Functionalized fluoropolymers for fuel cell membranes

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A Functionalized fluoropolymers for fuiel cell membranes: *Novel fluorinated copolymers based on commercially available fluoroalkenes tetrafluoroethylene (TFE), vinylidene fluoride (VDF) and chlorotrifluoroethylene (CTFE) with various fluorinated and non-fluorinated comonomers were synthesized by radical copolymerization either in bulk, solution and emulsion. TFE functional copolymers containing vinyl perfluoroethers with sulpho- or carboxylic pendant groups were used as proton exchange membranes at low temperatures. VDF based copolymers were synthesized by iodine transfer controlled radical polymerization with hexafluoropropene (HFP) and -trifluoromethacrylic acid (MAF). -Diiodoperfluoroalkanes were used as the chain transfer agents (CTAs) and according to the CTA concentrations in the feed, molecular weights were ranging from 2,000 to 220,000 g/mol. The terpolymers were functionalized by chemical modification with heterocyclic benzimidazoles using Eaton's catalyst or with aromatic sulphoacides by Mitsunobu reaction. On the basis of functionalized CTFE copolymers containing vinyl ether imidazole or aromatic sulphoacids, original medium temperature (90-200 ^{0}C) membranes for fuel cells were obtained.*
The main properties of the membranes synthesized, such as: chemical inertness, decomposition and glass transition temperatures, proton and dual conductivities, water uptake and ion-exchange capacity were also investigated.

Key words: *functionalized fluorinated copolymers, synthesis, properties, membranes for fuel cells*

INTRODUCTION

Fluorinated functional polymers [1] exhibit remarkable properties (thermal and oxidative stabilities, chemical inertness, low refractive index, good surface properties, etc) that enable them to find numerous applications in high tech fields: aerospace, energy, automotive industries, optics, microelectronics, and engineering.

Fluoropolymers for energy are nowadays seeing an enormous growth in both their number and variety. Although most membranes for fuel cells are made from perfluorosulfonic acid polymers such as Nafion®, Flemion®, Hyflon®, Fumion®, M® membranes, or Aciplex® [2-4], produced from the radical copolymerization of tetrafluoroethylene (TFE) with aliphatic perfluorinated vinyl ethers, few have been achieved from aromatic functional fluoropolymers [5-6].

The objectives of this presentation was to synthesize a new generation of original membranes prepared from aliphatic fluorinated copolymers incorporating fluoromonomers for alkaline, protonic and quasi-anhydrous membranes.

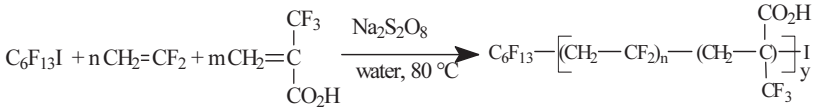
EXPERIMENTAL

Vinylidene fluoride (VDF), hexafluoropropene (HFP) and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium. α-Trifluoromethacrylic Acid (MAF) was kindly supplied by Tosoh F- Tech Company (Shunan, Japan). The NMR spectra were recorded on Bruker AC 200 and AC 250 instruments, using deuterated acetone as the solvent and TMS (or $CFCl_3$) as the references for ^{1}H (or ^{19}F) nuclei.

Infrared spectra were recorded on a Nicolet 510P Fourrier Transformed spectrometer from KBr pellets. Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer. Thermogravimetric analyses were performed with a Texas Instrument TGA 51-133 apparatus in air at a heating rate of 10°C.min^{-1} from room temperature up to a maximum of 600°C. Size Exclusion Chromatography (SEC) analyses were carried out in tetrahydrofuran at 30°C, at a flow rate of 0.8 mL/min, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer.

RESULTS AND DISCUSSION

The syntheses of a new generation of original membranes prepared from aliphatic fluorinated copolymers (Scheme 1) incorporating chain transfer agent (CTA) and fluoromonomers such as vinylidene fluoride (VDF, $F_2C{=}CH_2$), -trifluoromethacrylic acid (MAF), and hexafluoropropene (HFP, $F_2C{=}CFCF_3$), was provided according to the following reaction :



Scheme 1: Free emulsifier iodine transfer copolymerization of VDF with α-trifluoromethacrylic acid (MAF) in the presence of $C_6F_{13}I$ as the chain transfer agent.

1. Iodine transfer copolymerization (ITP) of VDF with α-trifluoromethacrylic acid (MAF)

Poly(fluoroolefins) are usually synthesized in emulsion or suspension radical polymerization of fluoroalkenes [1] in the presence of surfactants. More recent works focus on the original radical copolymerization in emulsion of vinylidene fluoride (VDF) with α - trifluoromethacrylic acid (MAF). That reaction was initiated with sodium persulfate at 80 °C and was carried out in the presence of 1-iodoperfluorohexane, 1,6-diiodoperfluorohexane or 1,4-diiodoperfluorobutane as the chain transfer agents (CTAs) making this polymerization controlled (CRP) [i.e. i) the experimental molecular weights are close to the targeted ones [7], ii) the polydispersity indexes are narrow (1.1 to 1.6 for CRP in contrast to 2.2-10 for conventional radical polymerization)] (Table 1).

Table 1. Iodine transfer copolymerization of VDF and MAF in the presence of various chain transfer agents (CTAs) $C_6F_{13}I$ or IC_4F_8I. Experimental conditions and results

a- $R_0 = [CTA]_0/[M]_0$; b- number of MAF units in copolymer; c- number of VDF units in copolymer; d- M_n, ^{19}F NMR = $n^{MAF} \times 140 + n^{VDF} \times 64 + M_{CTA}$, with M_{CTA} is the molar mass of CTA, e- $M_{n,\ targeted} = 1/R_0 \times$ (composition of copolymer $^{PMVE} \times 166$ + composition of copolymer $^{VDF} \times 64$) + M_{CTA}, with M_{CTA} is the molar mass of CTA

CTA	Molar feed (mol%)		Composition of copolymer (mol%)		R_0 [a]	Yield (%)	n^{MAF} [b]	n^{VDF} [c]	$M_{n,\ Targeted}$ (g/mol)	$M_{n,\ ^{19}F\ NMR}$ (g/mol)
	VDF	MAF	VDF	MAF						
IC_4F_8I	85	15	90	10	$3.3\ 10^{-3}$	70	27	243	22,500	20,000
IC_4F_8I	85	15	92	08	0.05	60	2	18	1,900[e]	1,850[d]
$C_6F_{13}I$	85	15	93	07	0.10	90	1	8	1,200[e]	1,100[d]
IC_4F_8I	40	60	55	45	0.01	50	42	46	11,000[e]	9,200[d]

The results have shown that the radical copolymerization (and terpolymerization) of VDF and MAF (and HFP) was successfully achieved in emulsion in good yields (60-90 %) even without any surfactant. Interestingly, the obtained emulsions were stable for several

months leading to monodispersed particles sizes of ca. 100 nm. In addition, the experimental molar masses close to targeted one, showing certain control of that radical copolymerization.

2. Characterization of poly(VDF-ter-MAF-ter-HFP) terpolymers

The mol % of VDF, MAF and HFP units incorporated in the terpolymers were assessed according to the following equations (Eq.1a-1c) from the integrals of the characteristic signals of ^{19}F NMR (Figure 1):

$$\text{Mol \% of VDF in the terpolymer} = x_{VDF} = \frac{I_A}{I_A + I_B + I_C} \times 100 \qquad \text{(Eq.1a)}$$

$$\text{Mol \% of HFP in the terpolymer} = x_{HFP} = \frac{I_B}{I_A + I_B + I_C} \times 100 \qquad \text{(Eq. 1b)}$$

$$\text{Mol \% of MAF in the terpolymer} = x_{MAF} = \frac{I_C}{I_A + I_B + I_C} \times 100 \qquad \text{(Eq. 1c)}$$

$$I_A = \frac{I_{-91.1} + I_{-93.8} + I_{-110.1} + I_{-113.4} + I_{-115.7}}{2}$$

$$I_C = \frac{I_{-68.1}}{3} \qquad I_B = \frac{I_{-71.2} + I_{-74.8}}{3}$$

The molecular weights, M_n, were assessed as follow:

$$M_n = M_{CTA} + (\#VDF) \times 64 + (\#HFP) \times 150 + (\#MAF) \times 140, \qquad \text{(Eq. 2)}$$

where # represents the number of monomeric unit. Molecular weights of these of poly(VDF-ter-MAF-ter-HFP) terpolymers were ranging between 2,000 and 220,000 g/mol according to the initial amount of iodinated CTA. It was noted that emulsion polymerization led to higher M_n than from solution and that the lower the CTA concentration, the higher the M_n.

The kinetics of copolymerization of VDF and MAF under ITP led to the assessment of the reactivity ratios of both comonomers to be r_{VDF} = 1.6 and r_{MAF} = 0 at 80 °C (Figure 2) while they worth 0.34 and 0 at 60 °C, respectively under solution copolymerization.
That novel process was also extended to the radical terpolymerizations of VDF with MAF and HFP and was also successfully achieved.

Thermal stabilities of these copolymers depended on the content of MAF and it was noted that the higher the MAF content, the lower the thermal stability of the resulting co- (or terpolymers) (Table 2) mainly related to the decarboxylation of MAF units.

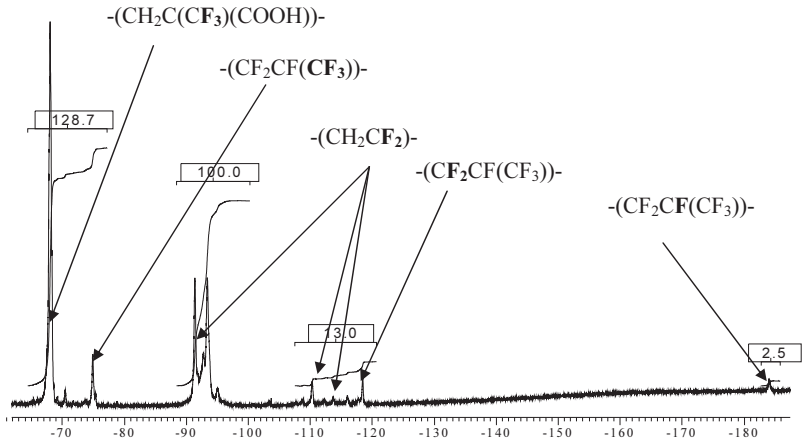


Figure 1: ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-MAF) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane /($[VDF]_0$ + $[HFP]_0$ + $[MAF]_0$) = 0.9 %, 134°C, 6 hours and VDF / HFP / MAF initial molar ratio in the feed = 69.2 / 17.1 / 13.7.

3. Modification of poly(VDF-ter-HFP-ter-MAF) terpolymers

Various chemical modifications of these poly(VDF-ter-HFP-ter-MAF) terpolymers were investigated. Interestingly, the carboxylic side groups were reduced into primary alcohols hence improving the thermal stability. Subsequently, these hydroxyl groups underwent etherification reaction with 4-phenol sulfonic acid, *via* a Mitsunobu reaction, to lead to original fluoropolymers bearing sulfonic acid side groups as precursors of fuel cell membranes. The overall scheme is as follows (Scheme 2).

Table 2. Determination of the Monomer/Terpolymer composition of poly(VDF-*ter*-HFP-*ter*-MAF) terpolymers *versus* the reaction conditions in the radical terpolymerization of VDF, HFP with MAF. Terpolymerization conditions:[2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane]$_0$/($[VDF]_0$ + $[HFP]_0$ + $[MAF]_0$) = 0.9 mol %, 134 °C, 10 hours. Average molecular weights, M_n and M_w assessed from SEC with poly(styrene) standards. T_g (glass transition temperature) values were assessed by DSC.

Exp. #	Mol % of VDF in feed	Mol % of HFP in feed	Mol % of MAF in feed	Mol % of VDF in the terpolymer	Mol % of HFP in the terpolymer	Mol % of MAF in the terpolymer	Massic yields (%)	Tg (°C)	Mn (g/mol)	PDI
1	69.2	17.1	13.7	56.8	3.5	39.7	54	- 18	10100	1.6
2	74.1	16.8	9.1	57.7	5.4	36.9	54	- 19	11100	1.7
3	72.7	21.2	6.1	59.5	5.1	35.4	55	- 19	11500	1.8
4	71.4	23.2	5.4	80.4	12.4	7.2	61	- 21	14000	1.8
5	77.9	18.9	3.2	86.2	10.4	3.4	65	- 26	19500	1.6
6	83.9	14.6	1.5	88.8	10.1	1.1	64	- 27	21400	1.6

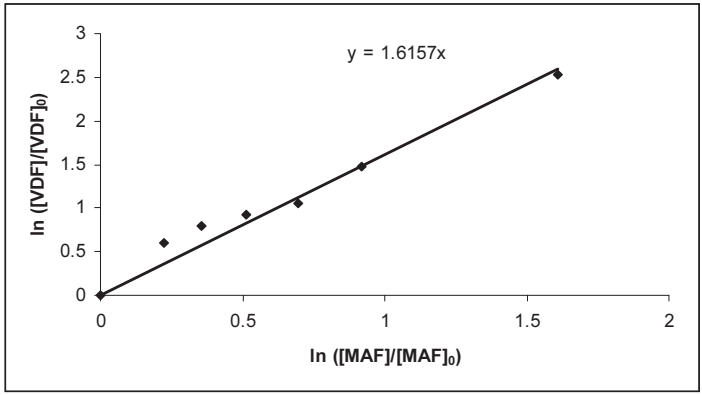
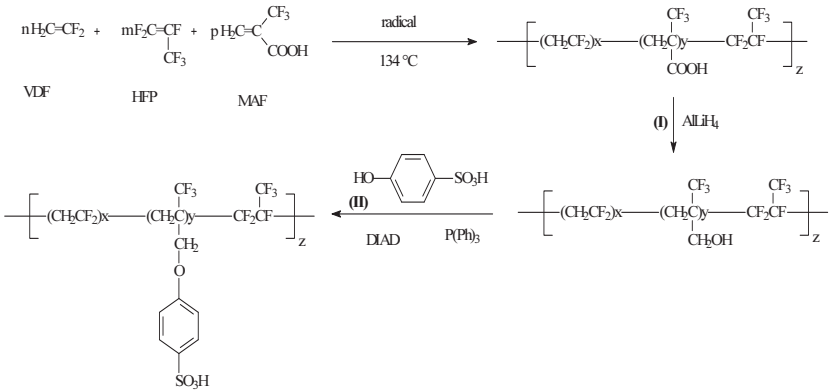
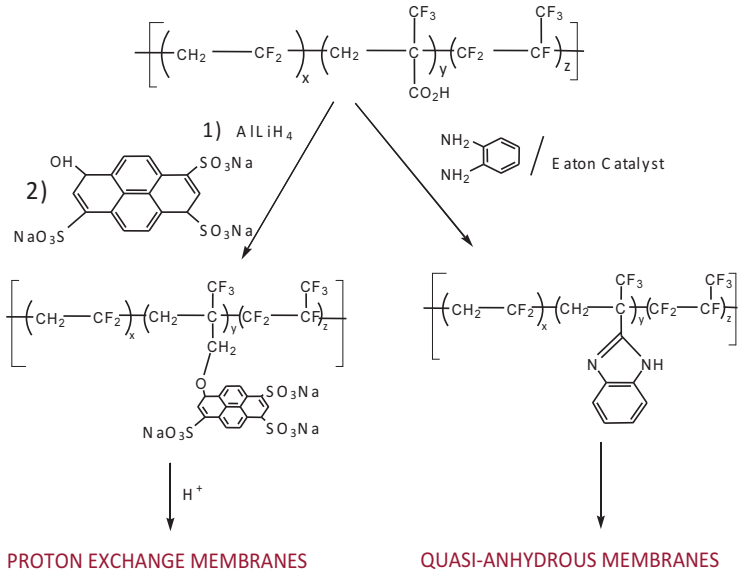


Figure 2: Determination of the reactivity ratios of MAF and VDF by the Evolution of ln $[VDF]/[VDF]_0$ *versus* ln$[MAF]/[MAF]_0$ for the radical copolymerization of VDF and MAF. Feed composition in VDF and MAF (mol-%) 95/5 in aqueous medium (Macret's Law)

Original membranes from these functionalized graft terpolymers were casted from various solvents and their physico-chemical, thermal and electrochemical properties were assessed, with conductivities reaching 20 mS/cm.
Further work has recently been investigated on the use of other sulfonated synthons (such as (or tris(sodium sulfonate) dies) to graft onto these poly(VDF-ter-MAF-ter-HFP) terpolymers (Scheme 3)[8].



Scheme 2. Chemical transformation of poly(VDF-ter-MAF-ter-HFP) terpolymer into sulfomembrane by Mitsunobu reaction.



Scheme 3. Synthesis of proton exchange and quasi-anhydrous membranes by modification of poly(VDF-ter-HFP-ter MAF) copolymers.

However, perfluorosulfonic polymers suffer from three limitations (methanol crossover, high cost and loss of performance from ca. 85 °C since the membrane start to dry). Beside, Kreuer [9-11] and then, Jannash [12-13]'s groups have pioneered novel concepts where H_2O is replaced by an amphiteric immobilized solvent; i.e. a system which exhibits a donor-acceptor behavior. These teams used nitrogeneous heterocycles as suitable candidates for amphoteric solvents and our choice is benzimidazole function which has the property to enable proton conduction. This new challenge allow us to prepare fluorinated membranes [8] which keep certain conductivity at T > 120 °C since it is known that nowadays requirements for car industry and for stationary are such that the membrane could bear severe conditions for 5,500 hrs (10) and 40,000 hrs, respectively.

That is why a second chemical modification of the carboxylic acid side groups of the initial copolymers was successfully achieved by condensation (on the presence of Eaton catalyst). These modified copolymer show better thermostability than the initial ones and are potential candidates as original sulfonic and quasi-anhydrous membranes with benzene orthodiamine (Scheme 3).

CONCLUSIONS

This paper has shown that the radical copolymerization (and terpolymerization) of VDF and MAF (and HFP) was successfully achieved in emulsion in good yields without any surfactant. Interestingly, the obtained emulsions were stable for several months leading to monodispersed particles sizes of ca. 100 nm. In addition, the experimental molar masses close to targeted one, showed a certain control of that copolymerization. Then, successful chemical modifications of the carboxylic acid side groups of the resulting copolymers were successfully achieved in two different ways: by reduction and

etherification with sulfonic acid paraphenol or by condensation (on the presence of Eaton catalyst) with benzene orthodiamine. These modified copolymers with improved thermostability than the initial ones and are valuable candidates as original sulfonic and especially quasi-anhydrous membranes.

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The paper is reviewed.