

RECENT ADVANCES IN THE SYNTHESIS AND PROPERTIES OF FUNCTIONAL FLUOROPOLYMERS FOR FUEL CELL MEMBRANES

Georgi Kostov^{1*}, Bruno Ameduri¹

¹ *Ingénierie & Architectures Macromoléculaires, UMR (CNRS) 5253,
Ecole Nationale Supérieure de Chimie de Montpellier,
8, rue Ecole Normale, 34296 Montpellier, Cedex 5, France*

^{*} *Dept of Org. Chem. Techn., Burgas Prof. A. Zlatarov University
1, Prof. Yakimov Str., 8010 Burgas, Bulgaria, E-mail: gkkostov@yahoo.com*

ABSTRACT

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 or by radiation grafting onto fluoropolymer films. 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 α -trifluoromethacrylic acid (MAF). $\alpha\omega$ -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 sulphoacids by Mitsunobu reaction. On the basis of functionalized CTFE copolymers containing vinyl ether imidazole or aromatic sulphoacids, original medium temperature (90-200 °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 of Nafion®, Flemion®, Hyflon®, Fumion®, 3M® Membranes, or Aciplex® (2), produced from the radical copolymerization of tetrafluoroethylene with aliphatic perfluorinated vinyl ethers, few have been achieved from aromatic functional fluoropolymers (3).

Earlier, we synthesized a copolymer of tetrafluoroethylene with 2-(1-pentafluoro-2-propenyloxy)-tetrafluoroethanesulfonyl fluoride to get membranes with proton-exchange capacity from 0.7 to 1.2 mEq/g, melting temperature 280-290 °C and thermal stability higher than 300 °C (4). Another way was a radiation grafting of acrylic acid onto fluorinated polymers which takes place predominantly on the polymer films surface (PTFE, TFE/E, TFE/HFP, TFE/PFAVE) and progresses inward through the grafting layer into polymer matrix depth (5).

Experimental

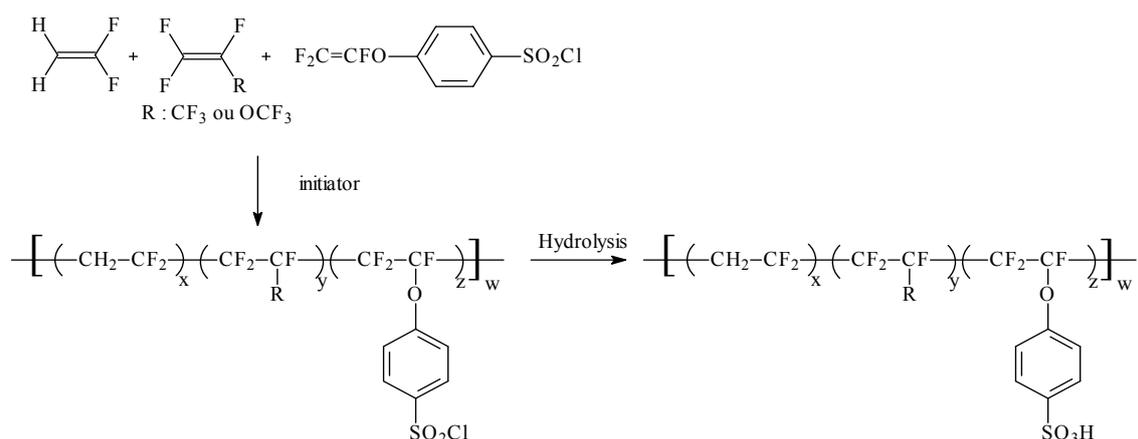
Vinylidene fluoride (VDF), hexafluoropropene (HFP) and 1,1,1,3,3-pentafluorobutane were kindly offered by Solvay Solexis S.A., Tavaux, France and Brussels, Belgium. α -

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 ^1H (or ^{19}F) nuclei.

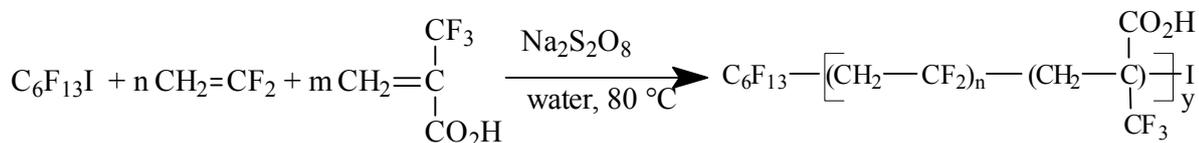
Infrared spectra were recorded on a Nicolet 510P Fourier Transformed spectrometer from KBr pellets. Differential scanning calorimetry (DSC) measurements were conducted using a Perkin-Elmer Pyris 1 instrument connected to a micro-computer. Thermogravimetric analyses were performed with a Texas Instrument TGA 51-133 apparatus in air at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ 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 $0.8\text{ mL}/\text{min}$, by means of a Spectra Physics Winner Station, a Waters Associate R 401 differential refractometer.

RESULTS AND DISCUSSION

The objective of this presentation deals with the syntheses of new generations of original membranes prepared from aromatic (6-7) (Scheme 1) and aliphatic fluorinated (Scheme 2) copolymers incorporating fluoromonomers such as vinylidene fluoride ($\text{F}_2\text{C}=\text{CH}_2$), hexafluoropropene ($\text{F}_2\text{C}=\text{CF}_2$), and an aromatic fluorinated monomer functionalized by a sulfonic acid, or α -trifluoromethacrylic acid (MAF) according to the following reactions:



Scheme 1: Radical terpolymerization of vinylidene fluoride (VDF) with hexafluoropropene (HFP) and trifluorovinylparaphenyl sulfonyl chloride, precursors of original fuel cell membranes



Scheme 2: Free emulsifier iodine transfer copolymerization (ITP) of VDF with α -trifluoromethacrylic acid (MAF) in the presence of $\text{C}_6\text{F}_{13}\text{I}$ as the chain transfer agent

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 VDF with MAF. That reaction was initiated with sodium peroxydisulfate at 80°C and was carried 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, ii) the polydispersity indexes are narrow (1.1 to 1.5 for CRP in contrast to 2.2-5 for conventional radical polymerization)].

The first part has 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 a certain control of that radical copolymerization.

The numbers of VDF, MAF and HFP units incorporated in the terpolymers were assessed by ^{19}F NMR from the integrals of the characteristic signals (Figure 1)

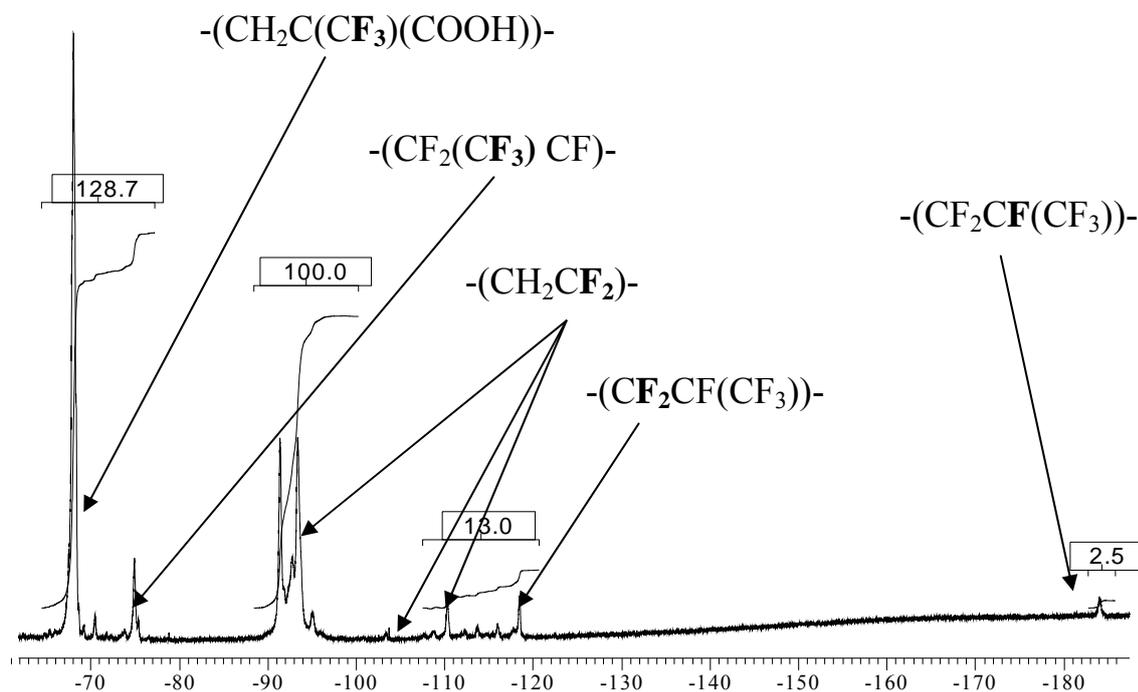


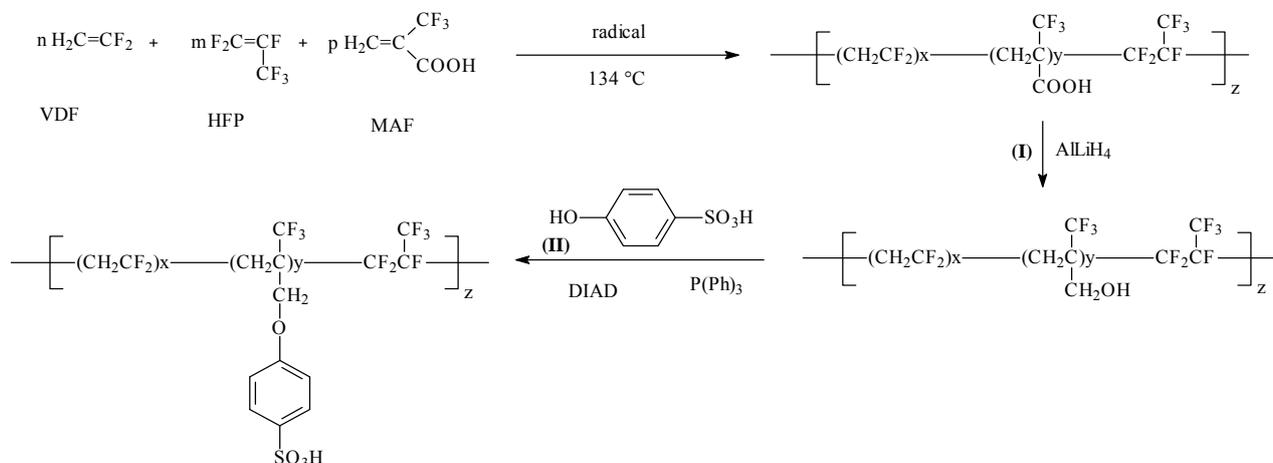
Figure 1 ^{19}F NMR spectrum of poly(VDF-*ter*-HFP-*ter*-MAF) terpolymer, recorded in deuterated acetone. Terpolymerization conditions: [2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane / ([VDF] $_0$ + [HFP] $_0$ + [MAF] $_0$) = 0.9 %, 134°C, 6 hours and VDF / HFP / MAF initial molar ratio in the feed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

The molecular weights, M_n , were assessed as follows:

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

where # represents the number of monomeric unit. Molecular weights of these 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(7). 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) mainly related to the decarboxylation of MAF units (Table 1) (8).

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 (9). The overall scheme is as follows:

Scheme 3. Synthesis of VDF/MAF/HFP terpolymers and their next modification to original sulphonic acid membranes.

Table 1: Determination of the monomer/graft poly(VDF-*ter*-HFP-*ter*-MAF) terpolymer compositions from solution terpolymerization in the absence of CTA. Average molecular weights, M_n assessed from SEC with poly(styrene) standards. T_g and T_d values were determined by DSC and TGA, respectively.

Ionomers	Mol % of VDF in the terpolyme r	Mol % of HFP in the terpolyme r	Mol % of grafted MAF in the terpolymer	Grafting conversion rates (%)	T_g (°C)	T_d (°C) Δm (10%) under air	M_n (g/mol)
A	76	8	12	75	6	170	10,800
B	82	3	8	53	2	190	12,000
C	86	5	6	66	-2	210	14,900
D	94	3	1.5	50	-17	230	22,000

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 (9-10).

Further work has recently been investigated on the use of other sulfonated synthons (such as tris(sodium sulfonate) dies) to graft onto these poly(VDF-*ter*-MAF-*ter*-HFP) terpolymers (10). 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). Besides Kreuer (11) and then, Jannash (12)'s groups have pioneered novel concepts where H_2O is replaced by an amphoteric 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 conductivity.

This new challenge should allow us to prepare fluorinated membranes which keep certain conductivity at $T > 120\text{ }^{\circ}\text{C}$ 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 and 40,000 hrs, respectively(13). This 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) with benzene orthodiamine (10, 14).

These modified copolymer show better thermostability than the initial ones and are potential candidates as original sulfonic and quasi-anhydrous membranes (10).

CONCLUSION

The first part 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 membrane

Acknowledgements:

The authors thank FNI-MON-Bulgaria for financial support and Tosoh F-Tech Company (Shunan, Japan) for the generous gift of MAF.

REFERENCES

1. Ameduri, B. and B. Boutevin, *Well-Architected Fluoropolymers: Synthesis, Properties and Applications*, Elsevier, Amsterdam (2004).
2. a) Arcella, V., A. Ghielmi and G. Tommasi, *Ann. N.Y. Acad. Sci.*, New-York, **2003**, 984, 226;
3. b) Doyle, M., and G. Rajendran, *Perfluorinated Membranes in Handbook of Fuel Cells-Fundamentals, Technology and Applications*, W. Vielstich, H.A. Gasteiger and A. Lamm, Editors, vol. 3, Chapter 30, pp.351-395 (2003); c) Souzy, R. and B. Ameduri; *Prog. Polym. Sci.* **2005**, 30, 644.
4. Steck, A.E. and C. Stone, US Patent 5,985,942 (assigned to Ballard Power System) (1999).
5. Kostov G.K., St.V. Kotov, G.D. Ivanov and D. Todorova, *J.Appl. Polym. Sci.*, **1993**, 47, 735.
6. Kostov, G.K., A.N. Atanassov, *J. Appl. Polym. Sci.*, **1993**, 47, 1269.
7. a) Marsacq, D.; M. Pineri, R. Souzy and B. Ameduri, FR 2843398 (assigned to CEA) (2004);
8. b) Souzy,R., P. Capron, G. Gebel, B. Boutevin and B. Ameduri, *Fuel Cell*, **2005**, 5, 383.
9. Souzy, R. and B. Ameduri, in *Functional Fluoropolymers for Fuel Cell Membranes*, T. Nakajima and H. Groult, Editors; *Fluorinated Materials for Energy Conversion*, Elsevier, Amsterdam, Chapter 21, pp 496-509 (2005).
10. Boyer,C. and B. Ameduri; Japanese Patent Application 2007/51201(assigned to Tosoh F-Tech) (2006).
11. Souzy; R., B. Ameduri., B. Boutevin and P. Capron; WO 2006/042996 (assigned to CEA), (2006).
12. Kostov, G.K. and B. Ameduri, in preparation.
13. a) Kreuer, K. D. *Solid State Ionics*, **2001**, 45, 85; b) Kreuer, K. D., *Chem. Mat.*, **2004**, 16, 329; c) Scharfenberger C. and K. D. Kreuer, *Fuel Cell*, **2006**, 3-4, 237.

14. Persson, C. and P. Jannasch, *Solid State Ionics*, **2006**, 177, 6; b) Persson, C. and P. Jannasch, *Chem. Mat.*, **2006**, 18, 3096.
15. Weiser, C., *Fuel Cell*, **2004**, 4, 245.
16. Jouanneau, J., *Ph D Disertation*, University of Savoie (France) (**2006**).