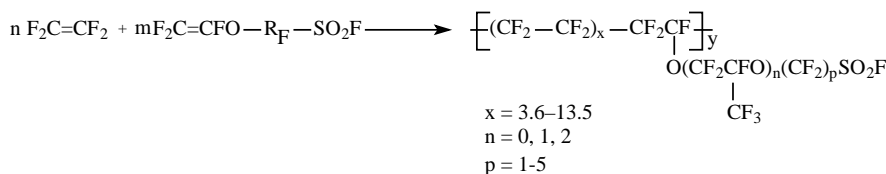
Scheme 11. Alternative of synthesis of methyl perfluoro(5-oxa-heptanoic-6-ene ester) [63].



Scheme 12. Strategy of synthesis of aliphatic perfluorovinyl ether bearing phosphonic acid [62,64].



Scheme 13. Strategy of synthesis of trifluorovinyl phosphonic acid [67].



Scheme 14. Aliphatic perfluorofunctional copolymers bearing sulfonyl fluoride side group by radical copolymerization.

drawn interest from many academic and industrial groups) concerns the copolymerization of TFE with a perfluorovinyl ether with or without hexafluoropropylene oxide (HFPO) units, and bearing carboxylic or sulfonyl fluoride end-group, as in Scheme 14.

The hydrolysis of the sulfonyl fluoride group of copolymers in Scheme 14 led to the corresponding sulfonic acid derivative used for membranes in chloroalkali, ion-exchange membranes for electrolysis, or fuel cell applications. Since 1962, the most known commercially available copolymers are Nafion<sup>®</sup> and Flemion<sup>®</sup> [1,40,71–80] (from DuPont and Asahi Glass Co., respectively) with  $n=1$  and  $p=2$ , and more recently Fumion<sup>®</sup> (from Fumatech), although Tosflex<sup>®</sup> ( $n=0, 1$  and  $p=1$  or  $5$ ), for which the functional end-group is an anion-exchange unit [71], is produced from Tosoh Co. Ltd. In addition, Dow<sup>®</sup> and Hyflon<sup>®</sup> Ion H (from Dow Chemical and Solvay-Solexis, respectively) with  $n=0$  [45,72] and Aciplex<sup>®</sup> (from Asahi Chemicals Co.) with  $n=2$  [1,45,63,73–80] have also led to potential membranes for the above applications [1,71–74] (Table 2).

Three very interesting reviews on such copolymers for obtaining proton exchange membranes (PEMs) devoted to fuel cells have recently been published by Li et al. [4], Doyle and Rajendran [40], and Arcella et al. [45]. In addition, a recently published review by Mauritz and Moore [81] that extensively reports the morphological characterization (by X-rays, neutron scattering, and microscopy) of Nafion<sup>®</sup> supplies molecular simulations, mechanical properties, and the nature and the behavior of ions, water and other solvents in Nafion<sup>®</sup>. Current research on fuel cell membranes, efforts have concentrated on PEMs with lower methanol permeabilities [82a] and lower cost

than Nafion<sup>®</sup> ( $>780$  US \$  $\text{m}^{-2}$ ) [5,82b] and longer durability. However, it has recently been reported that new solution cast Nafion<sup>®</sup> membranes (NR-111) would allow the cost to drop to 50 US \$  $\text{m}^{-2}$  with volume production of  $\sim 2$  million  $\text{m}^2$  per year [83].

For similar strategic fuel cell applications, other monomers with longer chain lengths [84–86] have also been used in the copolymerizations with TFE, while original studies have concerned the use of monomers bearing phosphonate or phosphonic acid end-groups [87–89] such as  $\text{F}_2\text{C}=\text{CFOC}_3\text{F}_6\text{P(O)(OH)}_2$ .

In addition, functional perfluoroalkoxyalkyl vinyl ethers and mainly those containing a sulfonyl fluoride

Table 2

Fuel cell membranes prepared from poly(perfluorosulfonic acid) arising from copolymers of tetrafluoroethylene (TFE) and perfluorovinyl ether alkyl sulfonyl fluoride

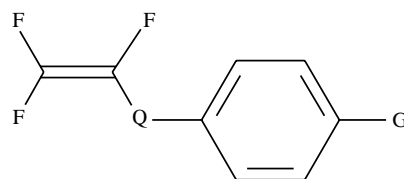
Structural parameters (and monomer contents)	Supplier and trademark	Equivalent weight (IEC; mequiv. $\text{g}^{-1}$ )	Thickness ( $\mu\text{m}$ )
$n=1, x=5-13.5, p=2$	DuPont		
	Nafion <sup>®</sup> 120	1200 (0.83)	250
	Nafion <sup>®</sup> 117	1100 (0.91)	175
	Nafion <sup>®</sup> 115	1100 (0.91)	125
$n=0-1, p=1-5$	Nafion <sup>®</sup> 112	1100 (0.91)	50
	Asahi Glass		
	Flemion <sup>®</sup> T	1000 (1.00)	120
$n=0, p=2-5, x=1.5-14$	Flemion <sup>®</sup> S	1000 (1.00)	80
	Flemion <sup>®</sup> R	1000 (1.00)	50
	Asahi Chemicals		
$n=0, p=2, x=3.6-10$	Aciplex <sup>®</sup> S	1000–1200 (0.83–1.00)	25–100
	Dow Chemical		
$n=0, p=2, x=3.6-10$	Dow <sup>®</sup>	800 (1.25)	125
	Solvay		
	Hyflon <sup>®</sup> Ion	900 (1.11)	

or their derivatives were also successfully copolymerized with vinylidene fluoride (VDF) in various processes [47,85,90–95]. Connolly and Gresham [47] disclosed the copolymerization of VDF with perfluorosulfonyl fluoride ethoxy propyl vinyl ether (PSEPVE) and the terpolymerization involving hexafluoropropylene (HFP) in an emulsion process, using a small amount of functional comonomer, so that only 0.2–5.0 mol% was present in the copolymer. More recently, we have disclosed that VDF copolymerizes with PSEPVE [92] in all proportions. The addition of HFP in this system enabled the functional PSEPVE monomer to improve its reactivity and to produce original elastomers with a higher thermostability [93]. In addition, Feiring et al. [90] have investigated the copolymerization of VDF with various functional comonomers  $F_2C=CFOCF_2CF(CF_3)OC_2F_4R$ , where R represents  $NHSO_2CF_3$  (described by DesMarteau [85]),  $SO_2CLi(SO_2CF_3)_2$ ,  $SO_2NLiSO_2CF_3$  and  $SO_2F$  (PSEPVE). In the case of the last system, the copolymers have a  $T_g$  of  $-20^\circ C$ , and no weight-loss was noted up to  $375^\circ C$ . Hence, these copolymers with pendant groups containing fluorosulfonyl methide or fluorosulfonyl imide derivatives are original fluorinated ionomers that can be used in applications such as electrolysis cells, ion exchange membranes, sensors, electrochromic windows, in electrochemical capacitors for modified electrodes, and also for batteries and fuel cells [1].

Further work reported terpolymerization involving brominated [94] or nitrile [95] fluorinated comonomers. Interestingly, cure site monomers bearing Br or CN groups induced a crosslinking reaction [31] that made the resulting network insoluble in all solvents. By contrast, fluorinated monomers containing a  $CO_2H$  end-group did not have the same fate as that of the sulfonic acid derivatives [96,97] because of the weaker acidity of the ionic group, although various studies were developed [1,96]. Nevertheless, the kinetics of copolymerization of TFE with  $F_2C=CFO-R_F-CO_2H$  [97] and of VDF with  $H_2C=CF_2OCF(CF_3)CF_2OCF(CF_3)CO_2CH_3$  [98] were investigated.

### 3.1.2. PEMFC based on aromatic fluorinated polymers

This sub-section seeks to report the preparation and the characterization of proton exchange membrane for



TFS: Q equivalent to “-”, TFVOB: Q equivalent to O  
G: sulfonic or phosphonic acid

Fig. 2. Formula of functionalized or non-functionalized- $\alpha,\beta,\beta$ -trifluorostyrene.

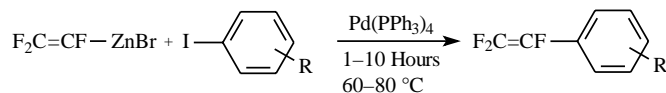
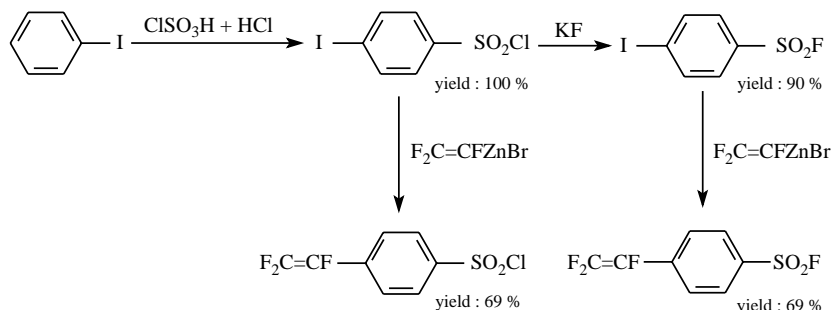
fuel cell (PEMFC) based on aromatic (per)fluorinated polymers. In the past few decades, attention has focused on the preparation of new fluorinated monomers and aromatic fluoropolymers. This topic was recently reviewed [99], summarizing the characteristic effects of the aromatic group on the physico-chemical properties (e.g.  $T_g$  and the thermostability of the obtained polymers).

To our knowledge, aromatic fluorinated macromolecules for PEMFCs may be prepared by direct radical (co)polymerization from two groups of functionalized aromatic perfluorinated monomers: (i)  $\alpha,\beta,\beta$ -trifluorostyrene (TFS), and (ii) [ $(\alpha,\beta,\beta$ -trifluorovinyl)oxy] benzene (TFVOB), sketched in Fig. 2.

The first part covers PEMFCs obtained by direct (co)polymerization of functionalized TFS. Various routes dealing with the synthesis and characterization of (co)polymers containing functionalized TFVOB are presented in a second part.

**3.1.2.1. PEMFC based on functionalized  $\alpha,\beta,\beta$ -trifluorostyrene.** Several syntheses of TFS are first reported, followed by a discussion of the preparation and the characterization of PEMFCs including (co)polymers of TFS functionalized by acid groups (sulfonic and phosphonic).

**3.1.2.1.1. Synthesis and polymerization of  $\alpha,\beta,\beta$ -trifluorostyrene.** The synthesis of  $\alpha,\beta,\beta$ -trifluorostyrene (TFS) and its (co)polymerization with different comonomers have been reported by several authors [100–105]. The most interesting methods of TFS synthesis were reviewed by Heinze and Burton [106] in 1988. TFS was prepared after a coupling reaction of perfluoroalkenylzinc reagents [ $F_2C=CFZnX$ , (Z)  $F_3C-CF=CF-ZnX$ , (E)  $F_3C-CF=CF-ZnX$  with X equivalent of bromide or iodide] with aryl iodides in

Scheme 15. Synthesis of  $\alpha,\beta,\beta$ -trifluorostyrene by Heinze and Burton [106].Scheme 16. Synthesis of 4-fluorosulfonate- $\alpha,\beta,\beta$ -trifluorostyrene [107].

the presence of  $\text{Pd(PPh}_3)_4$  as catalyst to yield the corresponding fluoroalkenes (Scheme 15).

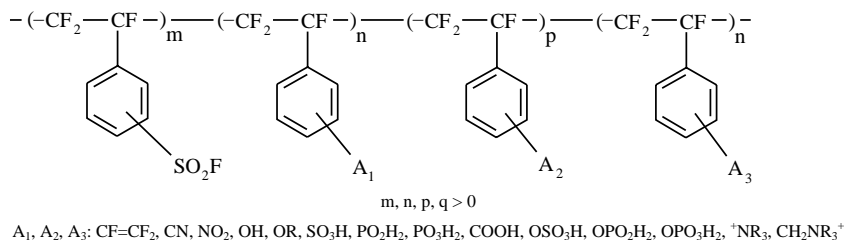
The synthesis of *p*-sulfonic acid- $\alpha,\beta,\beta$ -trifluorostyrene was patented by the Ballard Power System Company [107] (Scheme 16). First, the action of chlorosulfonic acid onto iodobenzene was achieved from the Sanecki's synthesis [108] and the chlorosulfonate or fluorosulfonate trifluorostyrene compound was obtained via a Burton reaction [106]. The corresponding sulfonic acid monomer was obtained by hydrolysis of the *p*-halogenosulfonate- $\alpha,\beta,\beta$ -trifluorostyrene.

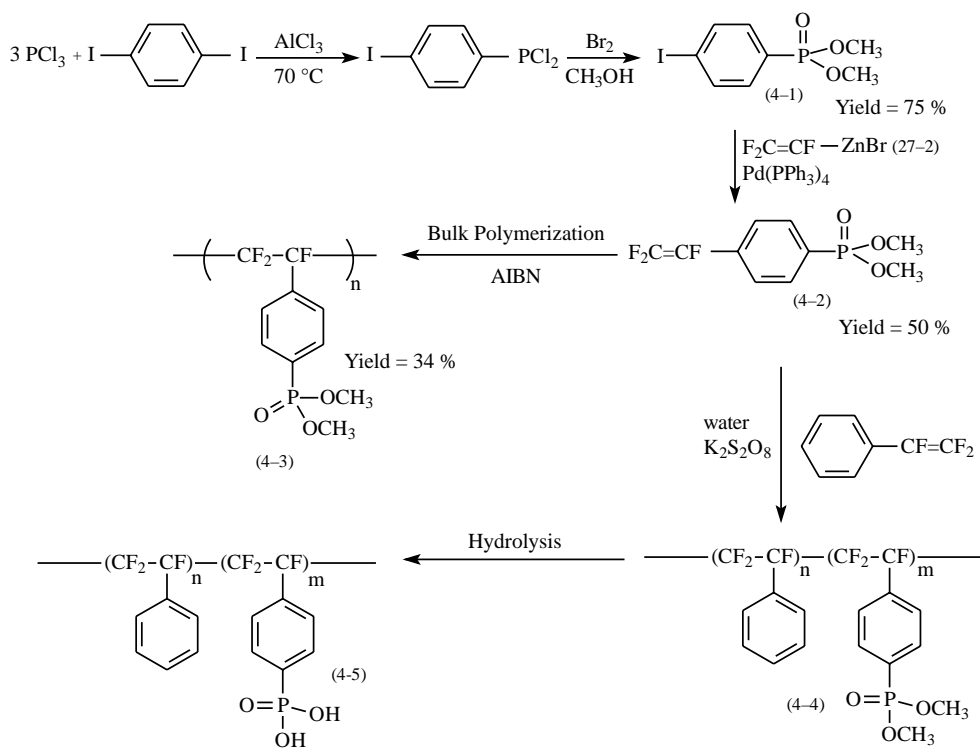
It has been shown that dimers or dienes can be prepared by a cyclodimerization reaction of TFS [109–111].

The bulk polymerization of TFS in the presence of benzoyl peroxide at 70–75 °C, and with boron trifluoride at 1–4 °C was achieved for the first time by Prober [101] in 1953. The softening points of the copolymers ranged between 207 and 225 °C. In 1981,

Tevlina et al. [112] copolymerized  $\alpha,\beta,\beta$ -trifluorostyrene (I) with vinyl fluoromonomers, such as *N*-vinylpyrrolidone (II),  $\text{H}_2\text{C}=\text{CF}-\text{CN}$  (III),  $\text{FHC}=\text{CF}-\text{COOMe}$  (IV) and  $\text{F}_2\text{C}=\text{C}(\text{CF}_3)\text{COOMe}$ , in the presence of AIBN. The low reactivity of (I) was attributed to the presence of fluorine in both  $\beta$ -positions of the vinyl group. The high polarity of bonds in compounds III, IV and V arises from the electron acceptor effect of the fluorine atom. Compounds II, III and IV were highly reactive in copolymerization with I.

3.1.2.1.2. *Poly( $\alpha,\beta,\beta$ -trifluorostyrene) incorporated in PEMFC.* *p*-Chloro or fluorosulfonate- $\alpha,\beta,\beta$ -trifluorostyrene synthesized by Stone et al. [107] and patented by the Ballard Power System was copolymerized in emulsion (in the presence of dodecylamine hydrochloride) with trifluorostyrene, functionalized or not (Scheme 17). However, the thermal properties ( $T_g$ ,  $T_d$ ), the molecular weights, the polydispersity index of copolymers, and the electrochemical

Scheme 17. Copolymerization of fluorosulfonate- $\alpha,\beta,\beta$ -trifluorostyrene [107].



Scheme 18. Synthesis and homopolymerization of dimethylphosphonate-4-substituted- $\alpha,\beta,\beta$ -trifluorostyrene according to Stone et al. [113].

properties of the PEMFC like ion exchange capacity (IEC), swelling rates, proton conductivity were not reported.

In 1999, Stone et al. [113] proposed a PEMFC based on phosphonic acid trifluorostyrene. Polymers were prepared in two basic steps (Scheme 4): (i) the synthesis of 4-iodobenzene phosphonic acid dimethyl ester (4-1), and (ii) the synthesis of the *p*-dimethyl phosphonate- $\alpha,\beta,\beta$ -trifluorostyrene (4-2). The authors showed that the monomer either homopolymerized or copolymerized (Scheme 18).

Although, it is known that  $\alpha,\beta,\beta$ -trifluorostyrene does not homopolymerize under radical conditions, these authors reported the homopolymer (4-3) of monomer (4-2). They achieved the highest degree of ionization and the lowest equivalent weight for an ionomer of this structure by using a variety of standard techniques, including emulsion polymerization, solution polymerization (in toluene), and bulk polymerization. The best yields were obtained in bulk polymerization initiated by AIBN. The polymer was characterized by a low intrinsic viscosity, and its

membranes exhibited very poor mechanical properties. Nevertheless, the homopolymer (4-3) was hydrolyzed to afford an ionomer mixture soluble in aqueous base. As a consequence, the physical properties of ionomer did not fulfill the requirements for use as a PEMFC.

In a second method, Stone et al. [113] copolymerized monomer (4-2) with  $\alpha,\beta,\beta$ -trifluorostyrene (TFS) (Scheme 18) by emulsion polymerization in 21% isolated yield. The optimized ratio between TFS and the dimethylphosphonate-substituted- $\alpha,\beta,\beta$ -trifluorostyrene monomer in the copolymer (4-5) was 2.4:1. The molecular weights of the resulting copolymer were 38,100 and 105,900 g/mol, for  $M_n$  and  $M_w$ , respectively.

Homopolymer (4-3) (membrane A) was hydrolyzed in acid conditions (hydrochloric acid in dioxane,  $100^\circ\text{C}$ , 20 h). The yield and the equivalent weight of acid functions were 95% and 130 g/mol, respectively. Copolymer (4-4) was hydrolyzed by the authors using two processes: (i) basic conditions (potassium hydroxide,  $84^\circ\text{C}$ , 64 h), membrane C<sub>1</sub>, and (ii) acid

Table 3

Electrochemical characteristics of different ionomer membranes achieved by Stone et al. [113], Xu and Cabasso [114], and Kotov et al. [66], compared to those of Nafion<sup>®</sup>

Ionomer	EW (g/mol)	EW effective (g/mol) <sup>1</sup>	Transverse proton conductivity (mS cm <sup>-1</sup> )	Water absorption at 100 °C (%)	Reference
A (membrane based on homopolymer 4–3)	130	215	–	–	[113]
C <sub>1</sub> (membrane based on copolymer 4–4)	350	670	0.01–0.1	15	[113]
C <sub>3</sub> (membrane based on copolymer 4–4)	200	380	–	77	[113]
D (membrane based on 3.86:1 ratio <i>n:m</i> )	357	357	76	22	[66]
[CF <sub>2</sub> –CF <sub>2</sub> ] <sub><i>n</i></sub> [CF <sub>2</sub> –CFX] <sub><i>m</i></sub> with X = O(CF <sub>2</sub> ) <sub>3</sub> P(O)(OH) <sub>2</sub>					
E (membrane based on 4.63:1 ratio <i>n:m</i> )	370	370	69	21	[66]
[CF <sub>2</sub> –CF <sub>2</sub> ] <sub><i>n</i></sub> [CF <sub>2</sub> –CFX] <sub><i>m</i></sub> with X = O(CF <sub>2</sub> ) <sub>3</sub> P(O)(OH) <sub>2</sub>					
F (membrane based on poly(dimethylphenylene oxide phosphonic acid))	111	202	–	–	[114]
G (membrane based on poly(dimethylphenylene oxide diposphonic acid))	70	107	–	–	[114]
Nafion <sup>®</sup>	1100–1500		50–110		[40,49,73,82]

EW, equivalent weight.

conditions with a DMF pre-treatment, membrane C<sub>3</sub>. The electrochemical properties of these membranes are gathered in Table 3 and compared to other copolymers bearing phosphonic acid groups [66,114]. Finally, the authors concluded that the best results were obtained with an acidic hydrolysis, and that membranes based on sulfonic acid- $\alpha,\beta,\beta$ -trifluorostyrene gave better results than those obtained from the phosphonic acid homologue.

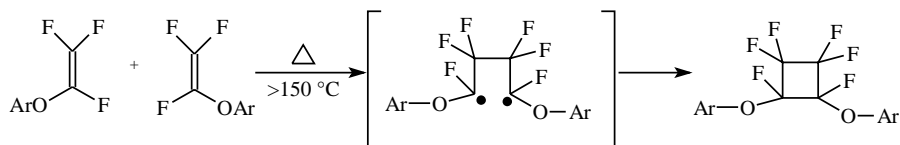
**3.1.2.2. PEMFC based on functionalized [ $\alpha,\beta,\beta$ -trifluorovinyl]oxy benzene.** In this sub-section, two main kinds of aromatic PEMFC incorporating functionalized [ $\alpha,\beta,\beta$ -trifluoroethenyl]oxy benzene (TFVOB) are presented: (i) polymers prepared by thermocyclodimerization, (ii) and macromolecules obtained by direct (co)polymerization of TFVOB with commercially available fluoroalkenes [115].

**3.1.2.2.1. PEMFC prepared by direct thermal cyclodimerization of TFVOB.** [ $\alpha,\beta,\beta$ -Trifluorovinyl]oxy]benzene and polymers incorporating such a

monomer are very interesting materials [99,115]. They have received considerable attention by a number of groups [116], industries [115,117], and are currently used as materials for microphonics [118], optics [119], liquid crystals [120], interlayer dielectrics [121], circuit board laminates [122], coating applications [123], ion exchange resins [116g, 117d,124], and for the preparation of ionomer membrane and fuel cells [107,113,125].

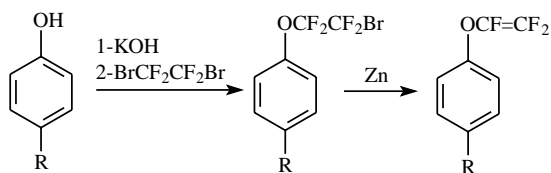
The most interesting property of perfluoroalkyl [ $\alpha,\beta,\beta$ -trifluorovinyl]oxy benzene is its thermal cyclopolymerization [ $2\pi + 2\pi$ ] with temperature (up to 150 °C) (Scheme 18). The formed perfluoroalkyl-polymer is a thermoplastic and thermoset perfluoro-cyclobutane (PFCB) (Scheme 19) [116c,g,126,127].

Initially pioneered by Beckerbauer [126] in 1968, the preparation of functionalized TFVOB has been important in numerous investigations [115,116c,117d, 123b,127c,128,129]. As explained in prior communications [130], trifluorovinyl ethers are usually prepared in two steps: the first involves a fluoroalkylation



Scheme 19. Formation of aromatic perfluorocyclobutane (PFCB) [116c,g,126,127].





Scheme 20. General synthetic route of TFVOB preparation.

with  $\text{BrCF}_2\text{CF}_2\text{Br}$ , while the second one deals with a zinc mediated elimination of 'FBr' (Scheme 20).

Babb et al. [127c,128a] developed a series of TFVOB prepared from bis- and tris-phenols, such as tris(hydroxyphenyl)ethane. These perfluorinated aryl ethers were thermocyclodimerized giving thermoset polymers ( $T_g = 180^\circ\text{C}$ ) endowed with good thermal stability (they are stable up to  $434^\circ\text{C}$ ), thermal/oxidative stability and mechanical properties [123b, 127d]. In addition, in 1996, these authors [116c] prepared perfluorocyclobutane (PFCB) aromatic polyethers containing a siloxane group. Their syntheses involved an aryl Grignard reagent from 4-[(trifluorovinyl)oxy]bromobenzene that led to 4-[(trifluorovinyl)oxy]phenyldimethylsilane in a high-yield (87%). The latter was finally dehydrogenatively hydrolyzed in situ and then condensed to produce bis[1,3-(4-[(trifluorovinyl)oxy]phenyl)]-1,1,3,3-tetramethyldisiloxane in 43% yield. Such a monomer was

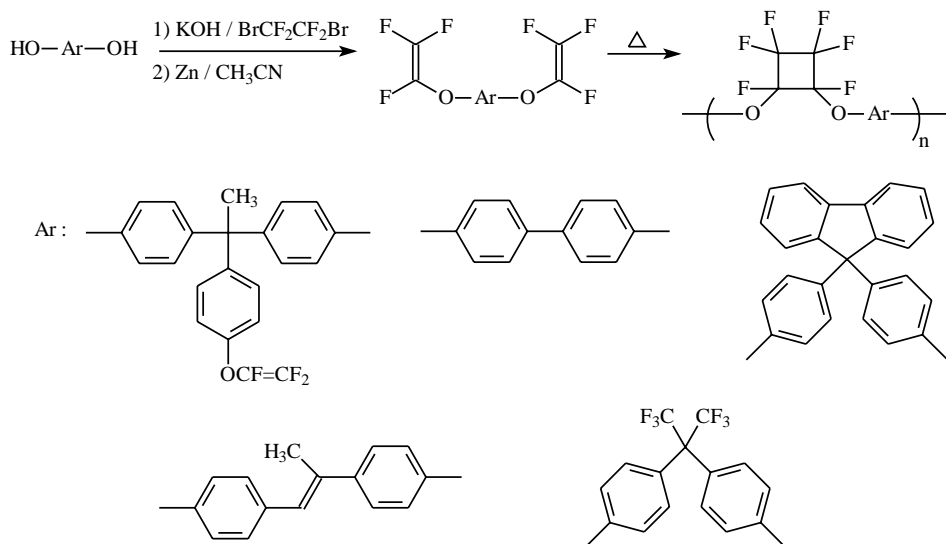
thermocyclodimerized (by heating the monomer at  $210^\circ\text{C}$  for 14 h) to yield the siloxane PFCB.

In 2000, Smith et al. [123b] reported the synthesis of different PFCB polyarylethers (Scheme 21).

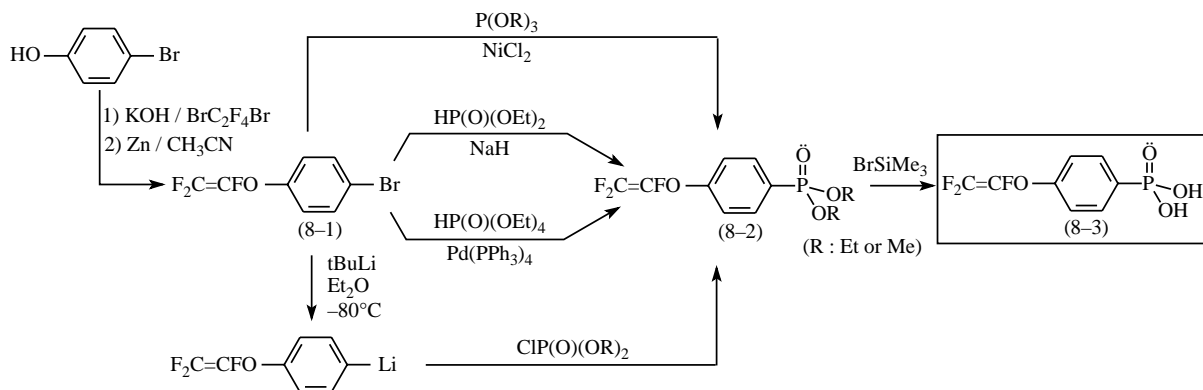
Interestingly, the reactive Grignard [131] or Lithium [128b,132,133] compound of 4-[(trifluorovinyl)oxy]bromobenzene [116c] gained access to an increasing number of organic/inorganic fluorinated compounds [116c,128b,132–134].

The current intensified interests in the preparation of PEMFC based on electrolyte polymers has prompted us to synthesize aromatic monomers such as trifluorovinyl ethers functionalized by acid groups. In particular, we reported the first preparation of 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy] benzene phosphonic acid [129] (Scheme 22). [( $\alpha,\beta,\beta$ -Trifluorovinyl)oxy] benzene dialkyl phosphonate was prepared by several phosphonation methods, such as Michaelis–Arbuzov, Michaelis–Becker or palladium catalyzed-arylation in the presence of various reactants. The reaction involving palladium triphenyl phosphine as the catalyst led to the best yield [129].

In 2000, Ford et al. [133] reported the synthesis of aromatic perfluorovinyl ether monomers containing sulfonamide and the sulfonic acid functionality for different applications, such as the proton exchange membrane fuel cell (PEMFC) [135]. As in the former



Scheme 21. Poly aryl vinyl ether synthesized by Smith et al. [123b].



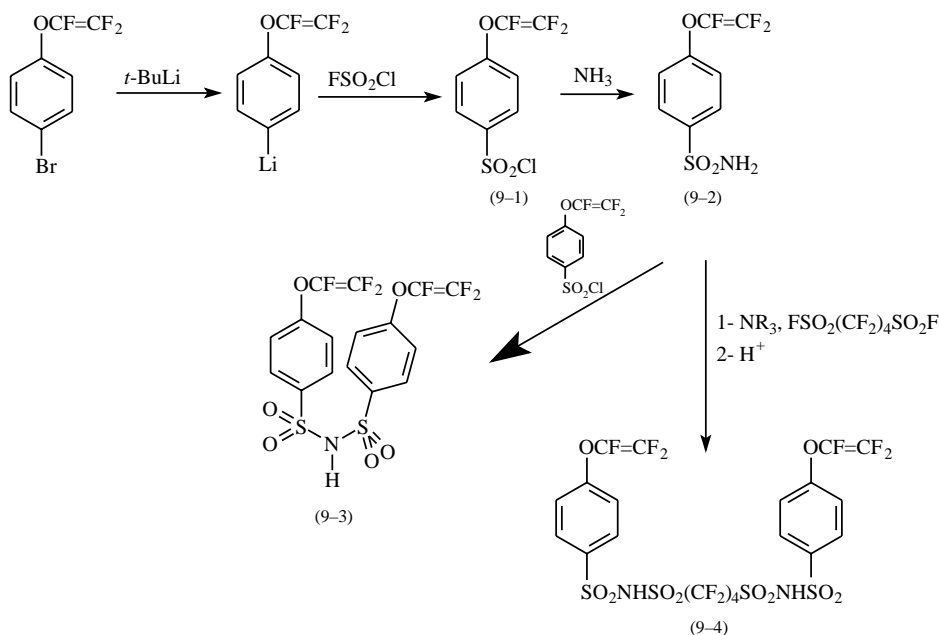
Scheme 22. Synthesis of new aromatic perfluorovinyl ether monomers containing phosphonic acid functionality [129].

example, Ford et al. used [*p*-((trifluorovinyl)oxy)phenyl]lithium, which was cross-coupled with  $\text{FSO}_2\text{Cl}$  to give 4-[(trifluorovinyl)oxy]benzenesulfonyl chloride in 65% yield (**(9-1)**, Scheme 23).

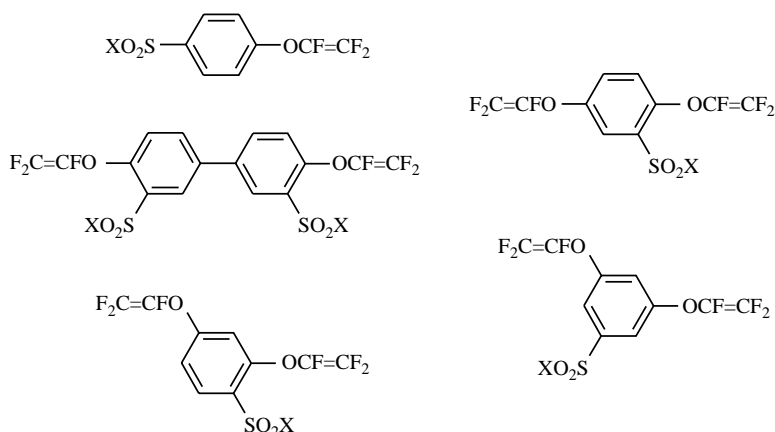
Monomers **(9-2)**, **(9-3)** and **(9-4)** were prepared in 91, 85 and 80% yield, respectively. The thermal behavior of monomer **(9-3)** was studied by DSC. The exothermic polymerization was in the range 175 °C ( $T_{\text{onset}}$ ) to 214 °C ( $T_{\text{max}}$ ).

These different monomers having similar structures as that of monomer **(9-1)** (Scheme 23) and polymers prepared by thermocyclodimerization of these monomers were patented by the 3M Innovative Properties Company [117d] in 2001 for PEMFC applications (Scheme 24).

3.1.2.2.2. PEMFC synthesized from direct radical terpolymerization of  $\alpha,\beta,\beta$ -trifluorovinyl benzyl ethers. Souzy et al. [136] studied the radical



Scheme 23. Synthesis of aromatic perfluorovinyl ether monomers containing the sulfonamide and the sulfonic acid functionality according to Ford et al. [133].

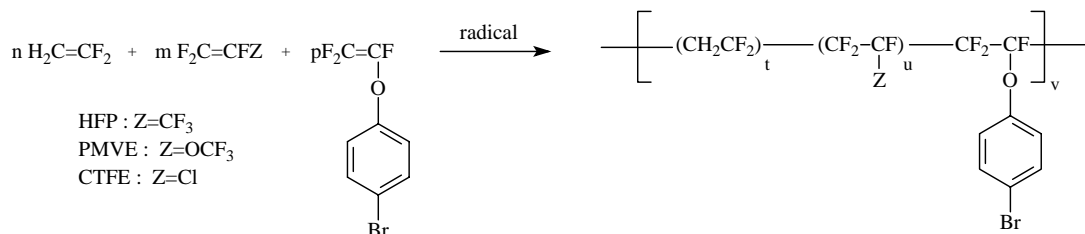


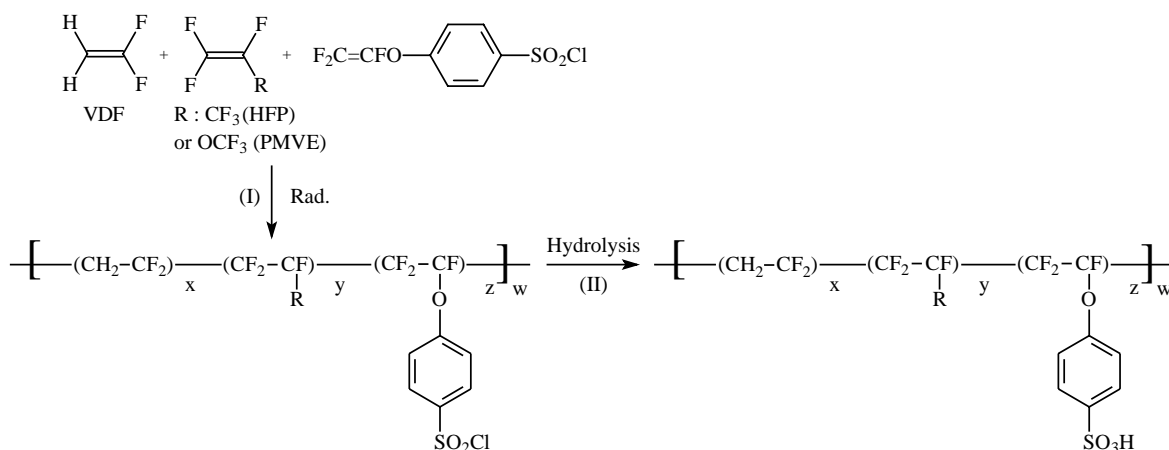
Scheme 24. Functionalized polyarylene vinyl ethers according to 3M Innovative Properties company [117d].

homo-, co-, and terpolymerization of 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy] bromobenzene with commercially available fluoroalkenes such as vinylidene fluoride (VDF) and/or chlorotrifluoroethylene (CTFE), and/or hexafluoropropylene (HFP), and/or perfluorovinyl methyl ether (PMVE) (Scheme 25). As mentioned above,  $\alpha,\beta,\beta$ -trifluorovinyl benzyl ethers are interesting monomers because they can lead to thermostable fluoropolymers. The authors optimized the conditions of co- and terpolymerization and even tetrapolymerization taking into account the nature of the radical initiators, the nature of solvents (fluorinated or non-halogenated) and the relative reactivities of the comonomers. Furthermore, terpolymers incorporating 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy] bromobenzene were synthesized and it was shown that the VDF/PMVE mixture enhanced the incorporation of the  $\alpha,\beta,\beta$ -trifluorovinyl benzyl ethers in the terpolymers.

Using the optimal conditions for the radical terpolymerization of 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy] bromobenzene with the fluoroalkenes above, these

authors reported the synthesis of new polymer electrolyte membranes based on fluoropolymers incorporating aromatic perfluorovinyl ether sulfonic acids [115,137]. In fact, a novel synthetic route for the preparation of perfluorovinyl ether monomer containing sulfonic functionalities, 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy]benzene sulfonic acid (TFVOBSA) was proposed. This monomer was synthesized in 72% overall yield. Further, the radical (co) and terpolymerization of 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy]benzene sulfonyl chloride (TFVOBSC) with VDF, HFP, and PMVE (Scheme 26) were also investigated. The incorporation of the aromatic functional monomer was limited (9%) and it was noted that the higher its feed content, the lower the yield. Poly(VDF-*ter*-HFP-*ter*-TFVOBSC) and poly(VDF-*ter*-PMVE-*ter*-TFVOBSC) were hydrolyzed by a slight alkali treatment without affecting both the content of fluoromonomers in the terpolymers and without inducing any dehydrofluorination of VDF units [137]. Moreover, membranes were formulated with

Scheme 25. Terpolymerization of 4-[( $\alpha,\beta,\beta$ -trifluorovinyl)oxy] bromobenzene with Fluoroalkenes (VDF, HFP, PMVE and CTFE) [136].



Scheme 26. Radical terpolymerization (I) of TFVOBSC with VDF and/or HFP and/or PMVE, and hydrolysis (II) of the corresponding terpolymers [115,137].

a commercially available fluoropolymer by casting and demonstrated good film-forming properties. IEC values ranged between 0.4 and 0.6 mequiv.  $\text{g}^{-1}$ . The corresponding protonic conductivities and swelling rates were characterized, and the thermal properties studied. Analytical evidence showed that these materials incorporated sulfonic acids. However, the conductivity values, still under improvement, ranged between 0.01 and 0.10  $\text{mS cm}^{-1}$ , far less than those for Nafion<sup>®</sup> (Table 4).

**3.1.2.3. Conclusion.** Functional [ $\alpha,\beta,\beta$ -trifluorovinyl]oxy benzenes are interesting precursors which can undergo thermal cyclopolymerization yielding low molecular weight perfluoroalkylpolymers. They lead to high- $T_g$  thermoset polymers endowed with a good thermal stability. These perfluorinated aryl ethers are currently used for the preparation of ion exchange resins and ionomer membranes.

Recently, investigations dealing with radical terpolymerization of those aromatic fluoromonomers functionalized by sulfonic acid groups [137] or phosphonic acid [129] with VDF, CTFE, HFP and PMVE led to fluoropolymers bearing acid functionality with, however, low yields and low conductivity values.

### 3.1.3. Conclusion

Various strategies for the syntheses of either aliphatic or aromatic functional fluorinated monomers

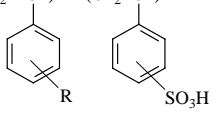
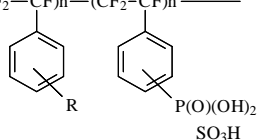
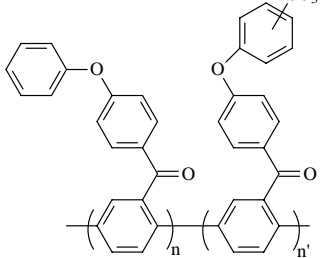
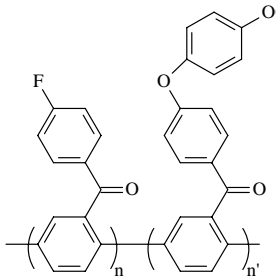
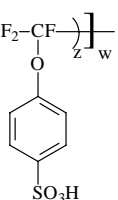
have been proposed in the literature. Because of their costs, they have been involved in copolymerization with fluoroalkenes, and although a lack of basic research is noted (e.g. no assessment of the reactivity ratios), many applied investigations have been developed. In fact, most companies producing fluorinated monomers and derivatives have solved the challenge to prepare fluorocopolymers bearing sulfonic acid side groups. Nevertheless, quite a few studies concern phosphonic acid function. Compared to direct copolymerization, the alternative to prepare fluorofunctional copolymers by chemical modification of polymers is often employed.

## 3.2. Fluorinated graft copolymers for PEMFC by chemical modifications

### 3.2.1. Introduction

Various fluorinated graft copolymers have been synthesized by chemical modification of hydrogenated or fluorinated copolymers [30b]. Different reactions have been used: hydrosilylation of poly(methyl hydrogenosiloxane)s with fluorinated unsaturated synthons, condensation of fluorinated alcohols onto maleic acid containing copolymers, direct addition of fluorinated reactants onto poly(diene)s, etc. The fluorinated group or function brings the desired property, and hence leads to potential applications such as oil and water repellent materials, surfactants for radical polymerizations in supercritical

Table 4  
Ionic exchange capacities and proton conductivities of different PEMFC

Membrane	Film thickness ( $\mu\text{m}$ )	IEC (mequiv. $\text{g}^{-1}$ )	Proton conductivity ( $\text{mS cm}^{-1}$ )	Reference
$-\text{[(CF}_2\text{CF}_2)_x-\text{[CF}_2\text{-CF[OCF}_2\text{CF(CF}_3\text{)]}_p\text{OCF}_2\text{CF}_2\text{-SO}_3\text{F]}_n-$ (p: 0 or 1) Nafion <sup>®</sup> 117	175	0.67–1.25	50–110	[46,47]
$-\text{-(CF}_2\text{-CF)}_n-\text{-(CF}_2\text{-CF)}_{n'}-\text{-}$ 	75	1.1–2.6	2–10	[107]
<b>BAM3G</b> $-\text{-(CF}_2\text{-CF)}_n-\text{-(CF}_2\text{-CF)}_{n'}-\text{-}$ 	90	1.5	0.10	[113]
	110	1.3	2.0	[22]
Sulfonated poly( <i>p</i> -phenoxybenzoyl-1,4-phenylene) (sPPBP)	40	1.3	8.5	[26]
				
Sulfonated poly( <i>p</i> -fluorobenzoyl-1,4-phenylene)- <i>co</i> -poly( <i>p</i> -ethoxytetrafluoro- <i>p</i> -phenoxybenzoyl-1,4-phenylene) (GPS)	71	0.4	0.037	[115,137]
$-\left[ \left( \text{CH}_2\text{-CF}_2 \right)_x \left( \text{CF}_2\text{-CF} \right)_y \left( \text{CF}_2\text{-CF} \right)_z \right]_w$ 	95	0.5	0.082	
	51	0.6	0.059	
R : CF <sub>3</sub> (HFP) or OCF <sub>3</sub> (PMVE)				
Blend of commercially poly(VDF- <i>co</i> -HFP) copolymers (80/20 wt%) with poly(VDF- <i>ter</i> -HFP or PMVE- <i>ter</i> -[trifluorovinyloxy]benzene sulfonic acid)				

CO<sub>2</sub>, original amorphous and soluble polymers for optics. This sub-section supplies non-exhaustive examples of grafted copolymers involved in fuel cell applications from either hydrogenated (grafted with fluorofunctional synthons) or fluorinated polymers (grafted with hydrogenated functional reactants).

### 3.2.2. Chemical modifications of poly(paraphenylenes)

An original approach was suggested by Le Ninivin [22a] who synthesized novel poly(paraphenylenes) (PPPs) bearing 2-sulfonic acid-1,1,2,2-tetrafluoroethyl side groups. They were obtained by nucleophilic substitution of *para*(1-sulfonic acid-1,1,2,2-tetrafluoro)phenate onto poly(*p*-fluorobenzoyl-1,4-phenylene) in 95% yields. With 1.2 equiv. excess of sulfonated phenolate, the degree of sulfonation was 95%, leading to a hydrosoluble graft copolymer, whereas a 0.4 equiv. of this fluorinated derivative led to 41% degree of sulfonation, as depicted in Scheme 27.

These amorphous polymers ( $T_g = 156\text{ }^\circ\text{C}$ ) exhibited fair to high molecular weights (as deduced with PS standards):  $M_n = 26,000$  and  $M_w = 65,000$ . Interestingly, the electron-withdrawing C<sub>2</sub>F<sub>4</sub> adjacent group enabled sulfonic acid to exhibit enhanced acidic character. From a certain amount of grafting, nanoscale organization was demonstrated by small angle X-ray scattering measurements. A distance of 3 nm between the ionic clusters was assessed; the ionic part being far enough from the rigid poly(paraphenylene) backbone [22].

These fluorinated PPPs led to original membranes endowed with a good thermal stability (films were stable in air up to 310 °C), interesting electrochemical properties, very low methanol crossover (its intrinsic permeability to methanol was lower than that of Nafion<sup>®</sup> for the same thickness), high ionic exchange capacity (1.3 mequiv. H<sup>+</sup> g<sup>-1</sup>) and satisfactory conductivity (8.5 mS cm<sup>-1</sup>) for a thickness of 40 μm. All

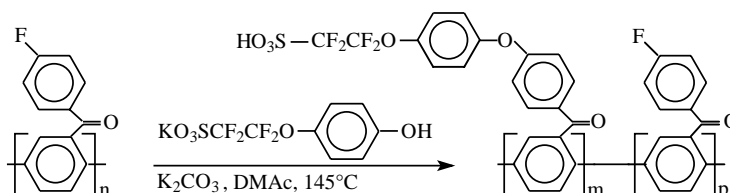
these relevant characteristics show that these membranes are potential candidates for direct methanol fuel cells [22b].

### 3.2.3. Chemical modification of fluoropolymers from irradiation followed by chemical grafting

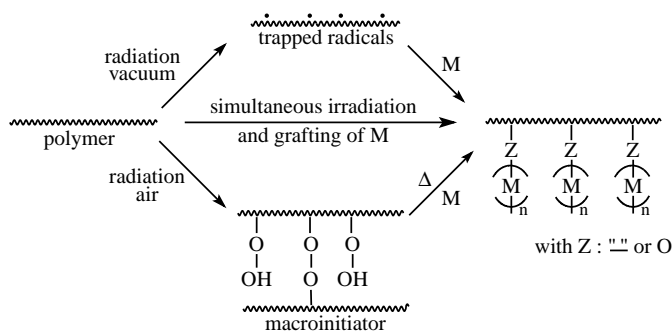
#### 3.2.3.1. Introduction.

The synthesis of original fluorinated graft copolymers achieved from the introduction of grafts via macroinitiators has recently been reported [30b]. These macroinitiators can be obtained by either of two different routes: (i) from the co- or terpolymerization of fluoromonomers, one of them containing an initiating species which does not participate in the (co)polymerization; or (ii) from the activation of the fluoropolymers under thermal initiation, ozone, plasma, swift heavy ions, X-rays or electron beam [138–145]. Then, these macroinitiators enable one to initiate the radical (co)polymerizations of various monomers leading to graft copolymers. Such a process, starting from the initiating functions born by the polymer, is called the ‘grafting from’ technique.

Many studies have been devoted to the synthesis of fluorinated graft copolymers involving a first step of activation of the fluoropolymer. Although such halogenated polymers are resistant to certain irradiations, they can be activated on their surface or even in bulk by various systems. Regarding the synthesis of functional graft copolymers from the activation process, the polymer is exposed to radiation, which leads to the formation of radicals on the macromolecular chain. The following three different methods may be used for the radiation-initiated grafting process [138,144]: (i) if the (pre-)irradiation is carried out in air, radicals react with oxygen leading to the formation of peroxides and hydroperoxides so that in contact with monomer, the irradiated polymer initiates grafting by thermal



Scheme 27. Synthesis of original paraphenylene containing *para*(1-sulfonic acid-1,1,2,2-tetrafluoro)phenate) side group [22].



Scheme 28. Various ways of obtaining fluorinated graft copolymers by 'grafting from' Technique.

decomposition of hydroperoxides; (ii) in the absence of air, these macromolecular radicals remain trapped in the polymeric matrix and initiate grafting in the presence of a monomer; and (iii) simultaneous radiation grafting is a single-step process, whereas pre-irradiation method involves two-steps [138,144,145]. These three methods are sketched in Scheme 28.

The extent of any degradation largely depends on the chemical nature of the polymer. Among fluorinated polymers, PVDF and PTFE have been widely used for the grafting of various monomers (see sections below). The latter has a very low resistance to high-energy radiation, which causes degradation even for low doses of gamma radiation [140]. However, the poly(tetrafluoroethylene-*co*-hexafluoropropylene) copolymer (FEP) shows a much higher resistance to gamma radiation. However, to the best of our knowledge, only one example arising from the thermal activation of hydrogenated polymer (for final fuel cell applications) has been proposed, by the DuPont Company [146], which claimed to graft  $\text{H}_2\text{C}=\text{CHC}_2\text{F}_4\text{OC}_2\text{F}_4\text{SO}_2\text{F}$  onto polyethylene in the presence of *ditert*-butyl peroxide, leading to the corresponding graft copolymer, with  $T_m=115^\circ\text{C}$  and 10% wt loss by TGA at  $380^\circ\text{C}$  under nitrogen.

A number of fluoropolymers have been activated by various techniques [30b,138–145]: thermal, corona, ozone, swift heavy ions, plasma, electron beam, or X-rays. Indeed, ozone smoothly activates fluoropolymers, in contrast to electron beam or X-ray radiation, which irradiate all the bulk and producing peroxides in high amount. This sub-section deals with the synthesis of fluorinated graft copolymers by the 'grafting from' method, i.e. the fluorinated polymers have been first activated by ozonization or other

various means (plasma, thermal,  $\gamma$  ray or electrons) (first part), followed by a subsequent reaction of grafting (second part). In each part, the fluorinated comb-like copolymers can be prepared from different F-homopolymers (e.g. PTFE, PVDF and PCTFE), and also those arising from their different families of F-copolymers, such as poly(TFE-*co*-HFP) (FEP), ETFE, and poly(TFE-*co*-PAVE) (PFA).

Grafting the required monomer to introduce the desired function properly has been thoroughly investigated by many authors and recently reviewed [30b]. The corresponding materials offer a wide range of well-architected copolymers involved in many applications, such as biomaterials (e.g. artificial hearts, cardiovascular prostheses), compatibilizing agents, the protection of substrates (e.g. metals), pH-sensitive membranes, membranes for purification of water and fuel cells.

**3.2.3.2. Synthesis of graft copolymers from the ozone-activation of the polymer.** Ozone, commonly written  $\text{O}_3$ , is an inexpensive gas (quite soluble in fluorinated solvents), but it is well-known for environmental concerns. The ozonization (or ozonation) of polymers has been investigated by many authors and was recently reviewed [147]. It allows the activation of a wide range of polymers, mainly polyolefins (polyethylene, polypropylene, PVC) but also PS, poly (dienes), PDMS, polyurethanes and finally copolymers [147].

PVDF containing peroxide initiated the polymerization of poly(ethylene oxide) methacrylate (PEOMA) at  $100^\circ\text{C}$  in NMP from [PEOMA]/[PVDF] with weight ratio ranging from 1:1 to 6:1 [148]. The structures of the resulting PVDF-*g*-PEOMA graft copolymers were investigated by FTIR and XPS,



showing, as expected, that the graft concentration increased with increasing PEOMA macromonomer concentration [148]. In addition, various electrochemical properties of these membranes were studied. These materials exhibited (i) very high capacity of liquid electrolyte uptake (these membranes could absorb 74 wt% of liquid electrolyte—higher than the best ones which absorb 65% in the presence of inorganic fillers [149]); (ii) an ionic conductivity of  $1.6 \times 10^{-3} \text{ S cm}^{-1}$  at 30 °C; (iii) a satisfactory transference number of 0.15, suitable for polymer electrolytes or concentrated solutions [150]; and (iv) electrochemical stability. These properties enabled the membranes to have good prospects for applications in lithium ion rechargeable batteries.

### 3.2.3.3. Activation by electron beam and gamma ray.

3.2.3.3.1. *Introduction.* Radiation induced grafting can also be used for the synthesis of original graft copolymers [138,143–145]. For this method, a polymer endowed with the required mechanical, chemical or thermal properties is irradiated with electron beams or  $\gamma$ -rays (usually emitted from various radioactive isotopes:  $^{60}\text{Co}$  obtained by beaming  $^{59}\text{Co}$  with neutrons in a nuclear reactor, and  $^{137}\text{Cs}$  which is a product of fission of  $^{235}\text{U}$ ) [138,143–145]. Generally, the use of an electron beam enables activation on the surface. Hence, the polymer to be activated can first be processed into thin films. By contrast,  $\gamma$  irradiation is efficient in the bulk of the substrate and thicker films can hence be treated. The irradiation causes free radical centers formed in the polymeric matrix.

3.2.3.3.2. *Types of radiation.* Different types of high-energy radiation are available for use in the grafting process [138–141,144], although crosslinking may occur, as Forsythe and Hill reported [145a] (for example, the radiation-chemical effects in PVDF showed that crosslinking proceeds mainly through an alkyl macroradical). This radiation may be either electromagnetic, such as X-rays and gamma rays, or charged particles, such as beta particles or electrons. The most widely used gamma radiation source is the  $^{60}\text{Co}$  source which emits radiations of 1.17 and 1.33 MeV (mean value: 1.25 MeV).

Radical generation throughout the film thickness is necessary. Fortunately, all of the radiation discussed above have sufficient energy to penetrate into the bulk of fluorinated films, which are usually 25–200  $\mu\text{m}$

thick. This is the advantage of the high-energy radiation grafting over UV-induced photochemical grafting in the presence of a sensitizer (although it introduces an impurity). The UV radiation cannot, however, penetrate into the bulk of the polymeric film. As a result, the grafting involving UV radiation remains confined virtually to the surface layers of a film, leaving a bulk unmodified film. Photochemical grafting is, therefore, interesting for applications where only surface properties of a polymer need to be altered. The physical states of the matrix polymers to be grafted may be films, membranes, fibers, powders, or beads. The irradiation and grafting can be carried out in one step, in two, or in more steps.

This remainder of this sub-section is divided into two parts: (i) investigations on the activation of fluorinated homopolymers followed by the grafting, and (ii) methods starting from the irradiation of fluorinated copolymers, with a subsequent grafting step.

#### 3.2.3.3.3. Activation of fluorinated homopolymers.

3.2.3.3.3.1. *Synthesis of PVDF-g-PM graft copolymers from the irradiation of PVDF Followed by grafting.* This sub-section supplies non-exhaustive examples of syntheses, properties, and applications of graft copolymers starting from the activation of PVDF. Table 5 lists the conditions of irradiation and grafting, leading to PVDF-g-PM graft copolymers.

3.2.3.3.3.1.1. *Synthesis and properties of PVDF-g-PMAAc graft copolymers.* Several authors have chosen to irradiate PVDF in order to graft various monomers (M) for the preparation of PVDF-g-PM graft copolymers. In 1976, Machi et al. [159] synthesized poly(fluoroalkene)-g-poly(acrylic acid) after irradiation of poly(fluoroolefin) films by a 20 Mrad electron beam, followed by immersion into acrylic acid (AAc). The resulting membranes exhibit a low electrical resistance of  $6.2 \Omega \text{ cm}^{-2}$ , compared, for example, to a film that does not contain any AAc ( $10\text{--}15 \Omega \text{ cm}^{-2}$ ).

3.2.3.3.3.1.2. *Synthesis, properties, and applications of PVDF-g-PS and functionalized PVDF-g-PS graft copolymers.* Pertinent surveys on the activation of PVDF were investigated by a Scandinavian team, a Swiss Institute, and an English Laboratory summarized in the following.

(A) *Studies from the Sundholm Laboratory.* This Finnish group [161–163,181–187] synthesized and

Table 5

Fluorinated graft copolymers and their properties compared to those of Nafion<sup>®</sup> membrane, achieved from the irradiation of fluoropolymers (FP) followed by grafting of M monomer, for fuel cell applications

FP	Way of activation	M	d.o.g. (%)	IEC (mequiv. g <sup>-1</sup> )	Properties	Reference
PTFE (film)	Total dose: 20 kGy dose rate: 110 Gy min <sup>-1</sup>	S then sulfonation (ClSO <sub>3</sub> H)	1–31	0.7–0.9	$\sigma$ up to 11.8 mS cm <sup>-1</sup> SFT = 73–140 $\mu$ m	[151]
PTFE	<sup>60</sup> Co (1.3–15.0 Gy h <sup>-1</sup> )	S then sulfonation	Variable	0.4–1.2	Water uptake, good thermal, chemical and mechanical stabilities	[152–155]
PTFE	$\gamma$ rays	S then sulfonation (ClSO <sub>3</sub> H)	Variable	Variable	Variable $\sigma$	[156]
PTFE	<sup>60</sup> Co (1–50 kGy)	4-VP then quaternisation	0.7–13.0	Low specific electr. resistance	High transport number (0.93) and diffusion coefficient, good mech. properties, low specific resistance, AEM	[157,158]
PVDF	e Beam (20 Mrad)	AAc and 4-AS	Variable	Variable	Elect. resist. 4.2 $\Omega$ cm <sup>-1</sup> IEM	[159]
PVDF	$\gamma$ rays (3 Mrad)	S then sulfonation (H <sub>2</sub> SO <sub>4</sub> )	18–30	0.7–1.7	$\sigma$ = 30 ms cm <sup>-1</sup> , Elect. resist. 1.4 $\Omega$ cm <sup>-1</sup> H <sub>2</sub> O uptake 37–60 SFT = 100–111 $\mu$ m	[160]
PVDF	e Beam (20–200 kGy) 175 kV	S then sulfonation (ClSO <sub>3</sub> H)	Variable up to 100%	Variable	$\sigma$ up to 120 Ms cm <sup>-1</sup> 57% swelling rate at 95 °C good thermostability	[161–163]
PVDF (80 $\mu$ m film)	15 Mrad	S then sulfonation (H <sub>2</sub> SO <sub>4</sub> )	18–30	0.68–1.70	37–60% H <sub>2</sub> O uptake $\sigma$ = 20–30 ms cm <sup>-1</sup> SFT 100–111 $\mu$ m, overall cell resistance 6.5 $\Omega$ cm <sup>-2</sup>	[164]
PVDF	<sup>60</sup> Co (6.3 Mrad)	VBC then amination	26	0.68–1.70	8–30 ms cm <sup>-1</sup> 37–60% H <sub>2</sub> O uptake SFT = 100–111 $\mu$ m Alkaline AEM	[165,166]
FEP	<sup>60</sup> Co (10–30 kGy)	AAc	Variable	IEC vs d.o.g.	Resistance vs d.o.g. EWC = 50–65%, variable $\sigma$	[167,168]
FEP	<sup>60</sup> Co (3.5 kGy)	AAc then sulfonation	5–32	0.5–2.8	4–40% H <sub>2</sub> O uptake, stable performances after 100 h at 50 °C	[169]
FEP	<sup>60</sup> Co (6 Mrad)	S then sulfonation (ClSO <sub>3</sub> H)	19	1.39	68% H <sub>2</sub> O uptake, SFT = 78 $\mu$ m	[160]
FEP	<sup>60</sup> Co	S then sulfonation	Variable	Variable	Variable	[170,171]
FEP	60 kGy	TFS then sulfonation	19	1.27	Crosslinking rate 12%, swelling rate 16% in H <sub>2</sub> O at 100 °C, specif. resistance 35 $\Omega$ cm <sup>-1</sup>	[172]
FEP	<sup>60</sup> Co (10–30 kGy)	VBC then amination	3–30	Variable	$\sigma$ = 20 ms cm <sup>-1</sup> , thermal stability	[165,166,173]
ETFE	<sup>60</sup> Co	AAc	Variable	Variable	Mechanical and thermal stabilities, IEM	[167]
ETFE	<sup>60</sup> Co (12.7 kGy h <sup>-1</sup> )	S then sulfonation	Variable	Variable	Variable $\sigma$	[167]
ETFE	<sup>60</sup> Co	S then sulfonation	Variable	1.9–2.0	Variable $\sigma$ , low methanol crossover, good power performance, promising for DMFC	[174]
ETFE	e Beam (1.5 MeV) 80 kGy	S then sulfonation (ClSO <sub>3</sub> H)	Variable	1.39	Crosslinking by DVB, reduction of MeOH crossover	[175]
ETFE	e Beam	STFS	Variable	Variable	IEM for fuel cell	[172]

(continued on next page)

Table 5 (continued)

FP	Way of activation	M	d.o.g. (%)	IEC (mequiv. g <sup>-1</sup> )	Properties	Reference
PFA	e Beam (100–1200 kGy)	S then sulfonation	Variable	Variable	variable mechanical properties and electrochem. properties vs d.o.g.; PEMFC	[176–180]
Nafion	None	None	None	0.67–1.25	37% H <sub>2</sub> O uptake, SFT: 209 μm spec. resist. 12.8 Ω cm <sup>-1</sup> , σ: 50–110 ms cm <sup>-1</sup>	[40,49,73,82]

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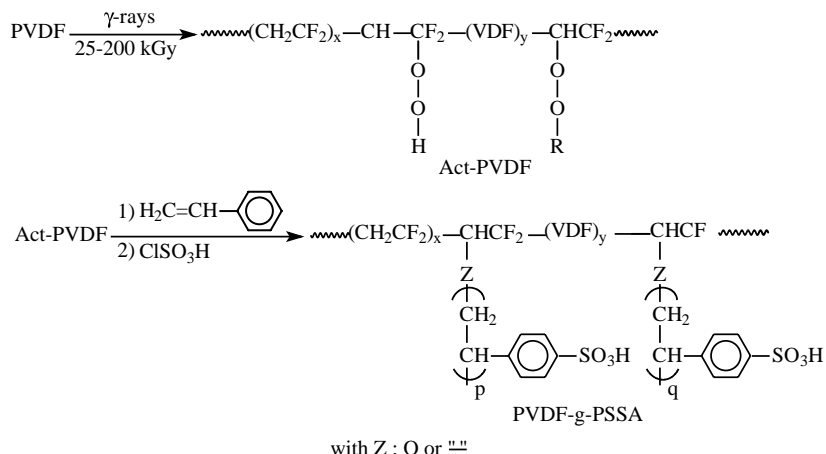
AAC, AEM, 4-AS, DVB, d.o.g., eBeam, EWC, FP, IEC, S, SFT, STFS, 4-VP and  $\sigma$  stand for acrylic acid, anion-exchange membrane, 4-acetoxy styrene, divinyl benzene, degree of grafting, electron beam, equivalent weight capacity, fluoropolymer, ionic exchange capacity, styrene, swollen film thickness, substituted trifluorostyrene, 4-vinyl pyridine and conductivity, respectively.

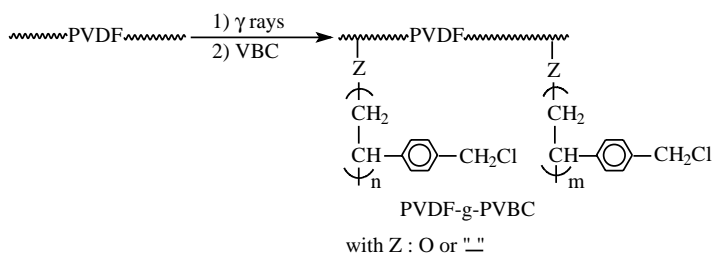
fully characterized novel sulfonated PVDF-*g*-PS (or PVDF-*g*-PSSA) copolymers in a three step-procedure: first, the irradiation of porous films of PVDF by electron beam at various doses (25–200 kGy), followed by the grafting of styrene, and in a final step, the sulfonation of the aromatic ring in the presence of chlorosulfonic acid. Activation of PVDF was carried out under nitrogen atmosphere at an acceleration voltage of 175 kV [161]. As expected, it was observed that the higher the dose-rate and the longer the grafting-time, the higher the degree of grafting (d.o.g.); interestingly, the authors claimed that no homopolystyrene was formed. Then, the PVDF-*g*-PS membranes were immersed in chlorosulfonic acid in methylene chloride for 2–12 min, leading to a degree of sulfonation of 11–71% [161]. Reaction for 2 h with a doubled ClSO<sub>3</sub>H concentration was required to achieve 95–100% of sulfonation. In these conditions,

the authors did not observe any trace of chlorine atom in the PVDF-*g*-PSSA membranes. This procedure is summarized in Scheme 29.

These authors provided evidence on the structure [161,162], thermal behavior [161–163,181] and conductivities (up to 120 mS cm<sup>-1</sup> at room temperature) [161–163,181,182], slightly higher than that of Nafion<sup>®</sup>. Unexpectedly, these authors claimed that the PVDF-*g*-PSSA membranes were stable up to 370 °C under air atmosphere, and to 270 °C in a highly oxidizing atmosphere [162,181] (PS grafts started to decompose from 340 °C [181]).

The grafting reaction of styrene, initiated in the amorphous regions, and at the surfaces of the crystallites in the semi-crystalline PVDF matrix [182], was quite efficient, with a high degree of grafting (50–86%), and with grafts formed both from C–H and C–F branch sites of PVDF. Grafting was

Scheme 29. Synthesis of PVDF-*g*-PSSA graft copolymers [161–163].



Scheme 30. Synthesis of PVDF-g-PVBC graft copolymers after irradiation of PVDF and grafting of vinyl benzyl chloride (VBC) [188].

assumed to take place in the amorphous regions of PVDF [162]. The sulfonation step was realized in high yields (up to 100%), occurring mainly in the *para* position of the phenyl ring. The presence or absence of C–O bond (that could arise from the formation of peroxides) was not mentioned.

These novel films were characterized by Raman [161] and NMR [183] spectroscopies, wide angle X-ray scattering (WAXS), and small angle X-ray scattering (SAXS) [161,162,184]. Tests of swelling in various solvents and in water, and results of conductivity (by impedance spectroscopy) indicated that these films were potential proton exchange membranes for fuel cell applications [163,185]. Indeed, the higher the content of sulfonic acid functions, the higher the conductivity, and these values were enhanced when the crystallinity-rate was decreasing [162].

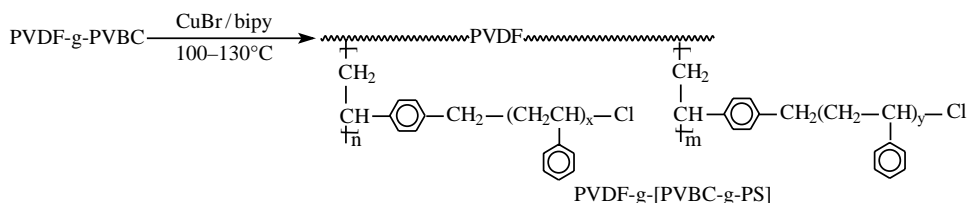
Sundholm's research was well-summarized in a review article [163], including the description and characterization of novel polymer electrolyte membranes for low temperature fuel cells. Membranes made of PVDF-g-PSSA graft copolymers, crosslinked by divinylbenzene (and/or bis(vinylphenyl)ethane) [182,185,186], were compared to non-crosslinked membranes. The authors observed that the ion conductivity of the crosslinked membranes was lower than that of non-crosslinked ones (induced by

the inefficient sulfonation of the crosslinked materials and also by low water uptake at a low degree of grafting). Confocal Raman spectroscopy was used to characterize the PVDF-g-PSSA membranes in fuel cell conditions [187], finding that the crosslinked membranes did not undergo the degradation noted with the non-crosslinking films.

In addition, this group synthesized PVDF-g-PVBC graft copolymers according to the same strategy (also reported in Section 3.2.3.3.3.1.3), where VBC stands for vinyl benzyl chloride (Scheme 30) [188].

These PVDF-g-PVBC copolymers acted as suitable macroinitiators via their chloromethyl side groups in the atom transfer radical polymerization [189] of styrene, with a copper bromide/bipyridine catalytic system, leading to controlled PVDF-g-[PVBC-g-PS] graft copolymers, as in Scheme 31 [188].

The high degree of grafting achieved would not be possible with conventional uncontrolled radiation-induced grafting methods owing to termination reactions. The polystyrene grafts were sulfonated, leading to well-defined PVDF-g-[PVBC-g-PSSA] graft copolymers for use in the design of proton-exchange membranes for fuel cells applications. The highest conductivity measured for these membranes was  $70 \text{ mS cm}^{-1}$ , which is similar to that claimed for Nafion<sup>®</sup>. The SEM/energy-dispersive X-ray results



Scheme 31. Synthesis of PVDF-g-PVBC-g-PS by ATRP of styrene initiated by PVDF-g-PVBC copolymers [188].

showed that the membranes had to be grafted through the matrix with both PVBC and PS to become proton-conducting after sulfonation [188].

(B) *Studies from the Paul Scherer Institute.* Similar investigations were also extensively realized at the Paul Scherer Institute [190,191]. PVDF was activated by  $\gamma$  rays from a  $^{60}\text{Co}$  source (dose of 20 kGy at 1.33 MeV with a dose rate of  $5.9 \text{ kGy h}^{-1}$  at room temperature in air). The grafting of styrene occurred at  $60^\circ\text{C}$ . The PVDF-*g*-PS graft copolymers were sulfonated to produce PVDF-*g*-PSSA as useful ion-exchange membrane for electrochemical applications [190,191]. Additional investigations by this Institute devoted to the synthesis, properties and applications of ETFE-*g*-PM and FEP-*g*-PM graft copolymers are reported in Sections 3.2.3.3.3.3.1 and 3.2.3.3.3.3.2, respectively.

(C) *Studies from the Kronfli Laboratory.* The grafting of acrylate (Acr) onto PVDF was also accomplished by Kronfli's team [192], motivated for possible use in novel lithium batteries. The PVDF-*g*-poly(Acr) graft copolymer led to an improvement in the adhesion of composite electrode to current collectors, and to an increase of electrolyte solvent uptake. Graphite-LiCoO<sub>2</sub> cells containing such modified PVDF-*g*-PM showed good rate performance and stable cycle life. The same group also achieved an improved process to prepare microporous membranes for solid electrolytes for Li cells by casting the graft copolymer solution.

(D) *Studies of Flint and Slade.* In a similar strategy, Flint and Slade [164] synthesized PVDF-*g*-PSSA graft copolymers, and investigated the physical and electrochemical properties of the resulting membranes. The grafting occurred in styrene at 80, 90 and  $100^\circ\text{C}$ . These membranes were involved as MEA used in fuel cell conditions. The conductivity of the membrane containing 30% graft was  $30 \text{ mS cm}^{-1}$  with an overall resistance of  $6.5 \Omega \text{ cm}^{-2}$ . The authors compared the physical and electrochemical properties of these obtained PVDF-*g*-PSSA graft copolymers with those of FEP-*g*-PSSA and Nafion<sup>®</sup>.

3.2.3.3.3.1.3. *Synthesis and applications of PVDF-*g*-poly(vinyl benzyl chloride) graft copolymers.* More recently, by grafting vinyl benzyl chloride (VBC) onto either of two grades of PVDF activated by  $\gamma$ -rays  $^{60}\text{Co}$  at a dose of 6.3 Mrad at  $70^\circ\text{C}$  for 1 week, Danks et al. [165] synthesized PVDF-*g*-PVBC graft

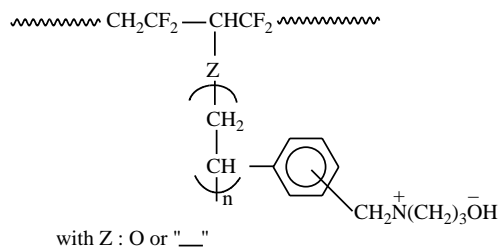


Fig. 3. Formula of PVDF-*g*-poly(vinyl benzyl ammonium chloride) graft copolymers for anionic exchange membranes.

copolymers. According to the grade, the degree of grafting was either 38 or 54%, while the average thickness was  $54 \mu\text{m}$ . The chloromethyl end groups of the grafts then underwent an amination reaction into benzyl trimethylammonium (BTMA) hydroxide [165] or BTMA chloride (BTMAC) [166] for anion exchange membrane applications (Fig. 3).

These quaternary ammonium side groups allowed these novel membranes to be used as alkaline fuel cells for portable applications, thanks to the conductivity of hydroxide ions. Unfortunately, this last step led to PVDF-*g*-PBTMAC graft copolymers too brittle for use because of degradation of the polymer backbone by the expected dehydrofluorination of PVDF. Hence, the resulting materials, which possessed lowered ion exchange capacity ( $\text{IEC} = 0.31$  and  $0.71 \text{ mequiv. g}^{-1}$ ), was unsuitable for use as membranes for fuel cells or electrochemical devices. These authors used the same strategy with a perfluorinated copolymer, a poly(TFE-*co*-HFP) or FEP copolymer which is not base-sensitive, to obtain a membrane endowed with a suitable IEC of  $1.0 \text{ mequiv. g}^{-1}$  (Section 3.2.3.3.3.3.2).

3.2.3.3.3.2. *Synthesis, properties, and applications of PTFE-*g*-PM graft copolymers.* The sensitivity of PTFE to ionizing radiation has been known since the early 1950s [138]. In fact, radiolysis of PTFE has extensively been studied in various books or reviews [138–141,193,194].

Indeed, irradiated PTFE can still be used for grafting polymerization several years after it has been exposed [193]. The easy availabilities of PTFE and of functional vinyl monomers led to many investigations on the synthesis of PTFE-*g*-PM graft copolymers, pioneered by Chapiro [138]. Many monomers were used ranging from acrylic acid [195], methyl



trifluoroacrylate (MTFA) [196], styrene [151–156], vinyl pyrrolidone [157,158,197], and in a lesser extent, *N*-vinyl pyrrolidone (NVP) [198]. Usually, decrease of the crystallinity content and of melting point of PTFE are noted.

A Bulgarian group [157,158] extensively developed research on the grafting of fluoropolymers (mainly PTFE), reproducing some of Chapiro's results [138]. Kostov's team observed that  $T_g$  and the enthalpies of melting and of crystallization decreased with increasing degrees of grafting (d.o.g.) of acrylic acid (AAc) or vinyl pyrrolidone (VP) (Table 5). The resulting graft copolymers were used not only for ionomers and ion exchange membranes, but also for enzyme biosensors [195b]. Nasef et al. [152–155] investigated the synthesis of PTFE-*g*-PSSA graft copolymers for proton exchange membranes, followed by structural studies and evaluation of thermal [152], chemical and mechanical stability [152–155]. Studies on the grafting kinetics were also attempted [158,195b].

More recently, Liang et al. [151] used a similar strategy ( $^{60}\text{Co}$  beam, under 20 kGy at 110 Gy/min) to prepare PTFE-*g*-PSSA graft copolymers for fuel cell membranes. Grafting was achieved directly on 70  $\mu\text{m}$  thick films having  $T_g$  of 117 °C, with degrees of grafting ranging between 0.9 and 31.2%. These materials were evaluated for the ion-exchange capacity, water uptake, dimension charge percentage, and specific resistance vs the degree of grafting. They obtained grafted copolymers with  $T_g$ , thicknesses and resistances ranging between 117.5 and 125 °C, 73 and 140  $\mu\text{m}$ , and 11.9 and 48.6  $\Omega\text{ cm}^{-2}$ , respectively. However, these membranes start to suffer from oxidative degradation from 60 °C. These three teams studied the effect of grafting and the experimental conditions on the d.o.g., the kinetics of grafting and the properties of the grafted films (Table 5).

#### 3.2.3.3.3. Activation of fluorinated copolymers followed by the grafting of various monomers.

Various VDF containing grafted copolymers have already been developed [30b], but none have yet been utilized in fuel cell applications. By contrast, those containing TFE base-units are potential candidates for these applications. The following sub-sections consider three examples: poly(*E-co*-TFE), poly(TFE-*co*-HFP) and poly(TFE-*co*-PPVE) copolymers where E,

HFP and PPVE stand for ethylene, hexafluoropropylene and perfluoropropyl vinyl ether, respectively.

3.2.3.3.3.1. *Activation of poly(E-co-TFE) copolymers followed by grafting.* Copolymers containing ethylene and TFE, called ETFE copolymers are commercially available, produced by DuPont (Tefzel<sup>®</sup>), Asahi Glass (Aflon<sup>®</sup>), Daikin (Neoflon<sup>®</sup>), and in the past Ausimont (Halon<sup>®</sup>) [30a,199].

Many surveys on the synthesis of ETFE-*g*-poly(M) have been carried out involving a number of monomers M: acrylic acid [167,168,200], ethyl acrylate [201], methyl acrylate [201], dimethylaminoethyl methacrylate [202], *N,N*-methylene-bis-acrylamide [203], NVP [202], 1-vinyl imidazole [202], styrene [167,174,175,204–206] and trifluorostyrene [172]. Acrylic acid, styrene and trifluorostyrene} have been used for the preparation of ion exchange membranes (IEM) (Table 5). To improve the ion-exchange capacity (IEC), some of ETFE-*g*-PAAc membranes were sulfonated [200a], leading to both sulpho- and carboxyl groups and an increase of the IEC (1.75 mequiv.  $\text{g}^{-1}$ ). Some of IEMs were suitable for fuel cell applications after sulfonation of ETFE-*g*-PS graft copolymers [167,174,175,204–206] (Table 5).

Various correlations [167] between the membranes properties and compositions, IECs and their respective fuel cell performances have been reported [167, 168], with most of the work in this area accomplished by Horsfall and Lowell [167,168,204,205] or at the Paul Scherer Institute [191,206,207]. The former team showed that oxygen diffusion coefficient and permeability increased when decreasing equivalent weight, while the proton conductivity also increased with the water content [205]. These laboratories also noted that the new types of membranes perform well in comparison to the Nafion<sup>®</sup> standard [204]. Some membranes were found to have stable resistivities at high current density and high power density, greater than 1  $\text{A cm}^{-2}$  [167]. Scherer's group also investigated on the surface properties and has reported the increasing total surface energy series, as follows: ETFE film—irradiated film < grafted film < sulfonated membrane. Interestingly, this group compared the performances of the membranes prepared from ETFE-*g*-PSSA, PVDF-*g*-PSSA, and FEP-*g*-PSSA and found that the first exhibited better mechanical properties, attributed to: (i) the higher molecular weight of ETFE; (ii) better compatibility of ETFE

with the graft component, and (iii) the reduced extent of radiation—induced chain scission occurring on ETFE [191,195,206,207].

3.2.3.3.3.2. *Activation of poly(TFE-co-HFP) or FEP, followed by grafting.* FEP (or fluorinated ethylene–propylene) resin is a linear, semicrystalline fluoroplastic containing TFE and HFP base units [30a, 208]. The introduction of a trifluoromethyl side group disrupts the chain packing and results in a decrease in crystallinity (from 98% for PTFE to 70% for FEP). The mole percent of HFP may vary depending on the grade of the resin, but typically is about 8.5 mol%.

Early investigations on the radiation chemistry of FEP were achieved by Florin and Wall [209]. It is known that FEP undergoes a degradation when it is irradiated in vacuum below its  $T_g$  (80 °C) [30a,145, 208]. Forsythe and Hill [145] reviewed the influence of the intensity of the dose on the activation, crosslinking or degradation of FEP. They interpreted zero strength time (ZST) measurements to conclude that an initial dose of about 160 kGy induced crosslinking first, followed by chain scissioning.

Lovejoy et al. [210] found that  $CF_4$  was the major gaseous radiolytic product in e-beam irradiation of finely divided FEP resin (containing 9 mol% HFP). This gas was generated from the recombination of  $\cdot CF_3$  and  $F\cdot$  radicals arising from the radiochemical cleavage of the  $CF_3$  side groups. With higher dose (2000 kGy)  $\gamma$ -radiolysis of FEP, Rosenberg et al. [211] demonstrated that FEP undergoes chain scission when irradiated at room temperature.

FEP has been grafted successfully by a number of monomers: acrylic acid [167–169,212], MMA [171], styrene [160,170,171,173,213,214], divinyl benzene [177–180], substituted trifluorostyrene [172], and vinylbenzyl chloride [165,166,173]. In addition, useful crosslinking agents such as divinyl benzene [175,214] or *N,N*-methylene-bis-acrylamide [203] were grafted to enhance the mechanical properties of the membranes. As above, most investigations were developed on the synthesis of FEP-*g*-PS by Horsfall and Lowell [167,204,205], Nasef et al. [171,213], Slade's team [165,166,173], and the Scherer group [170,206,207,214], as precursors of novel FEP-*g*-PSSA (after sulfonation of the aromatic rings) (Table 5). These well-defined FEP-*g*-PSSA copolymers were rather stable (the desulfonation occurring from 200 °C) and were used as novel proton exchange

membranes. Rouilly et al. [170] reported with a d.o.g. higher than 30%, specific resistivity values as low as 2  $\Omega$  cm (at 20 °C) were measured, lower than that of Nafion<sup>®</sup> 117 (12  $\Omega$  cm). Horsfall and Lovell [167, 168] presented correlations between the d.o.g., the IEC, and the equilibrium water content for materials prepared from various fluorinated (co)polymers, such as PVDF, PTFE, FEP, ETFE, and PFA.

Danks et al. [165,166] compared the chemical and thermal behaviors of PVDF-*g*-PVBC and FEP-*g*-PVBC graft copolymers. They showed that the former underwent a dehydrofluorination in the functionalization step (amination), but this step was successfully achieved for the FEP-*g*-PVBC graft copolymer, for which ammonium sites were introduced for potential membranes in alkaline fuel cell applications [165, 173]. Although, the ion exchange capacity decayed rapidly at 100 °C, amino FEP-*g*-PVBC graft copolymers were stable at 60 °C, for at least 120 days. The conductivity values at room temperature of these graft copolymers were satisfactory (0.01–0.02 S  $cm^{-1}$ ).

3.2.3.3.3.3. *Poly(TFE-co-perfluoropropylvinylether), poly(TFE-co-PPVE) or PFA.* Copolymers of TFE and perfluoroalkyl vinyl ether (PAVE,  $CF_2=CFOC_nF_{2n+1}$ ;  $n = 1$  and principally  $n = 3$ ) are called PFA [30a,215]. As expected, melting point of PFA, ranging from 305 to 315 °C (according to the PAVE content), is lower than that of PTFE. By contrast to the huge attention on the synthesis of graft copolymers starting from the irradiation of ETFE or FEP, there has been relatively little work on the activation of PFA. In addition to a few studies dealing with the crosslinking of PFA via radiation in an electron beam [216], the groups of Nacef [176–180] and Cardona [217] worked on the synthesis of PFA-*g*-PM comb-like copolymers by irradiation of PFA followed by grafting. The former team [176–180] investigated the irradiation of PFA followed by the grafting of styrene to achieve PFA-*g*-PS graft copolymers, which were then sulfonated to yield PFA-*g*-PSSA as precursors of fuel cell membranes (Table 5). These authors optimized the conditions of activation/grafting in terms of the monomer concentration, irradiation dose and dose-rate, and the choice of solvent chosen for the grafting process ( $CH_2Cl_2$  was found to greatly enhance the grafting process) [176]. As in the above cases, the higher the d.o.g., the greater the monomer



concentrations until it reached the highest styrene concentration of 60 vol%.

Nasef et al. [177–180] extensively studied the morphology and various electrochemical, thermal and physicochemical properties of these membranes and showed that these properties were dependent upon the d.o.g. The morphology of the membrane plays an important role in the chemical degradation of the membrane [179]. These authors also studied the physicochemical properties: swelling behavior, ion exchange capacity, hydration number, ionic conductivity, and water uptake, which increased with increasing d.o.g., just as in the thermal and chemical stabilities [178]. These membranes were also characterized by FTIR, X-ray diffraction, XPS [179,180] and mechanical properties (tensile strength and elongation percentages). They also noted that the degree of crystallinity decreased with an increased grafting, and that both the tensile strength and elongation decreased with increasing d.o.g. [177]. In addition, XPS was used by the authors to monitor the membrane degradation after fuel cell tests to show that oxidation degradation took place in the PFA-*g*-PSSA membrane during fuel cell tests, mainly due to chemical attack at the tertiary H of  $\alpha$ -carbon in PS side chains [177,179,180].

### 3.2.4. Conclusion

A wide range of different fluorinated polymer-*g*-poly(M) graft copolymers have been synthesized by activation of fluoropolymers (mainly by gamma rays, or electrons) followed by grafting, and used as novel PEMFCs. Their mechanical, physico-chemical, thermal, and electrochemical properties have been studied. The quality of the well-defined fluorinated copolymers depends upon the nature of the activation of the fluoropolymer and the compromise to generate as many radicals as possible without affecting the properties of the fluoropolymeric backbone. This is still a challenge. Both basic and applied research has been carried out, including investigations on the assessment of the concentration of macroradicals (peroxides or hydroperoxides) and their half-lives, and specific properties for several applications (fuel cell membranes, compatibilisers, biomaterials, etc.), respectively.

Various fluoropolymers, in different states (powders and films), have been activated, but most studies have utilized PVDF, PTFE, ETFE, FEP, or PFA. A

number of articles have reported comparison of membranes prepared under similar conditions with these (co)polymers. For example, considering the isomers PVDF and ETFE, Danks et al. [165,166] noted that amination of PVDF-*g*-PVBC led to dehydrofluorination, with a drastic influence on properties. Conversely, ETFE was a better candidate, that offered potential membranes for alkaline fuel cells [165,166]. The comparison of grafting monomers to various polymeric substrates and the performance of the resulting graft copolymers has been examined by a number of teams [168,184,204]. Correlations between the d.o.g., IEC and equilibrium water content were shown to be independent of the chemical nature of the starting fluorinated polymer [168].

### 3.3. Reinforced polymers and hybrid polymers in fuel cells

Three principal types of reinforcement are available for polymeric membranes:

- (i) use of a non-conducting polymer to improve the mechanical properties;
- (ii) incorporation a conducting or a non-conducting inorganic phase to improve thermal stability along with conductive and water uptake properties;
- (iii) incorporation of a compound which is easily oxidized, to limit the degradation of the conducting polymer.

#### 3.3.1. Reinforcement by a polymer

The appropriate mechanical properties for a membrane to be used in a fuel cell may be obtained by impregnation of a non-conductive porous substrate by a solution of a functionalized polymer. Usually, the porous substrate is made of an organic polymer that exhibits both a mechanical and a chemical resistance. PTFE could be a good candidate but its use is limited by poor adhesion onto the conducting polymer. In addition, PTFE increases the electrical resistance of the membrane.

Composite perfluorosulfonic acid membranes with reinforcement either via a porous PTFE sheet in the form of ultrathin membranes (from Gore [218]), or by micro PTFE fibril (from Asahi Glass Co. [219]) make

possible the development of thin membranes. Nafion<sup>®</sup> impregnation of other substrates and other strategies and properties of membranes have been well-reviewed by Li et al. [4], and were discussed at the ‘Solid State Protonic Conductors 12’ Conference [220]. In addition, Ishisaki and Kinoshita [221] claimed the elaboration of a polymer reinforced by a fluorinated copolymer in fibrillar state. The copolymer, containing at least 95% PTFE (the reinforcing polymer), and the conductive fluoropolymer were mixed and extruded as droplets which were sputtered and processed into membranes. These membranes exhibit weaker resistance to current-flow and a higher power than with a porous substrate. (After 1000 h-use at 80 °C, the current density through the membrane was 0.2 A cm<sup>-2</sup>.) However, the minimal thickness of 100 or 200 μm may limit the fuel cell applications of such membranes.

### 3.3.2. Composite membranes

Organic–inorganic composites represent a useful approach. Li et al. [4] or a recent conference [220] reported interesting reviews or presentations on the preparation of original high temperature-DMFC membranes arising from composites made of fluoropolymers doped with fillers or solid inorganic proton conductors (zirconium hydrogen phosphates, hygroscopic oxides, heteropolyacids, (HPA), phosphotungstic acid (PWA), etc.). These membranes were tested at temperatures up to 120 °C under ambient pressure and up to 150 °C under pressure of 3–4 atm.

Preparing organic/inorganic hybrid polymers is an interesting way to improve the thermal stability of membranes. Three alternatives are possible to incorporate silica into organic matrices.

- (i) formation of two interpenetrating network (organic and inorganic);
- (ii) elaboration of a silica gel by acidic catalysis around a polymeric film;
- (iii) ‘copolymerization’ of an organic monomer with a silylated derivative.

The use of polysiloxanes gives copolymers with lower  $T_g$ , increased thermal stability of the hybrid system and decreased methanol crossover. Silica particles increase the water retention and hence the protonic conduction at high temperature.

**3.3.2.1. Nafion<sup>®</sup>/Silica system.** Jung et al. [222] have reported the synthesis of a Nafion<sup>®</sup>/Silica composite membrane obtained via the sol–gel acidocatalyzed of tetraethoxysilane (TEOS) in a Nafion<sup>®</sup> 115 membrane (equivalent weight 1100). The amount of TEOS impregnated in the membrane varied with the reaction time. These authors noted that the water absorption of the composite membrane increased with the silica content, while the proton conductivity decreased. The silica particles inhibited the proton transfer. The methanol permeability of that membrane was that of Nafion<sup>®</sup>, and the performance of the membrane in fuel cell improved up to a silica content of 12.4%, leading to potential applications in DMFC; for 0.5 V, the current density at 125 °C was 650 mA cm<sup>-2</sup>.

**3.3.2.2. Nafion<sup>®</sup>/silica/phosphotungstic acid (PWA) system.** The impregnation of hybrid membranes by heteropolyacids such as phosphotungstic acid (PWA) or silicotungstic acid is used to increase the conductivity [223]. Hence, these heteropolyacids exhibit interesting conductivities (ca. 0.02–0.10 s cm<sup>-1</sup>) at room temperature. PWA must be immobilized in a silicagel because of its high stability, which could induce its dissolution in water. Hybrid Nafion<sup>®</sup>/SiO<sub>2</sub>/PWA have higher conductivities than that of the polymer itself, and at rather low humidity rate, the resulting membrane is claimed more mechanically and thermally stable than Nafion<sup>®</sup> thanks to the crosslinked structure of silica.

**3.3.2.3. Nafion<sup>®</sup>/zirconium phosphate.** Bauer and Willert-Poroda [224] obtained Nafion<sup>®</sup> 117 membranes filled with zirconium phosphate, characterized by various techniques (cryo scanning electron microscopy, dynamic mechanical analysis and X-ray diffraction). These authors noted that the water content of the membranes was increased by the fillers and a strong influence of the filler concentration on both the mechanical properties and the glass transition temperature. A decrease of the methanol permeation was also observed. Zirconium phosphate also behaved as stabilizers for the polymeric matrix.

**3.3.2.4. Miscellaneous.** As with Nafion<sup>®</sup>, other sulfonated hydrogenated heterocyclic polymers have been hosts for various fillers such as phosphoric acid [225], for sulfonated poly(arylene ether sulfone) [226]

or sulfonated polybenzimidazole [226] and even PTFE [227]. Other novel composite membranes have been developed by Prakash et al. [228] from the blend of PVDF and poly(styrene sulfonic acid), with encouraging conductivities.

### 3.3.3. Hybrid membranes

Recently, hybrid membranes have been prepared by casting a homogeneous solution prepared by sonicating a dispersion of PWA and SiO<sub>2</sub> particles in a solution of 5% Nafion<sup>®</sup> [223]. The membrane could be compressed to improve its mechanical stability. Analysis of the microstructure by SEM showed that the silica and PWA particles did not gather into aggregates, but they were uniformly distributed in the membranes. By X-ray analysis, the authors showed that the presence of SiO<sub>2</sub> increased the crystallinity of the membrane, but it was lowered in the presence of PWA. The thermal stability was improved, up to 350 and 340 °C for Nafion<sup>®</sup>/SiO<sub>2</sub> and Nafion<sup>®</sup>/SiO<sub>2</sub>/PWA, respectively, about that of Nafion<sup>®</sup>, which decomposes above 320 °C. Thanks to the hydrophilic effect of both fillers, the water uptake was increased with SiO<sub>2</sub> (34%) and SiO<sub>2</sub>/PWA (38%), about that of Nafion<sup>®</sup> (26%). The electrochemical performance of these hybrid membranes in cells was lower than those of Nafion<sup>®</sup> for the low range of temperatures, but the conductivity values were greater for higher temperatures [223]. However, the roughness of silylated derivatives weakened the membranes/electrode contact. In addition, Staiti et al. [4,229] recast Nafion<sup>®</sup> membranes from a blend of Nafion with silica-supported PWA and silicotungstic acid. At 145 °C in fuel cell conditions, maximum power densities of 400 and 250 mW cm<sup>-2</sup> were observed in O<sub>2</sub> and air, respectively.

### 3.3.4. Nafion<sup>®</sup>/sulfonated alkoxysilanes

The DuPont de Nemours Company [230] claimed the modification of TFE/perfluorovinylalkylsulfonate fluoride copolymers by alkylsiloxanes [(RO)<sub>3</sub>SiRR<sub>F</sub>SO<sub>2</sub>F]. Nafion<sup>®</sup>-type membranes swollen in protic solvents reacted with these functional silanes. The hydrolysis of alkoxysilanes enables the condensation that produces a network strongly linked to the polymeric matrix. The chains were then crosslinked, yielding a 3D-stability of the polymeric network.

The conductivity values were ranging between  $5.2 \times 10^{-2}$  and  $0.130 \text{ S cm}^{-1}$ .

### 3.3.5. Polymers stabilised by a reducing colloid solution

A stable suspension of a noble metal may be added to the polymeric matrix to improve the chemical stability of electrolyte membranes, especially against oxidation [231]. Indeed, in use condition, a noble metal can be oxidized more easily than the polymer in the membrane, thereby protecting the polymer. The most used metals are palladium, platinum, rhodium, ruthenium and iridium. Nafion<sup>®</sup> can also act as surfactant for the dispersion [231].

### 3.3.6. Multilayer membranes

Various authors have prepared multilayer membranes from hydrogenated polymers, but few surveys exist involving such a system with fluoropolymers. Park et al. [232] prepared a trilayer membrane from a copolymer matrix composed of a poly(VDF-co-HFP) copolymer doped with a 5% Nafion<sup>®</sup>/hydrated tungstic phosphoric acid solution. This constitutes the central thickness of the membrane (60 μm). Then, a 5% Nafion<sup>®</sup> solution was deposited on each side to obtain a trilayer membrane of 70 μm. Finally, that membrane was pressed and laminated to obtain a composite membrane of 30 μm thick. The Nafion<sup>®</sup> layer deposited on both sides of the membrane improved the conductivity at the membrane/electrode interface and also limits the oxidation of hydrogen on the central polymer. Furthermore, Nafion<sup>®</sup> acts as an adhesive to insure better contact between the membrane and the electrode [232]. Such composite membrane allows to limit the methanol crossover for its use in DMFC which is the main drawback of that standard polymer.

## 4. Conclusions

Fluoropolymers are used in many high-tech fields and their good characteristics also enable their use in fuel cell membranes. Indeed, the fluorine atoms bring interesting properties such as: (1) the improvement of the thermal, chemical and oxidizing stabilities of the resulting (co)polymers and, to some extent, the mechanical properties; (2) the acid behavior of

a sulfonic acid function is enhanced when a fluorinated group is adjacent to it, allowing the resulting membrane to exhibit good protonic conductivities.

This review provides an up-to-date summary of the syntheses, properties, and applications of membranes for fuel cell applications. Various main routes have been successfully used to produce fluoropolymers of controlled architectures, basically falling into two main families:

- (a) Those achieved from the direct radical copolymerization of functional groups (i.e.  $\text{SO}_2\text{X}$ , with  $\text{X}=\text{F}$ ,  $\text{ONa}$ ,  $\text{OK}$ ,  $\text{OH}$ , or  $\text{CO}_2\text{H}$ ,  $\text{P}(\text{O})(\text{OH})_2$ ) with commercially available fluoroalkenes (TFE, VDF, HFP, CTFE, etc.). Most work has been achieved on aliphatic copolymers, and some are already produced on pilot or industrial scales, in contrast to fluorinated aromatic copolymers, for which some research has been carried out (except for the BAM3G membrane);
- (b) The chemical modification by irradiation of fluoropolymers (PTFE, PVDF, ETFE, FEP, and PFA) followed by grafting of proton-exchange monomers or polystyrene (PS post-functionalizable into sulfonic acid PS). The obtained copolymers seem to suffer from oxidizing decomposition, concomitant to the thermal degradation. Although some conductivity values seemed interesting, the presence or absence of the oxygen atom as a link between the polymeric backbone and the grafts is sometimes not mentioned. In addition, the chemical modification needs a special, heavy and expensive equipment to enable the irradiation, and the industrial production is probably difficult to achieve.

However, the development of fluorinated materials for electrolytes for fuel cells requires the synthesis of original functional fluorinated monomers to obtain new polymers and to optimize the characteristics of existing polymers in terms of molecular weight, crosslinking, new functional groups (e.g. too few polymers bear phosphonic acid function) formation of hybrid or composite membranes or those made of multilayers. Nevertheless, although recent developments seem encouraging [49], in spite of its cost, permeability to methanol and poor recyclability,

Nafion<sup>®</sup> seems to be the only fluorinated copolymer currently available that exhibits the mechanical, chemical and proton exchange properties useful for membranes for fuel cells. This continues to motivate scientists to pursue such exciting research to find out new alternatives to Nafion<sup>®</sup>.

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