



# Preparation of Solid Alkaline Fuel Cell Binders Based on Fluorinated Poly(diallyldimethylammonium chloride)s [Poly(DADMAC)] or Poly(chlorotrifluoroethylene-co- DADMAC) Copolymers

David Valade, Frédéric Boschet, Stéphanie Roualdes, Bruno Ameduri

## ► To cite this version:

David Valade, Frédéric Boschet, Stéphanie Roualdes, Bruno Ameduri. Preparation of Solid Alkaline Fuel Cell Binders Based on Fluorinated Poly(diallyldimethylammonium chloride)s [Poly(DADMAC)] or Poly(chlorotrifluoroethylene-co- DADMAC) Copolymers. *Journal of Polymer Science Part A: Polymer Chemistry*, 2009, 47, pp.2043-2058. 10.1002/pola.23290 . hal-00379230

**HAL Id: hal-00379230**

**<https://hal.science/hal-00379230>**

Submitted on 28 Apr 2009

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# **Preparation of Solid Alkaline Fuel Cell Binders Based on Fluorinated Poly(diallyldimethylammonium chloride)s (Poly(DADMAC)) or Poly(chlorotrifluoroethylene-co-DADMAC) Copolymers.**

David Valade<sup>1</sup>, Frédéric Boschet<sup>1</sup>, Stéphanie Roualdès<sup>2</sup>, Bruno Ameduri<sup>1\*</sup>

<sup>1</sup>*Institut Charles Gerhardt, Ingénierie et Architectures Macromoléculaires,  
UMR CNRS 5253, Ecole Nationale Supérieure de Chimie de Montpellier,  
8 Rue de l'Ecole Normale, 34296 Montpellier, France*

<sup>2</sup>*Institut Européen des Membranes, ENSCM, UM2, CNRS ;  
Université Montpellier 2, CC047, Place Eugène Bataillon, 34095 Montpellier, France*

*\* To whom correspondence should be addressed, Tel: +33-(0)467-1443-68; Fax: +33-(0)467-1472-20; Email: bruno.ameduri@enscm.fr*

(Dedicated to Prof. Bernard Boutevin on the occasion of his 60<sup>th</sup> birthday)

## **ABSTRACT**

A membrane or an electrode binder to be used in a Solid Alkaline Fuel Cell (SAFC) needs to (i) be insoluble in both aqueous solutions and in the required fuels, and (ii)

exhibit an hydroxide ion conductivity. To achieve these goals, two pathways were employed: (i) one consists of the radical copolymerization of diallyldimethylammonium chloride (DADMAC) with chlorotrifluoroethylene (CTFE) while (ii) the other one is based on the counter-ion exchange of a poly(DADMAC) by fluorinated anions. First, the radical copolymerization of CTFE with DADMAC under various experimental conditions was achieved in yields up to 85 % and DADMAC percentages in the copolymers were higher than those in the feed compositions. To obtain insoluble copolymers, high CTFE feed contents (> 70 mol%) were required.

The other route consisting of the partial replacement of the  $\text{Cl}^-$  counter-ions in the water-soluble poly(DADMAC) by bistrifluoromethanesulfonimide ( $\text{TFSI}^-$ ) did confer the starting material insolubility in water while maintaining its conductivity. When the fluorinated poly(DADMAC) was obtained from concentrated solutions of fluorinated surfactant, it was observed that the amount of counter-ions exchanged was difficult to control, which limits optimization. Nevertheless, under diluted conditions, membranes with ion exchange capacity up to  $0.7 \text{ meq.g}^{-1}$  and conductivities close to  $1 \text{ mS.cm}^{-1}$  were obtained. Although their conductivities were low, these membranes fulfill the requirements for a SAFC membrane in terms of solubility in DMSO, water insolubility, and thermal stability ( $T_{d,10\%} > 320 \text{ }^\circ\text{C}$ ). When used in a fuel cell as a binder in the membrane-electrodes assembly (MEA), significant improvements were noted (+50% of the open circuit voltage, +580 % in current density and +540 % in accessible power).

## KEYWORDS

Fluoropolymer, Radical copolymerization, Diallyldimethylammonium chloride, Chlorotrifluoroethylene, Solid Alkaline Fuel Cell, Membrane, Thermal properties, Electrochemical properties

## 1 INTRODUCTION

Among the different types of fuel cells, solid alkaline fuel cells (SAFCs) appear as an attractive solution to the energy crisis, global warming/green energy and the development of new sources of energy.<sup>1</sup> SAFCs are among the most recently reconsidered in fuel cells technology, trying in an attempt to combine the best advantages of both alkaline batteries and solid polymer electrolyte membranes for fuel cells (PEMFCs).<sup>2</sup> In contrast to other fuel cells, SAFCs, based on anion-exchange membranes, do not require rare and expensive noble metals (Pt, Ru...) as catalysts to function, which is one of the main drawbacks for the commercialization of PEMFCs based on proton-exchange membranes (these metals are rare and thus expensive).<sup>1,3</sup> Nevertheless, SAFCs are still in the early stages of development especially as membrane-electrodes assemblies (MEA).

Within this research, our goal is to prepare a polymeric membrane or binder to increase the contact surface between the electrode and the membrane, with a high conductivity, a high ionic exchange capacity and insolubility in both water and fuels (such as methanol, ethylene glycol...).

To achieve this goal, two pathways can be followed. The first route consists of preparing polymeric materials that are insoluble in water by inserting a hydrophobic co-monomer in the course of the copolymerization. Among the hydrophobic comonomers, fluoroolefins are suitable and can undergo a radical copolymerization with a monomer bearing a

conducting hydroxide ion-group. The other route consists of modifying an existing water-soluble polymer bearing ammonium groups especially through the counter-ion exchange to make it insoluble in water. The interest in this case is the simplicity of the synthesis of the material which usually consists of mixing two aqueous solutions of a polyelectrolyte and a surfactant.<sup>4</sup> Both the surfactant and the polyelectrolyte can be water-soluble but the resulting product should be water-insoluble. Other advantages to this method is that this approach usually leads to nanostructures that may have useful applications in coatings (complexes of polyelectrolyte/fluorinated amphiphiles<sup>5,6</sup>), or for CO<sub>2</sub> absorption (polymeric ionic liquids<sup>7-10</sup>).

Fluorinated materials are well-known for their insolubility in both common organic solvents and in water.<sup>11</sup> They also present several advantages in terms of thermal, chemical, corrosive, and oxidative stabilities and can be found in most PEMFCs membrane formulations.<sup>12</sup>

Then, for the first pathway employed to synthesize a hydroxide ions conducting water-insoluble polymer, the copolymerization of an ammonium-containing monomer with a fluorinated comonomer was considered. Given the instability in basic medium of the dimethylaminoethyl methacrylate (DMAEMA) and the high cost of vinylbenzyltrimethyl ammonium chloride (VBTMAC), two monomers often used for the preparation of functional membranes,<sup>13-16</sup> we focused on another commercially available monomer, such as diallyldimethylammonium chloride (DADMAC).<sup>17</sup> The DADMAC, in contrast to the (meth)acrylates, does not have any ester linkage, and is less susceptible to degradation. This monomer, synthesized from dimethylamine and allyl chloride<sup>18,19</sup> was

at the origin of the first generation of quaternary ammonium containing polymers<sup>17</sup> (Scheme 1) which are widely used especially in the field of paper industry, water treatments and cosmetics.<sup>17,20-24</sup> These interests arise mainly from its structure that induces a high glass transition temperature, hydrophilicity, and a low cost. The DADMAC homopolymer is highly soluble in water, and hence is one of the most widely used polyelectrolytes.<sup>25,26</sup>

### **Insert SCHEME 1**

Thus, the counter-ion exchange of poly(DADMAC) by some fluorinated counter-ions was considered to avoid the water solubility of the starting material for potential uses as an alkaline fuel cell membrane and/or as a binder. Such complexes of polyelectrolyte/surfactant<sup>4,27-30</sup> or polyanion/polycation<sup>31-34</sup> have been reported from poly(DADMAC) giving rise to water-soluble<sup>27,28,30</sup> and hydrophobic<sup>4</sup> complexes as well as low surface tension materials from fluorinated surfactants. Some of those complexes are well-known to be water insoluble but do present a solubility in organic solvents, depending strongly on the polyelectrolyte / surfactant ratio.<sup>4,35</sup>

Indeed, for the preparation of the SAFCs membranes or binders, it is worth modifying the poly(DADMAC) to get rid of its solubility in aqueous medium while maintaining its ionic conductivity. This can be achieved by two main strategies: i) to carry out the radical copolymerization of DADMAC with a hydrophobic monomer such as a fluorinated comonomer and, ii) to exchange the counter-ions of poly(DADMAC).

To the best of our knowledge, neither of these strategies for the preparation of SAFC membranes or binders has ever been reported in the literature. In addition, the copolymerization of DADMAC with a fluorinated comonomer has never been reported in the literature. Vinylidene fluoride (VDF) (co)polymers are base sensitive<sup>11</sup> and are not suitable for SAFC membranes<sup>36,37</sup> or binders and it was necessary to choose another commercially available highly fluorinated alkene. Hence, the objectives of the present study concern the radical copolymerization of DADMAC with a highly hydrophobic monomer, chlorotrifluoroethylene (CTFE), and the partial counter-ion exchange of commercially available poly(DADMAC) by fluorinated counter-ions (such as bistrifluoromethanesulfonimide (TFSI)). In the second part of this manuscript, the membrane/binder properties prepared from the synthesized polymers are described (such as water uptake, electrochemical and thermal properties).

## 2 EXPERIMENTAL

### 2.1 Materials:

The initiators, *tert*-butylperoxypivalate (TBPPI) and di-*tert*-butyl peroxide (DTBP), were kindly provided by Akzo (Compiègne, France). Chlorotrifluoroethylene (CTFE) and 1,1,1,3,3-pentafluorobutane (C<sub>4</sub>F<sub>5</sub>H<sub>5</sub>) were kindly provided by Solvay S.A. (Tavaux, France & Bruxelles, Belgium) and were used as received. A fluorinated surfactant, Forafac®, C<sub>6</sub>F<sub>13</sub>[CH<sub>2</sub>CH(CONH<sub>2</sub>)]<sub>x</sub>H was obtained from Elf Atochem (Pierre Bénite, France). 1-hexyl-3-methylimidazolium-bistrifluoromethanesulfonimide, used as an ionic liquid (I.L.), was kindly provided by Merck (Germany). Water (HPLC grade), methanol

(analytical grade), acetonitrile (analytical grade), dimethylformamide (analytical grade), bistrifluoromethanesulfonimide lithium salt (LiTFSI,  $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ ) (puriss., >99 %), pure diallyldimethylammonium chloride (DADMAC) (99 % dry), diallyldimethylammonium chloride (DADMAC) in aqueous solution (35 %), and Poly(DADMAC) were purchased from Aldrich Chemie (Saint Quentin-Fallavier, France). Poly(DADMAC) is available in two range of molecular weights (one has a molecular weight range below  $100,000 \text{ g.mol}^{-1}$  (35 wt% in water) while those of the second one range between 250,000 and  $350,000 \text{ g.mol}^{-1}$  (20 wt% in water)).

The ADP 5063 Membrane was also kindly provided by Solvay S.A. (Tavaux-France, and Bruxelles-Belgium) and was used as a reference membrane for our study. It consists of a poly(ethylene-*co*-tetrafluoroethylene)-*g*-poly(vinyl benzyl chloride) copolymer obtained by radiation grafting of VBC onto ETFE (where ETFE and VBC stand for poly(ethylene-*alt*-tetrafluoroethylene) copolymer and vinylbenzyl chloride, respectively) that was further chemically modified into an ammonium salt by reaction with an trimethylamine and a further exchange of the chlorine anions by hydroxide anions.<sup>38</sup>

## **2.2 Experimental**

### **2.2.1 First route: Radical copolymerization of DADMAC with CTFE.**

As CTFE is a gas, the reactions were carried out in a 160 mL Hastelloy autoclave Parr system equipped with a manometer, a rupture disk (3000 PSI), inlet and outlet valves and a magnetic stirrer. Prior to reaction, the autoclave was pressurized with 30 bars of nitrogen to check for leaks. The autoclave was then conditioned for the reaction with



several nitrogen/vacuum cycles ( $10^{-2}$  mbar) to remove any traces of oxygen. The liquid phase, composed of the initiator (1 mol% with respect to CTFE and DADMAC) and the solvent, was introduced via a tight funnel while the gases were introduced by double weighing (i.e. the difference of weight before and after filling the autoclave with the gas). Then, the autoclave was placed into an oil bath with a vigorous magnetic stirring, and was heated up to 70 °C. The reaction was allowed to proceed at that temperature for 15 hours. After an initial increase of the internal pressure due to the increasing temperature and hence to the expansion of the CTFE gas, the pressure dropped by consumption of the CTFE monomer to produce the copolymer in the liquid phase. After the reaction was completed, the autoclave was purged (to release the unreacted CTFE), and opened. The solvent of the total product mixture was evaporated and the copolymer was precipitated into pentane. Then, the products were vacuum dried at 70 °C until constant weight, and were recovered as white powders.

### **2.2.2 Second route: Ion Exchange procedure.**

The solution of fluorinated anions (LiTFSI) was added to the solution of poly(DADMAC) which led to the progressive formation of a white precipitate which corresponded to the modified poly(DADMAC). The precipitate was filtered and placed in a vacuum oven at 50 °C while the polymer that remained in solution was weighed after drying (by freeze drying). Only the water-insoluble part, a white powder, was further used.

### **2.2.3 Preparation of Membranes**

Whichever the chosen route, the obtained (co)polymers were dissolved in DMSO (ca. 1 g of polymer for ca. 2 g of DMSO) and cast into a membrane followed by a  $10^{-1}$  mmHg vacuum drying of 8 hrs at room temperature and then at 50 °C for another 24 hrs under vacuum. The membrane was then removed from the glass substrate by immersion into water.

Most products obtained had good solvent-casting and film-forming properties depending on if they were immersed in water. It was observed that these membranes were quite soft but shrank and became slightly brittle upon drying.

## **2.3 Characterization**

### **2.3.1 Nuclear Magnetic Resonance**

The Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker AC 400 instruments, using deuterated chloroform as the solvent and tetramethylsilane (TMS) (or  $\text{CFCl}_3$ ) as the references for  $^1\text{H}$  (or  $^{19}\text{F}$ ) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and part per million (ppm), respectively. The experimental conditions for recording  $^1\text{H}$  (or  $^{19}\text{F}$ ) NMR spectra were as follows: flip angle  $90^\circ$  (or  $30^\circ$ ), acquisition time 4.5 s (or 0.7 s), pulse delay 2 s (or 2 s), number of scans 128 (or 1024), and a pulse width of 5  $\mu\text{s}$  for  $^{19}\text{F}$  NMR.

### 2.3.2 Elemental analysis

The proportion of bistrifluoromethanesulfonimide (TFSI<sup>-</sup>) incorporated in the polymer was determined from the elementary analysis of carbon and sulfur to minimize the potential influence of water contained in the product. This was calculated from the following equations

$$x + y = 1 \quad (1a)$$

$$\frac{x}{y} = \frac{2 M_s - 10 M_c \times \frac{\%S}{\%C}}{8 M_c \times \frac{\%S}{\%C}} \quad (1b)$$

where x and y represent the molar fractions of DADMAC substituted with Cl<sup>-</sup> (reagent) and TFSI<sup>-</sup> (product), respectively. Ms and Mc are the respective molar masses of sulfur (62.066 g.mol<sup>-1</sup>) and of carbon atoms (12.011 g.mol<sup>-1</sup>). %S and %C are the respective weight fractions of sulfur and carbon determined by elementary analysis.

### 2.3.3 Electrochemical properties

Water uptake at 25 °C was calculated from the equation (2)

$$\text{Water uptake (\%)} = \frac{m_h - m_s}{m_h} \times 100 \quad (2)$$

where m<sub>h</sub> and m<sub>s</sub> stand for the weight (in grams) of the hydrated membrane and of the dry membrane before immersion in water, respectively.

Experimental ionic exchange capacity (IEC<sub>exp</sub>) at 25 °C was calculated from equation (3), as follows:

$$\text{IEC}_{\text{exp}} = \frac{[\text{Cl}^-] \cdot V}{m_s} \quad (3)$$

where  $[Cl^-]$ ,  $V$ , and  $m_s$  stand for the concentration of the exchange solution in  $Cl^-$  anions ( $mol.L^{-1}$ ), the volume of the exchange solution (mL), and the weight of the dry membrane (g), respectively.

Membrane conductivity was determined from the following equation:

$$\sigma = \frac{l}{RS} \quad (4)$$

where  $l$ ,  $R$  and  $S$  represent the membrane thickness, the resistance measured by impedance spectroscopy, and the active surface of the membrane ( $0.785 \text{ cm}^2$ ), respectively. The experimental device used for the resistance measurement was a Teflon two-compartment cell that clamped the humid membrane (100% relative humidity); each compartment was filled with liquid mercury and contained a platinum electrode. The impedance spectra were recorded at  $25 \text{ }^\circ\text{C}$ , in the frequency range  $0.1 \text{ Hz} - 1 \text{ MHz}$ , with a Solartron 1260 Frequency Response Analyzer connected to a Solartron 1287 Electrochemical Interface Potentiostat supplying the DC (direct current) bias potential and the AC (alternating current) sinusoidal perturbation. For all experiments, the DC bias potential was maintained at  $0 \text{ V}$  and the AC perturbation at  $10 \text{ mV}$ .

Prior to the conductivity assessment, it is necessary to perform a conditioning step to replace the chloride by hydroxide anions. This conditioning step consists of a 24 hrs-immersion of the membrane in a sodium hydroxide solution ( $0.1 \text{ M}$ ) followed by a 24hrs-immersion in deionized water to get rid of the trapped sodium salts. Even though the usual reaction time for the complete replacement of the chloride anions is shorter than 8 hrs, we chose an immersion time of 24 hrs to ensure a complete conversion. No change in color, solubility or physical state was observed during that conditioning step.

The polarization curves were obtained in fuel cell using hydrogen and air gases at atmospheric temperature and pressure, at the anode and cathode side, respectively. The membrane-electrodes assembly (MEA) consisted of a Solvay ADP 5063 membrane sandwiched between the anode and the cathode. The anode consisted of a Evionyx electrode inked with Pt/C ( $0.75 \text{ mg.cm}^{-2}$ ) and PTFE or our polymer as the binder (37 wt.%). The cathode composed of an Evionyx electrode doped with Cobalt Porphyrine and eventually the binder (37 wt.%).

#### **2.3.4 Thermogravimetric analyses**

Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and a Lauda RC6 CS cryostat apparatus, under air, at the heating rate of  $10 \text{ }^{\circ}\text{C.min}^{-1}$  from room temperature up to a maximum of  $580 \text{ }^{\circ}\text{C}$ .

### **3 RESULTS AND DISCUSSION**

Two strategies have been chosen for the preparation of the binders: i) the original radical copolymerization of diallyldimethylammonium chloride (DADMAC) with chlorotrifluoroethylene (CTFE) and ii) the chemical modification of commercially available poly(DADMAC) with bistrifluoromethanesulfonimide lithium salt (LiTFSI). Both are described herein.

#### **3.1 Radical copolymerization of DADMAC with CTFE.**

DADMAC has already been studied in copolymerizations to obtain high molecular weight polymers rather than in homopolymerization that is limited by a low propagation constant ( $k_p = 90 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-2}$  at 50 °C in aqueous media,<sup>39</sup>  $k_p = 100 \text{ L}^2 \cdot \text{mol}^{-2} \cdot \text{s}^{-2}$  at 60.5 °C in inverse emulsion<sup>40</sup>). Usual comonomers used for the radical copolymerization of DADMAC are acrylamide<sup>41,42</sup>, vinyl acetate<sup>43</sup>, styrene<sup>44</sup>, acrylic acid<sup>45</sup> and derivatives of DADMAC<sup>46,47</sup>. Nevertheless, to our best knowledge, the copolymerization of DADMAC with a fluorinated olefin has never been reported.

The Poly(CTFE-co-DADMAC) random copolymers were obtained by radical copolymerization of DADMAC with CTFE according to Scheme 2 initiated by either di-*tert*-butylperoxide (DTBP) at 140 °C or by *tert*-butyl peroxyphthalate (TBPPI) at 75 °C. Both initiators have a half-life of 1 hour at the given temperature.

### **Insert SCHEME 2**

Such a reaction was optimized and solvents, temperatures and monomer concentrations have been varied during these copolymerizations in the autoclave and the results are listed in Table 1.

### **Insert Table 1**

Water-soluble polymers were analyzed by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopies (Figures 1 and 2, respectively) that allowed the assessment of their microstructures due to the characteristic signals of each monomers in the NMR spectra:<sup>48-51</sup> CTFE (in the <sup>19</sup>F NMR

spectrum signals ranging between –95 and –130 ppm,  $-\text{CF}_2\text{CFCl}-$ ) and DADMAC (in the  $^1\text{H}$  NMR spectrum signals between 1.2 and 1.7 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}-\text{CH}_2-$ ), at 3.2 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}-\text{CH}_2-$ ) and 3.8 ppm ( $-\text{CH}_2-\text{CH}-\text{CH}_2-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{CH}-\text{CH}_2-$ )). However, an analysis with an internal standard containing both hydrogen and fluorine atoms was necessary to assess the composition of the copolymers. 1,3-Bis(trifluoromethyl)benzene, was chosen as the internal standard and its characteristic signals appear between 7.2 and 8.1 ppm (assigned to  $\text{C}_6\text{H}_4(\text{CF}_3)_2$  in the  $^1\text{H}$  NMR spectrum,) and -56 and -61 ppm (characteristic of  $\text{C}_6\text{H}_4(\text{CF}_3)_2$  in the  $^{19}\text{F}$  NMR spectrum). Composition in CTFE was obtained from equation (5) taking into account the different chemical shifts given above.

$$\% \text{CTFE} = \frac{\frac{\int_{-95 \text{ ppm}}^{-130 \text{ ppm}} \text{CF}_2\text{CFCl} / 3}{\int_{-56 \text{ ppm}}^{-61 \text{ ppm}} \text{CF}_3 / 6}}{\frac{\int_{-95 \text{ ppm}}^{-130 \text{ ppm}} \text{CF}_2\text{CFCl} / 3}{\int_{-56 \text{ ppm}}^{-61 \text{ ppm}} \text{CF}_3 / 6} + \frac{\int_{1.2 \text{ ppm}}^{1.7 \text{ ppm}} \text{CH}_2\text{CH} / 3}{\int_{7.2 \text{ ppm}}^{8.1 \text{ ppm}} \text{C}_6\text{H}_4 / 4}} \quad (5)$$

where  $\int \text{CF}_2\text{CFCl}$ ,  $\int \text{CF}_3$ ,  $\int \text{CH}_2\text{CH}$ ,  $\int \text{C}_6\text{H}_4$  represent the integrals of the signals of CTFE and of the internal standard in the  $^{19}\text{F}$  NMR spectrum, and the integrals of those of DADMAC and of the internal standard in the  $^1\text{H}$  NMR spectrum, respectively.

### **Insert FIGURE 1**

Among the results, it is worth noting that the use of a fluorinated surfactant Forafac®,  $\text{C}_6\text{F}_{13}[\text{CH}_2\text{CH}(\text{CONH}_2)]_x\text{H}$  (DV086, DV089) increased the yield. In addition, it was observed that the DADMAC proportion in the polymer is always higher than that in the

feed, which is attributed to the lower reactivity of the CTFE monomer as usually observed,<sup>11</sup> except for its radical copolymerization with vinyl ethers.<sup>52</sup> This is an important statement since DADMAC does not have a high propagation rate and maybe the pressure of the medium induces a higher reactivity. This higher DADMAC proportion is even more apparent as the polymerization is initiated by DTBP at high temperature (DV018). Higher polymerization temperature seemed to increase both yield and CTFE incorporation (DV018, DV026). Even though a lot of work has been done on the ionic liquids (IL), we did not observed any higher yield (DV075).<sup>53</sup> The polymer were obtained in good yields (up to 85 wt.%). It was noted that the reaction carried out from the DADMAC in powder yield an insoluble product in both organic solvents and water. The nature of the solvent appeared also to influence the yield and composition of the resulting copolymers.

### **Insert FIGURE 2**

The obtained copolymers were either water-soluble (DV018, DV026, DV038, DV048, DV085, DV086, DV089) or insoluble in common organic solvents (DV039, DV047). Water-insoluble polymeric products were obtained from high CTFE feed composition (>70 mol%) (DV039) or when we used the DADMAC in powder (DV047, DV075) instead of in an aqueous solution (See Table 1). Poly(CTFE) is a crystalline polymer well known for its insolubility<sup>54-56</sup> (only soluble in dichlorotetrafluorobenzene) which explains the insolubility of these copolymers with a large amount of CTFE (> 70 mol%).



Given that these copolymers were insoluble in common organic media, their characterization and film casting was impossible, and, for that reason, their synthesis was given up. In addition, the copolymers that do not contain a high proportion of CTFE, and that are characterizable, are often soluble in water which is not suitable for the requirements of a membrane or binder for SAFCs.

### **3.2 *Modification of the counter-ions in poly(DADMAC)***

The challenge, in this approach, is to obtain a water insoluble poly(DADMAC) due to the partial incorporation of some fluorinated counter-anions such as bistrifluoromethanesulfonimide (TFSI) in the structure while keeping some of the chloride anions (to be further replaced by hydroxide anions to ensure the conductivity). The reaction of exchange, summarized in Scheme 3, is then followed by the introduction of the hydroxide anions.

#### **Insert SCHEME 3**

LiTFSI as well as poly(DADMAC) bear electrostatic charges endowing them with a (poly)electrolyte behavior in solution. LiTFSI is known to have a good solubility and stability in water.<sup>57</sup> The reaction of exchange consists of mixing together two solutions: one containing the positively charged poly(DADMAC) and the other one containing the negatively charged TFSI<sup>-</sup> anions. Since the reaction of exchange is thermodynamically favorable, they react with each other. When a sufficient fraction of the polymer counter-anions has been exchanged for TFSI<sup>-</sup> anions, the polymer becomes insoluble and

precipitate from the solution. Due to the required properties, this insoluble polymer is the sole fraction that can be further used as a binder in the membrane-electrode assembly (MEA).

In a following step, called “membrane conditioning” (see section 2.3.3), the remaining chloride counter-ions on the polymer are replaced by hydroxide ions by exposing the polymer to a basic solution of sodium hydroxide.

TFSI anions in the solution can either be linked to a polymer chain or can be part of a micelle. It can be claimed that here appears to be a competition that takes then place between the anion exchange reaction and the micelle formation/equilibrium and that the micellization can occur either before or after the reaction of exchange.<sup>6</sup>

Two processes have been carried out to enable the substitution of chlorine atoms by LiTFSI onto poly(DADMAC): from concentrated or diluted solution of LiTFSI.

### **3.2.1 Concentrated surfactant solutions**

The chlorine ions of high molecular weight-poly(DADMAC) were exchanged by TFSI<sup>-</sup> anions from concentrated solution of LiTFSI ( $[\text{LiTFSI}] = 10^{-2} \text{ mol.L}^{-1}$ ). Time (1-48 hrs), temperature (22, 60 and 80 °C) and concentration in LiTFSI were taken into account as well as the nature of the solvent (water and methanol) to optimize the exchange reaction. The results are listed in Table 2.

#### **Insert Table 2**

As noted from Table 2 that the fraction of modified poly(DADMAC) increases with increasing amount of TFSI<sup>-</sup> anions in the medium ( $n_{\text{LiTFSI}}$  initial). This is in agreement with the fact that the yield and rate of the anion exchange reaction of substitution is affected by the concentration of both reagents. Nevertheless, other parameters can influence the fraction of modified polymer such as, for example, the dropwise addition of the surfactant solution that lowers the fraction of modified polymer (since the concentration in solution is low). Alternatively, replacement of water by methanol as the solvent does not lead to the precipitation of the polymer and this observation may arise from two reasons: (i) First, LiTFSI has a different solubility since that solvent is less polar than water; (ii) Second, if the exchange occurs, methanol allows the poly(DADMAC)-TFSI complex a better solubility to remain more soluble than in water.

Liquid solution state NMR spectrometry was not a suitable technique to monitor the exchange because we were not able to detect the reactant (N-Cl ionic bond cannot be characterized by <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR). However, the product (N-TFSI ionic bond) could be observed by <sup>19</sup>F NMR spectroscopy. Thus, the composition was assessed by elemental analysis and the results are listed in Table 2. The data shows that all the modified polymers contain more TFSI<sup>-</sup> anions than those predicted from the initial concentrations in surfactant. For example, DV168, DV169, DV170, DV179, DV180, and DV202 samples contain more than 87 % TFSI<sup>-</sup> anions. This observed difference shows that the anion exchange modification occurs, i.e. the modification of poly(DADMAC) by concentrated solutions leads to (i) highly exchanged polymers that rapidly precipitate from the aqueous media, and (ii) barely exchanged polymers that do not precipitate and

are thus eliminated by filtration. On considering these possibilities, a slow addition or a long reaction time should lead to a more homogeneous product.

In addition, two samples show lower substitution yields attributed to a dropwise addition of the lithium salt solution for the DV172 sample and, the stirring of the mixture for 48 hrs for the DV178 sample. Lower incorporation of the TFSI<sup>-</sup> anion allow more sites for OH<sup>-</sup> anions and as such, a better conductivity was noted (0.66 and 0.18 mS.cm<sup>-1</sup>) (see section 3.3.1).

In conclusion, it is noted that a slow addition of the ionic surfactant solution and a long reaction time leads to the formation of a more homogeneous modified poly(DADMAC). On the one hand, the introduction of TFSI<sup>-</sup> anions is necessary to bring water-insolubility to the poly(DADMAC) but on the other hand, an increased incorporation decreases the conductivity values of the resulting material. Both TFSI<sup>-</sup> and OH<sup>-</sup> anions are competing for the same sites on the polymer chain, for water-insolubility and conductivity, respectively. It is then a matter of finding the optimal balance between insolubility and conductivity to achieve the best membrane/binder.

### **3.2.2 Diluted surfactant solutions**

In this case, the reaction was carried out at room temperature, under dropwise addition and a continuous vigorous stirring for 24 hrs since a long period of exchange was required to favor a homogeneous distribution along the chain as demonstrated above.<sup>58</sup>

Such a reaction also occurred on both high and low molecular weight-poly(DADMAC) and the results are presented in Table 3.

### **Insert Table 3**

The polymers were modified to obtain a wide range of membranes endowed with different electrochemical properties and also to study how the counter-ion exchange occurred. From the corresponding experimental conditions, a homogeneous substitution by the TFSI<sup>-</sup> anions was expected which means that 100% of the starting polymer can be recovered as the precipitate. However, the amount of precipitate, at low or high level of substitution, usually varies with the amount of introduced surfactant. This demonstrates the heterogeneity of the counter-ion substitution, and consequently, the difficulty to control both the exchange and the composition of the polymer/surfactant complexes obtained, as shown in Table 3.

As for the concentrated surfactant solutions, most polymers show more TFSI<sup>-</sup> groups compared to the initial amount, except for DV313 and DV305 samples where the initial proportions between the fluorinated salt and the polyelectrolyte were stoichiometric. In Table 3, some variations were noted in the reproducibility of the counter ion exchange reaction from mixtures with the same initial composition but different product compositions (DV212 and DV262 samples). Moreover, the use of higher molecular weight-polyelectrolyte seems to favor a more homogeneous counter-ion exchange with products having a lower TFSI<sup>-</sup> content and closer to the expected value calculated from the initial concentrations.

### 3.3 Membranes properties

Membrane casting was carried out by pouring a concentrated solution of the polymer in dimethylsulfoxide (DMSO) into a mould or by spreading it onto a PTFE substrate. The DMSO was evaporated under vacuum at room temperature for 8 hrs, and was further dried in a vacuum oven at 50 °C for 24 hrs before it was removed from the substrate by immersion in water. The membranes were then conditioned and tested.

#### 3.3.1 Electrochemical properties

Table 4 displays the electrochemical properties of the membranes obtained from concentrated solutions of fluorinated anions compared to a reference (Solvay ADP 5063). The ADP 5063 consists of a poly(ethylene-*co*-tetrafluoroethylene)-*g*-poly(vinyl benzyl chloride) graft copolymer obtained by radiation grafting VBC onto ETFE (where ETFE and VBC stand for poly(ethylene-*alt*-tetrafluoroethylene) copolymer and vinylbenzyl chloride, respectively). Then it was further chemically modified into an ammonium salt by reaction with an triethylamine and a further exchange of the chlorine anions by hydroxide anions.<sup>38</sup> All prepared membranes, based on poly(DADMAC) counter-ion modification, fulfilled the SAFC requirements and were water-insoluble and DMSO-soluble. In addition, they show water uptakes, ionic exchange capacities ( $\text{IEC}_{\text{exp}}$ ) and conductivities ( $\sigma$ ) ranging from 13 to 68 wt.%, 0.1 to 0.7 meq.g<sup>-1</sup>, and 0.04 to 0.66 mS.cm<sup>-1</sup>, respectively. Though the ionic exchange capacity of the polymers varied as expected, the experimental values were less than the calculated ones. These differences arguably arise from a casting problem or some remaining DMSO having been trapped inside the membrane. Regarding the structure/properties relationships, some reasonable

expectations were observed. Indeed, the membranes having both lowest water uptake and  $IEC_{exp}$  values (those obtained from DV168, DV169, and DV170 polymers) are understandably the least conductive ( $< 0.07 \text{ mS.cm}^{-1}$ ). Although presenting a high water uptake (30 wt.%), the membrane prepared from the DV180 polymer has a very low conductivity ( $0.08 \text{ mS.cm}^{-1}$ ) that can be explained by its low  $IEC_{exp}$  ( $0.07 \text{ meq.g}^{-1}$ ). The other membranes show higher conductivities ( $> 0.18 \text{ mS.cm}^{-1}$ ) due to high water uptake (DV178: 68 wt.%, DV179: 42 wt.%) or high  $IEC_{exp}$  (DV172:  $0.4 \text{ meq.g}^{-1}$ , DV178:  $0.7 \text{ meq.g}^{-1}$ , DV202:  $0.19 \text{ meq.g}^{-1}$ ). These observations show that the conductivity, which relates to the presence, the quantity and the accessibility of the ammonium groups that carry hydroxide counter-ions, is dependent on both the water uptake and the IEC. Nevertheless, both latter properties are not the only ones that control the conductivity, which is also dependent on the arrangement of conductive groups on that form of ion-conduction pathways in the polymer matrix referred to the connectivity. This last point can explain the fact that the membrane obtained from the DV178 polymer, characterized by both highest water uptake (68 wt.%) and  $IEC_{exp}$  ( $0.7 \text{ meq.g}^{-1}$ ), is not the best conductive one:  $0.18 \text{ mS.cm}^{-1}$  (vs  $0.66 \text{ mS.cm}^{-1}$  for the most competitive one: the membrane obtained from the DV172 polymer with water uptake = 24.5 wt.%,  $IEC_{exp} = 0.4 \text{ meq.g}^{-1}$ ). This reflects the difficulty in interpreting the structure/properties relationships for ionic conductive membranes and thus properly controlling the different properties of such polymers by the variation of the synthesis parameters.

#### **Insert Table 4**

The electrochemical properties of the polymers modified by dilute solutions of fluorinated salt are presented in Table 5. Most products, and especially the low molecular weight ones, have a satisfactory solubility in DMSO (1 g of polymer for 2 g of solvent) but some of the high molecular weight samples (DV218, DV262, DV310) containing a lower ratio of TFSI<sup>-</sup> anions require a much larger amount of solvent for their dissolution. From this necessary high dilution, some difficulties arise in the membrane casting, i.e. the membrane is too fragile and too thin which makes it unusable for the determination of its electrochemical properties (DV262, DV310). However, the use of a mould instead of a surface, allowed obtaining an acceptable membrane in several cases (DV218).

#### **Insert Table 5**

Using dilute solutions of fluorinated salt leads to polymers having better electrochemical properties than the ones obtained from concentrated solutions. Ionic conductivities close to 1 mS.cm<sup>-1</sup> were obtained with IEC<sub>exp</sub> values ranging between 0.3 and 0.5 meq.g<sup>-1</sup>. Besides, as an indication of stability, prior to IEC measurements, the membranes were immersed 24 hrs in a basic solution (NaOH 0.1 M) and showed a good stability, i.e. no replacement of the TFSI<sup>-</sup> by hydroxide anions occurred, which is a crucial characteristic for SAFC application. It can be observed that the most competitive membranes obtained from the DV218 (0.68 mS.cm<sup>-1</sup>), DV273 (0.79 mS.cm<sup>-1</sup>) and DV302 (0.89 mS.cm<sup>-1</sup>) polymers are those showing the best compromise between both high water uptake and IEC<sub>exp</sub>.



To evaluate the binder performance under real conditions, the Solvay ADP 5063 membrane was used as the reference. In Figure 3, it can be noted that the membrane performances without any binders are lower (i.e., open circuit voltage: 0.6 V and a maximum exploitable current density of 2.5 mA.cm<sup>-2</sup>). However, when used in combination with the modified poly(DADMAC) as the electrode binder in the membrane-electrode assembly, the performances increased significantly (i.e., open circuit voltage up to 0.9 V and exploitable current density up to 17 mA.cm<sup>-2</sup>). Interestingly, it was noted that the power accessible in the presence of these anionic binders was also higher and increased from 0.5 to 3.2 mW/cm<sup>2</sup>. These results reflect the importance of a good contact between the electrode and the membrane and show how the performance can be drastically increased by using a different material to make the junction between the electrodes and the membrane.

**Insert FIGURE 3**

### **3.3.2 Thermostability**

The thermostabilities of the poly(CTFE-*co*-DADMAC) copolymers were assessed and the results (in Table 1) show that the decomposition temperature at 10 % weight loss under air is higher than 200 °C. The insoluble copolymers have higher decomposition temperatures which might relate to a higher CTFE content, as for thermostable fluoropolymers.<sup>11</sup>

The thermal stability of the polymers with the highest ionic conductivities (DV172, DV273, DV302) as well as the commercially available poly(DADMAC) and a fully

counter-ions exchanged poly(DADMAC) sample (DV305) were evaluated by thermogravimetric analyses and the thermograms are plotted in Figure 4.

#### **Insert FIGURE 4**

Since all polymers have similar molecular weights, the influence of the counter-ion nature on the thermal degradation of the membranes can be observed. All of them exhibit a thermal stability up to at least 210 °C but differences occur depending on the nature and the proportion of the Cl<sup>-</sup>, OH<sup>-</sup> and TFSI<sup>-</sup> counter-ions. For example, lower thermal stabilities were evaluated in terms of the temperature at which the membrane losses 10% in weight ( $T_{d,10\%}$ ). Lower thermostability was observed for polymers containing the largest proportion of chloride counter-ions ( $T_{d,10\%}$  (PDADMAC) = 303 °C while  $T_{d,10\%}$  (DV273) = 340 °C) compared to the hydroxide counter-ions ( $T_{d,10\%}$  (DV172) = 335 °C). This effect is enhanced with the presence of the fluorinated counter-ions ( $T_{d,10\%}$  (DV302) = 379 °C ;  $T_{d,10\%}$  (DV305) = 385 °C). Interestingly, the substitution of the Cl<sup>-</sup> by TFSI<sup>-</sup> anions not only has brought water-insolubility to the polymer but also has significantly increased its thermal stability. The modification of the chloride counterions of poly(DADMAC) into poly(DADMAF) significantly increased the thermostability of poly(DADMAC).

The TGA analysis of these materials does not enable us to conclude if the membrane is going to be thermally stable while operating in the SAFC. However, during the membrane preparation, the membrane was placed in an oven at 50 °C (same temperature conditions as in a SAFC) for 24 hrs and no changes occurred (no change in color, aspect,

mechanical properties...). This was also confirmed by TGA isothermal tests at 50 °C for 24 hrs where no weight loss was recorded.

## 4 CONCLUSIONS

The synthesis of water insoluble fluorinated polymers from diallyldimethylammonium chloride (DADMAC) and the modification of a water soluble commercially available poly(DADMAC) were simply achieved to obtain a membrane or binder that was insoluble in aqueous media and bearing ammonium groups. Two pathways were employed, one consisting of the radical copolymerization of DADMAC with chlorotrifluoroethylene (CTFE) while the other dealt with the counter-ion exchange of a poly(DADMAC) by fluorinated anions. The copolymerization of CTFE with DADMAC under various experimental conditions was successfully achieved in yields up to 85%. However, the obtained products were either water-soluble or insoluble in any common organic solvents and thus were not suitable as potential membranes or binders for Solid Alkaline Fuel Cell.

The other pathway consisted of the partial replacement of the  $\text{Cl}^-$  counter-ions by fluorinated  $\text{TFSI}^-$  anions. The starting material became insoluble in water while its conductivity was maintained. If these chemical modifications occurred from concentrated solutions of fluorinated surfactant, controlling the amount of counter-ions exchange was difficult, and obtaining optimal conditions that favored high conductivity became limited. However, with ionn-exchange diluted solution, electrochemical performances of the resulting membranes led to conductivities close to  $1 \text{ mS.cm}^{-1}$ , and to IEC values up to  $0.7 \text{ meq.g}^{-1}$ . Though these values were low, the produced polymers show satisfactory criteria

for a SAFC membrane in term of solubility in DMSO, insolubility in water, thermal stability ( $T_{d10\%} > 244$  °C). Their use in a MEA showed encouraging improvements in the performance of the fuel cell (with a 50% increase of the open circuit voltage, a 580 % in current density and a 540 % in accessible power). Further improvements in synthesizing poly(CTFE-*alt*-M) copolymers where M is a monomer bearing an ammonium group is under investigation<sup>50</sup>.

## ACKNOWLEDGEMENTS

The authors would like to thanks J. Salomon, A. Martinet, P. Capron and F. Gaillard from CEA Liten (Grenoble, France) for performing the polarization tests of the membranes. We acknowledge the financial support from the Alcapac Project. The authors also would like to thank Solvay (France and Belgium) for providing the ADP membrane, and some reagents. The authors would also like to thank all the other companies (Akzo, Elf Atochem, and Merck) that provided us with free material, which made this research possible. DV wants specially to thank Dr Benoit Gadenne for very helpful discussions.

## REFERENCES

1. Varcoe, J. R.; Slade, R. C. T. Fuel Cells 2005, 5, 187-200.
2. Larminie, J.; Dicks, A. Fuel Cell Explained, 2nd Ed; Wiley: Chichester, England, 2003.
3. Alaaeddine, A.; Boschet, F.; Ameduri, B. to be submitted 2009.
4. Ober, C. K.; Wegner, G. Adv. Mater. 1997, 9, 17-31.

5. Thuenemann, A. F. *Polym. Int.* 2000, 49, 636-644.
6. Thuenemann, A. F.; Sander, K.; Jaeger, W.; Dimova, R. *Langmuir* 2002, 18, 5099-5105.
7. Tang, J.; Sun, W.; Tang, H.; Radosz, M.; Shen, Y. *Macromol.* 2005, 38, 2037-2039.
8. Tang, J.; Tang, H.; Sun, W.; Plancher, H.; Radosz, M.; Shen, Y. *Chem. Comm.* 2005, 3325-3327.
9. Tang, J.; Tang, H.; Sun, W.; Radosz, M.; Shen, Y. *Polymer* 2005, 46, 12460-12467.
10. Tang, J.; Tang, H.; Sun, W.; Radosz, M.; Shen, Y. *J. Polym. Sci., Part A: Polym. Chem.* 2005, 43, 5477-5489.
11. Ameduri, B.; Boutevin, B. *Well-Architected Fluoropolymers: Synthesis, Properties and Applications*; Elsevier: Amsterdam, 2004.
12. Souzy, R.; Ameduri, B. *Prog. Polym. Sci.* 2005, 30, 644-687.
13. Quinn, R.; Laciak, D. V. *J. Membr. Sci.* 1997, 131, 49-60.
14. Shen, J.; Qiu, J.; Wu, L.; Gao, C. *Sep. Purif. Technol.* 2006, 51, 345-351.
15. Yamada, K.; Gondo, T.; Hirata, M. *J. Appl. Polym. Sci.* 2001, 81, 1595-1604.
16. Yang, J. M.; Ping Chang Chian, C.; Hsu, K.-Y. *J. Membr. Sci.* 1999, 153, 175-182.
17. Wandrey, C.; Hernandez-Barajas, J.; Hunkeler, D. *Adv. Polym. Sci.* 1999, 145, 123-182.
18. Harada, S.; Arai, K. *Makromol. Chem.* 1967, 107, 64-77.
19. Negy, Y.; Harada, S.; Ishizuka, O. *J. Polym. Sci., Part A: Polym. Chem.* 1967, 5, 1951-1965.
20. Butler, G. B. *Acc. Chem. Res.* 1982, 15, 370-378.

21. Ottenbrite, R. M.; Shillady, D. Polym. Amines Ammonium Salts, Invited Lect. Contrib. Pap. Int. Symp. 1980, 143-153.
22. Wandrey, C.; Jaeger, W.; Starke, W.; Wotzke, J. Wasserwirtschaft Wassertechnik 1984, 34, 185-187.
23. Jaeger, W.; Gohlke, U.; Hahn, M.; Wandrey, C.; Dietrich, K. Acta Polym. 1989, 40, 161-170.
24. Wandrey, C. Polym. News 1997, 22, 171-173.
25. Dautzenberg, H.; Jaeger, W.; Koetz, J.; Phillip, B.; Seidel, C.; Stscherbina, D. Polyelectrolytes: Formation, characterization and application; Hanser Gardner Publications: Munich, 1994.
26. Mandel, M. Encycl. Polym. Sci. Eng. 1987, 11, 738-829.
27. McQuigg, D. W.; Kaplan, J. I.; Dubin, P. L. J. Phys. Chem. 1992, 96, 1973-1978.
28. Swanson-Vethamuthu, M.; Dubin, P. L.; Almgren, M.; Li, Y. J. Coll. Interf. Sci. 1997, 186, 414-419.
29. Wei, Y.-C.; Hudson, S. M. J. Macromol. Sci., Rev. Macromol. Chem. Phys. 1995, C35, 15-45.
30. Xia, J.; Zhang, H.; Rigsbee, D. R.; Dubin, P. L.; Shaikh, T. Macromol. 1993, 26, 2759-2766.
31. Dautzenberg, H.; Loth, F.; Fechner, K.; Mehlig, B.; Pommerening, K. Makromol. Chem., Suppl. 1985, 9, 203-210.
32. Dautzenberg, H.; Lukanoff, B.; Eckert, U.; Tiersch, B.; Schuldt, U. Berichte der Bunsen-Gesellschaft 1996, 100, 1045-1053.

33. Phillip, B.; Dautzenberg, H.; Linow, K. J.; Koetz, J.; Dawydoff, W. *Prog. Polym. Sci.* 1989, 14, 91-172.
34. Schwartz, H. H.; Richau, K.; Paul, D. *Polym. Bull.* 1991, 25, 95-100.
35. MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* 1998, 31, 781-788.
36. Danks, T. N.; Slade, R. C. T.; Varcoe, J. R. *J. Mater. Chem.* 2002, 12, 3371-3373.
37. Danks, T. N.; Slade, R. C. T.; Varcoe, J. R. *J. Mater. Chem.* 2003, 13, 712-721.
38. Brunea, J. FR-2876298 A1 assigned to Solvay et Cie., Belgium.
39. Hahn, M.; Jaeger, W. *Angew. Makromol. Chem.* 1992, 198, 165-178.
40. Huang, P. C.; Reichert, K. H. *Angew. Makromol. Chem.* 1988, 162, 19-34.
41. Wandrey, C.; Jaeger, W. *Acta Polym.* 1984, 36, 100-102.
42. Schuller, W. H.; Price, J. A.; Moore, S. T.; Thomas, W. M. *J. Chem. Eng. Data* 1959, 4, 273-276.
43. Janietz, S.; Hahn, M.; Jaeger, W. *Acta Polym.* 1992, 43, 230-234.
44. Jen, Y. USA-2958673 assigned to American Cyanamid Co.
45. Bhattacharyya, B. R.; Dalsin, P. D. USA-4713431 assigned to Nalco Chemical Co.
46. Butler, G. B.; Do, C. H. *ACS Symp. Ser.* 1991, 467, 151-158.
47. Kevelam, J.; Engberts, J. B. F. N. *Langmuir* 1995, 11, 793-797.
48. Valade, D. Ph.D Thesis, Univeristé Montpellier II, Montpellier (France), 2007
49. Gaboyard, M.; Hervaud, Y.; Boutevin, B. *Polym. Int.* 2002, 51, 577-584.
50. Valade, D.; Boschet, F.; Améduri, B. to be submitted 2008.
51. Frutsaert, G.; Delon, L.; David, G.; Ameduri, B.; Jones, D. J.; Glipa, X.; Rozière, J. Submitted to *Chem. Mater.* 2008.

52. Takakura, T. In Modern Fluoropolymers; Scheirs, J., Ed.; Wiley Interscience: New York, 1997, p 557-564.
53. Wasserscheid, P.; Welton, T. Ionic Liquids in Synthesis; Wiley-VCH: Weinheim, Germany, 2003.
54. Bringer, R. P. *Encycl. Polym. Sci. Eng.* 1967, 7, 204-219.
55. Chandrasekaran, S. *Encycl. Polym. Sci. Eng.* 1985, 3, 463-480.
56. West, A. C. *Kirk-Othmer Encycl. Chem. Technol.*, 3rd Ed 1980, 11, 48-54.
57. Perron, G.; Brouillette, D.; Desnoyers, J. E. *Can. J. Chem.* 1997, 75, 1608-1614.
58. Fundin, J.; Brown, W. *Macromolecules* 1994, 27, 5024-5031.



## SCHEME CAPTIONS

**Scheme 1.** Cyclic radical polymerization of diallyldimethylammonium chloride (DADMAC) in the presence of an  $A_2$  initiator.

**Scheme 2.** Radical copolymerization of diallyldimethylammonium chloride (DADMAC) and chlorotrifluoroethylene(CTFE).

**Scheme 3.** Counter-ion exchange of poly(DADMAC) by LiTFSI followed by  $OH^-$  exchange for  $Cl^-$  anions.

## TABLE CAPTIONS

**Table 1.** Radical copolymerizations of chlorotrifluoroethylene (CTFE) and diallyldimethylammonium chloride (DADMAC).

**Table 2.** Experimental conditions for the modification of Poly(DADMAC) by concentrated solutions of TFSI<sup>-</sup> anions.

**Table 3.** Experimental conditions for the modification of Poly(DADMAC) by dilute solutions of TFSI<sup>-</sup> anions.

**Table 4.** Electrochemical characteristics of poly(DADMAC) membranes modified by concentrated solutions of TFSILi.

**Table 5.** Electrochemical characteristics of poly(DADMAC) membranes modified by dilute solutions of TFSILi.

## FIGURE CAPTIONS

**Figure 1.**  $^1\text{H}$  NMR spectrum of poly(CTFE-co-DADMAC) copolymer (DV089, % CTFE = 61 mol.%, % DADMAC = 39 mol.% in copolymer) recorded in  $\text{CD}_3\text{OD}$ .

**Figure 2.**  $^{19}\text{F}$  NMR spectrum of poly(CTFE-co-DADMAC) copolymer (DV089, % CTFE = 61 %, % DADMAC = 39 % in copolymer) recorded in  $\text{CD}_3\text{OD}$ .

**Figure 3.** Polarization curve for the membrane ADP 5063 with and without the anionic binder made from our polymers (the internal resistance of the cell was found to be 3.1, 0.34, 0.45, and 2.4  $\Omega$  without binder, with DV273, with DV302, and with DV183Q2, respectively).

**Figure 4.** TGA thermograms of various poly(DADMAC) polymers: DV172 (% TFSI- = 46 mol.% ; % OH- = 54 mol.%), DV273 (% TFSI- = 83 mol.%, % Cl- = 17 mol.%), DV302 (% TFSI- = 79 mol.%, % Cl- = 21 mol.%), DV305 (% TFSI- = 99 mol.%, % Cl- = 1 mol.%) and the commercially available poly(DADMAC) polymer, obtained under air at 10  $^\circ\text{C}.\text{min}^{-1}$ .