



Synthesis of Original para-Sulfonic Acid Aminoethylthioethylbenzenesulfonic by Telomerization, and Its Grafting onto Poly(VDF-co-HFP) Copolymers for Proton Exchange Membrane for Fuel Cell

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**Synthesis of Original Para-sulfonic Acid Aromatic Derivative
Bearing the New Compound Amino group *p*-
Aminoethylthioethylbenzenesulfonic by Telomerization, and its
Grafting onto Poly(VDF-*co*-HFP) Copolymers for Proton
Exchange Membrane for Fuel Cell**

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ABSTRACT

The synthesis of a novel aromatic sulfonic acid bearing an amino function $\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$ (**1**) from the radical addition of mercaptoethylamine hydrochloride onto styrene sodium sulfonate, and its subsequent grafting onto poly(vinylidene fluoride-*co*-hexafluoropropylene), poly(VDF-*co*-HFP), copolymer are presented. First, the radical telomerization, carried out under radical conditions and in water, led to various products (monoadduct (**1**), multiadducts and polymers), the amounts of which depend on the experimental conditions, and $[\text{mercaptan}]_0 / [\text{monomer}]_0$ initial molar ratio (R_0). An $R_0 \geq 1$ led to the monoadduct (**1**) only and achieved in ca. 85 % yield. The zwitterionic isomer was obtained mainly and its chemical modification was possible to get an original aromatic sodium sulfonate containing an amino end-group. A kinetic study of the telomerization was presented for $R_0 < 1$. Thermogravimetric analysis of the telomer showed that this compound was stable up to 200 °C. Second, the grafting of (**1**) onto poly(VDF-*co*-HFP) copolymer was also investigated. Such a grafting proceeded as expected by a classic mechanism of grafting of amines. Molar percentages of grafted telomer were assessed by ^1H NMR spectroscopy and by elemental analysis. Ion exchange capacity (IEC) values of the membranes were deduced from the mol.% grafted telomer. SEM pictures showed a good homogeneity in the cross section of membranes, and energy dispersive X-ray evidenced that all SO_3Na groups of the grafted amine were changed into SO_3H after treatment with concentrated HCl. Method involving an impedance analyzer, working at increasing high frequencies was used to assess the protonic conductivities, σ . These values were lower than that of Nafion117[®], but σ increased with the IEC to 4 mS.cm⁻¹ at room temperature and 95 % relative humidity. Water and methanol up takes were also assessed and it was shown that σ increased when water up takes increased. Membranes started to decompose from 170 °C, under air.

KEYWORDS

Telomerization, amine, poly(VDF-*co*-HFP) copolymer, grafting, proton exchange.

INTRODUCTION

Fluorinated polymers based on vinylidene fluoride (VDF) are well-known for their remarkable properties, that confer them lots of diverse applications in many fields¹⁻⁴. Those VDF-based fluorinated polymers can be modified by grafting several agents usually by amines, phenols and thiols, or by crosslinking⁵⁻¹⁷. Grafting allows to modify or to create properties by using hydrogenated and functionalized agents, whereas crosslinking enables one to increase the molecular weights, and hence to improve some properties of the fluorinated polymers^{17,18}.

Fluorinated polymers can also be grafted with the “grafted from” method⁴. The fluoropolymer is activated (by preirradiation) by using different techniques (such as γ -rays or electron beam)¹⁹⁻²⁴ on its surface or even in the bulk, thus creating trapped radicals that can act as macroinitiators able to initiate the polymerization of monomer (M). This last method was used to synthesize PVDF-*g*-PS and PVDF-*g*-PSSNa copolymers²⁵⁻³¹ where S and SSNa stand for styrene and styrene sodium sulfonate. Those PVDF-*g*-PSSNa copolymers are used as proton exchange membranes for fuel cells and are endowed with conductivities reaching 100 mS/cm.

To find application as proton exchange membrane in fuel cell, those grafted copolymers must fulfill the following requirements: they must exhibit a high protonic conductivity, a low electronic conductivity, a low permeability to fuel and oxygen, good chemical, oxidative and hydrolytic stabilities, good mechanical properties especially when swollen with water and a

good thermal stability³².

Proton exchange membranes for fuel cell can be made by grafting sulfonated aromatic agents onto fluorinated copolymers, such as poly(VDF-*co*-HFP) copolymers.

Previous studies were carried out using diamines and aromatic containing-amines^{17,33-36} grafted onto commercially available poly(VDF-*co*-HFP) copolymers. The mechanism of grafting amines onto VDF-containing copolymers is well-known, and proceeds in three steps^{17,37-41}: first, the amine must be basic enough to enable the dehydrofluorination of HFP/VDF/HFP triads and VDF/HFP diads, creating a --CF=CH-- double bond⁵. Then, a metal oxide (MgO) can trap released HF, and regenerates the amine in its NH_2 form^{38,41}. Finally, the amine can be added onto these double bonds by a Michael addition, creating the grafts onto the polymeric chain. It was previously demonstrated that the longer the spacer between the aromatic ring and the amino group, the faster the addition³⁶. Hence, it can be expected that an amine bearing a sufficiently long spacer between the sulfonated aromatic ring and the amino group is a suitable candidate to be grafted, and an amine containing sulfonated aromatic ring could be able to be grafted onto poly(VDF-*co*-HFP) copolymers.

Low molecular weight amines bearing aromatic rings can be synthesized by telomerization. The synthesis of difunctional amino-sulfonated telomer requires aminomercaptans known to behave as efficient chain transfer agents⁴²⁻⁴⁵ since they exhibit high transfer constants (C_T) when they are involved with various monomers^{43,46}. The monomer is used in its salt form because of the high purity amine⁴⁶, and because the higher the basicity of the amine, the higher the C_T ⁴⁵. Aminomercaptans were also used as chain transfer agents in free radical polymerization of acrylates⁴⁶, methyl methacrylate (MMA)⁴⁷, and of styrene⁴⁷. In fact, the telomerization of styrene with various mercaptans⁴⁸ yielded monoadducts mainly and selectively⁴⁹. However, no free radical telomerization of the styrene sulfonic acid, in the presence of an aminomercaptan as the chain transfer agent, has previously been reported.

Hence, the purpose of this article concerns first the synthesis of a new sulfonated amino telomer bearing aromatic ring by the telomerization of styrene sodium sulfonate with the mercaptoethylamine hydrochloride. Secondly, this telomer was grafted onto poly(VDF-*co*-HFP) copolymers and the thermal and electrochemical properties of the resulting films were measured to evaluate their potential in proton exchange membranes for fuel cells.

EXPERIMENTAL SECTION

Materials

4-Styrene sulfonic acid sodium salt monomer, methanol, dimethylacetamide (DMAC), *N*-methylpyrrolidinone (NMP) and the metal oxide MgO were purchased from Aldrich. 2-Mercaptoethylamine hydrochloride was purchased from Avocado. 2,2'-Azobis(2-amidino-propane) dihydrochloride, V50, supplied by Wako, and has a half life, $t_{1/2}$, of 10 hrs at 56 °C. FC-2230[®] and FC-2178[®] poly(VDF-*co*-HFP) copolymers (where VDF and HFP stand for vinylidene fluoride and hexafluoropropylene, respectively) containing 20 mol. % of HFP were kindly offered by 3M-Dyneon (Antwerp, Belgium), Kynar[®] poly(VDF-*co*-HFP) copolymer containing 10 mol. % of HFP, and was also kindly given by Arkema (King of Prussia, Pa, USA). The synthesized copolymer ("s. copo.") containing 17 mol. % of HFP was synthesized in our laboratory: after applying vacuum, 32.60 g (8.15 mol) of VDF, 31.40 g (0.21 mol) of HFP, supplied by Solvay, 0.48 g (0.0025 mol) of *tert*-amyl peroxyvalate, ($t_{1/2}$ =1 hr at 62 °C) and 80 g of CF₃CH₂CF₂CH₃ (solvent, kindly offered by Solvay) were introduced, under nitrogen atmosphere, in an autoclave equipped with inlet and outlet valves, a manometer, and a magnetic stirrer. The temperature was maintained at 72 °C for 400 min. The drop in pressure from 29 to 13 bars was evidenced for the good reactivity of both comonomers. After

reaction, cooling and release of unreacted gases, the copolymer was precipitated from pentane, dried and characterized by ^{19}F NMR to assess the mol. % of HFP (as determined in the literature^{50,51}).

1. Telomerization

1.1. Synthesis of the telomer (Experiment I)

13.84 g (0.1221 mol) of 2-mercaptoethylamine hydrochloride, 0.27 g (0.0010 mol) of 2,2'-azobis(2-amidino-propane) dihydrochloride, V50, and 50 ml of deionized water were placed into a three-necked round-bottom flask equipped with a condenser, a magnetic stirrer and a nitrogen flow outlet. 5.03 g (0.0244 mol) of the sulfonated styrene monomer, in the presence of 0.06 g (0.0002 mol) of V50 and 100 ml of deionized water were progressively added into the mixture heated at 80 °C. After 5 hrs at 80 °C, the round-bottom flask was cooled and the resulting precipitate was washed with cold water, filtered off and dried. 5.37 g of a white powder were obtained (yield = 84%). After purification, the product was characterized by ^1H and ^{13}C NMR spectroscopy (to assess the cumulated DP_n), by thermogravimetric analysis, and mass spectroscopy.

The initial $[\text{thiol}]_0 / [\text{monomer}]_0$ molar ratio, Ro , was fixed at 0.2 and 5, leading to Experiments I and II, respectively. The conditions of both experiments are reported in Table 1. The yield was calculated only in the case of experiment I, when only a monoadduct (1) was obtained. The synthesis of products of Experiments II (a and b) were the same as that produced from Experiment I and products resulting from Experiments II were also characterized by ^1H NMR spectroscopy.

1.2. Chemical modification

In a two-necked-round bottom flask equipped with a condenser and a magnetic stirrer, 5.00 g of the zwitterion telomer of Experiment I was dissolved in a minimum amount of deionized water (50 mL) and treated with 0.75 g NaOH (97% in mol) at 40 °C for 2 hrs.

Drying occurred for 16 hrs by means of a Christ Freeze Dryer (Alpha 2-4 LD). The obtained product (telomer salt) was analyzed by mass spectroscopy and elementary analysis.

1.3. Synthesis of the sodium sulfonate polystyrene

3.00 g (0.0145 mol) of the 4-styrene sodium sulfonate monomer, 0.19 g (0.0007 mol) of (2,2'-azobis(2-amidino-propane)dihydrochloride) and 30 mL of deionized water were put into a two-necked round-bottom flask equipped with a condenser, a magnetic stirrer and a nitrogen flow inlet. The reaction was carried out at 80 °C for 5 hrs. The mixture was lyophilized to remove water, and then it was characterized by ^1H NMR spectroscopy in D_2O .

1.4. NMR Spectroscopy, kinetics study and thermogravimetric analysis

The different pure products were characterized by ^1H and ^{13}C NMR spectroscopy at room temperature. NMR spectra were recorded on a Bruker AC 200 instrument (200 MHz) using deuterated water as the solvent, and TMS as the reference for ^1H nuclei. Coupling constants and chemical shifts are given in hertz and ppm, respectively. It was noted that the ^1H and ^{13}C NMR spectra of telomers obtained from experiments I and II were different.

The kinetics of telomerization for Experiment II was plotted from ^1H NMR spectra of the crude product and is reported in the supporting information section.

Thermogravimetric analyses are described in 2.8. Section.

1.5. Mass spectroscopy

The product of Experiment I was analyzed using an Alliance 2695-Z-Q-waters mass spectrometer, equipped with a photodiode Array Detector-996 Waters.

2. Grafting

2.1. Grafting of the $H_2N-C_2H_4-S-C_2H_4-C_6H_4-SO_3Na$ (I) telomer

All the experiments were carried out in the same solvent (DMAc), at the same temperature and time (100 °C, and 5 hrs) and by the same process. The following description concerns experiment M1 in Table 3 (“s. copo.” copolymers grafted by 150 mol % of telomer in DMAc).

The molar percentage of telomer as starting material (150 mol %) was calculated using the molar percentage of HFP. Indeed, 100 mol % of telomer means that 1 mol of telomer was added per mol of HFP:

$$_{mol}\%TELOMER = 100\%, \text{ when } m_{TELO} = M_{TELO} \frac{m_{COPO} * _{mol}\%HFP}{150 * _{mol}\%HFP + 64 * _{mol}\%VDF}$$

where $M_{TELO} = 284$ g/mol, $_{mol}\%HFP = 17\%$ and $_{mol}\%VDF = 83\%$ for “s. copo.”.

2.00 g of “s. copo.” poly(VDF-*co*-HFP) copolymer, 1.84 g ($6.5 \cdot 10^{-3}$ mol) of telomer, 0.17 g ($4.2 \cdot 10^{-3}$ mol) of MgO and 30 mL of dimethylacetamide (DMAc) were put into a two-necked round-bottom flask equipped with a condenser and a magnetic stirrer. The reaction was heated at 100 °C for 5 hrs. The total product mixture was then cooled to room temperature, precipitated from ether and rinsed with water to get rid off all the excess of unreacted telomer. It was noted that the mixture could not be precipitated from water because of its partial solubility. The precipitated sample was heated at 60 °C under vacuum for 5 hrs to remove all diethyl ether.

The sample was placed in a solution of 50 mL of concentrated HCl (35%) and 50 mL of deionized water at 80 °C for 12 hrs, to convert all SO₃Na groups into SO₃H groups. It was analyzed by ¹H NMR spectroscopy at room temperature. The grafting reaction was monitored by ¹H NMR spectroscopy. Spectra were recorded on a Bruker AC 200 instrument (200 MHz) using deuterated DMSO as the solvent, TMS as reference for ¹H nuclei. Coupling constants and chemical shifts are given in hertz and ppm, respectively.

Some membranes that were not stable in water at room temperature were crosslinked with 50 mol.% of 2,4,4-trimethyl-1,6-hexanediamine.

2.2. Calculation of the molar percentage of grafted telomer

The weight percentage of grafted telomer was either assessed by ¹H NMR spectroscopy or by elementary analysis (for crosslinked grafted copolymers), or both.

- By ¹H NMR spectroscopy (Figure 1):

¹H NMR spectroscopy was used to monitor the efficiency of the reaction of the telomer onto the fluorinated copolymer. Figure 1 represents the ¹H NMR spectra of the grafted telomer (Experiment M1 of Table 3) and of the telomer.

Insert Figure 1

Spectrum 1 (Figure 1) exhibits two peaks centered at 7.2 and 7.5 ppm assigned to the aromatic protons of the grafted telomer (as seen in spectrum 2). The signals in the 2.6 to 3.2 ppm range and from 3.2 to 3.7 ppm are assigned to the methylene groups of the grafted telomer, and to the CH₂ of the VDF of the polymeric chain (normal and tail to tail VDF chaining),

respectively. ^1H NMR spectrum 1 allowed us to assess the molar percentage of grafted telomer, as follows:

$$\text{mol.\%grafted telomer} = \frac{\int \text{peaks of aromatic protons} / 4}{(\int \text{peaks of VDF} - 2 * \int \text{peaks of aromatic protons}) / 2}$$

$$\text{mol.\%grafted telomer} = \frac{\int \text{peaks in } 7.4\text{ppm} / 4}{(\int \text{peaks in } 3.1\text{ppm} - 2 * \int \text{peaks in } 7.4\text{ppm}) / 2}$$

where \int peaks in i ppm represents the integral of signal centered at i ppm.

From Figure 1, it is deduced that 8.8 mol % of telomer was grafted onto the poly(VDF-co-HFP) copolymer.

- By elementary analysis:

For the crosslinked copolymer, the mol. % of grafted telomer was calculated from elementary analysis, that differentiates the contribution of the weight of nitrogen, carbon, hydrogen, sulfur and oxygen atoms in the total weight of the membrane. All calculations are presented in the *Supporting Information* section.

Afterwards, the average of both grafted telomer percentages obtained from ^1H NMR spectroscopy and from elementary analysis were investigated.

2.3. Casting of the membranes

The grafted polymer was first dissolved in *N*-methyl pyrrolidinone (NMP). The ratio between the amount of NMP to that of grafted polymer ($W_{\text{NMP}}/W_{\text{poly}}$) varied from 75/25 to 85/15, depending on the viscosity of the copolymer. After 5hr-stirring at room temperature, the mixture was deposited on a glass substrate by means of a hand coater, and the thickness was fixed at about 150 μm . After coating, the NMP was evaporated under vacuum, first at room temperature for 1 h, then at 60 °C for 1 h, then at 95 °C for 2 hrs, and finally at 120 °C for 2 hrs. The glass substrate was cooled to room temperature and put into a deionised water bath to inverse the membrane on a non-solvent. The membrane was washed into 200 mL deionized water at 100 °C for 2 hrs, to wash it.

2.4. Weight % of extractible compounds

Membrane was weighed (W_1) before being introduced into a Soxhlet extraction with deionized water equipped with a one round bottom flask full of deionized water, and with a condenser. The water was refluxed for 48 hrs and products were extracted to remove water-soluble materials from the membrane. It was weighed again (W_2) after cooling at room temperature. The weight % of extractible is given from the following equation:

$$\text{Wt. \% extractable} = (W_1 - W_2) / W_2$$

2.5. Water uptake assessments

The water uptake of membranes was determined by measuring the change in weight before and after the hydration. Membranes were swollen in deionized water and in methanol (at a concentration of 5 mol/L, as in a direct methanol fuel cell) at room temperature for 20 hrs.

$$\tau_s = ((W_s - W_D) / W_D)$$

where W_s and W_D represent the swollen and the dry weight, respectively.

2.6. Assessment of the ion exchange capacity (IEC)

IEC value is given in mmol. of SO_3H functions per gram of copolymer, and was determined as follows:

$$IEC = \frac{mol\% TELO}{(mol\% VDF*64)+(mol\% HFP*150)} * 1000$$

where mol.%TELO represents the average value between the molar percentages of grafted telomer calculated by 1H NMR, and elementary analysis. In the case of M2, where mol.%TELO= 5%, IEC = 0.69 meq/g

2.7. Measurement of the protonic conductivity

Membrane conductivity σ was determined from impedance spectroscopy measurements using a Hewlett-Packard 4192 impedance analyzer working in the frequency range of 5-1.3x10⁷ Hz at 0.1 V. Water swollen samples were held in a cell between stainless steel electrodes at ambient humidity and room temperature and assessments were carried out three times. More other information on the conductivity measurements is presented in the Supporting Information section.

2.8. Thermal analysis

Thermal stability was assessed by thermogravimetric analyses using a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus. 10 to 15 mg of sample were placed in a platinum pan and heated under air atmosphere from 30 to 590 °C, at a heating rate of 10 °C/min.

2.9. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectrometer

The morphology and the X-ray energy dispersive analysis of membranes were investigated by Scanning Electron Microscopy (SEM) analysis using LEO (ex LEICA, ex CAMBRIDGE) S260 equipped with a system of microanalysis-X. Accelerating voltage of 300 V to 3 kV (accelerating rate of 100 V) and 4 kV to 30 kV (accelerating rate of 1 kV) was applied.

Samples were put into liquid nitrogen to be cryofractured and the cross sectioned and was analyzed. Samples were vacuum coated with carbon, under vacuum.

RESULTS and DISCUSSION

An amine bearing a sulfonated aromatic ring was synthesized by telomerization and grafted onto commercially available poly(VDF-co-HFP) copolymers. The first part deals with the telomerization of styrene sodium sulfonate. Then, the second part deals with an investigation of the grafting of the synthesized telomer onto commercially available poly(VDF-co-HFP) copolymers to lead to original membranes.

1. Radical telomerization of styrene sodium sulfonate with mercaptoethylamine hydrochloride

2-Mercaptoethylamine hydrochloride and styrene sodium sulfonate were used as the telogen and the monomer, respectively, in the presence of a radical initiator. The reaction proceeds according to Scheme 1.

Insert Scheme 1

The conditions of the reaction (Table 1) were optimized. The telomerization was carried out in water, with 2,2'-azobis(2-amidino-propane)dihydrochloride (V50) as the initiator, and with an initial $[\text{initiator}]_0 / [\text{monomer}]_0$ molar ratio, C_0 , of 5 %. The initial $[\text{mercaptan}]_0 / [\text{monomer}]_0$ molar ratio, R_0 , was in the range of 0.2 to 5.0.

Insert Table 1

When $R_0 \geq 1$, only the monoadduct was obtained. With $R_0 < 1$ (Experiments IIa and IIb), several products were obtained: monoadduct, multiadducts and poly(styrene sodium sulfonate).

1.1. With $R_0 < 1$:

The product of Experiment IIb was characterized by ^1H NMR spectroscopy to identify the different products obtained with $R_0 < 1$, and hence to provide useful data on the mechanism of that reaction.

Figure 2 represents the ^1H NMR spectra of the transfer agent (mercaptoethylamine) (spectrum a), of the monoadduct (spectrum b), of the product of experiment IIb (after 135 min at 75 °C, and without any further treatment) (spectrum c), and of the polystyrene sodium sulfonate (prepared by radical polymerization in water of styrene sodium sulfonate initiated by 2,2'-

azobis (2-amidino-propane) dihydrochloride without any transfer agent) (spectrum d). Figure 2c shows five different groups of signals (named A to E) assigned to three different products after consumption of all monomer: the monoadduct (spectrum b), multiadducts (mainly di and triadducts), and the homopolymer of poly(styrene sodium sulfonate). The formation of the monoadduct is evidenced by signals ranging from 7.5 to 8.0 ppm for aromatic protons (peak A), and multiplets ranging from 2.7 to 3.2 ppm for aliphatic protons (signals C and D). The di- and triadducts are characterized by multiplets ranging from 2.1 to 2.9 ppm for aliphatic protons (multiplet D) and 7.2 to 8.0 ppm for aromatic ones (peak A). In addition, the presence of poly(styrene sulfonic acid) is evidenced in Figure 2c by multiplets ranging from 6.7 to 7.2 ppm assigned to both ortho protons on the pendant aromatic ring (peak B). Signals attributed to the meta protons on the sulfonated aromatic ring are centered at 7.6 ppm (peak A), as proved by spectrum d. The aliphatic protons of the polymer are characterized by a broad signal ranging from 1.2 to 2.0 ppm, as proved by spectrum d (peak E)⁵²⁻⁵⁵.

The molar percentages of each species in the mixture were assessed from the integrals of those signals and plotted in Fig. 2 of the Supporting information section.

The telomerization reactions with $R_o=0.2$ were carried out at 67 and 75 °C to evaluate the influence of the temperature. The details of the study are mentioned in the Supporting Information section (Fig. 2 and 3). This study shows that the telomerization of styrene sodium sulfonate (with a $R_o = 0.2$ (Experiments IIa and IIb) at 67 and 75 °C), led to the polystyrene sodium sulfonate as the main product. Then other products were produced from the telomerization (mono- and multiadducts). This result shows that mercaptoethyl amine hydrochloride is not an efficient transfer agent.

The transfer constant (C_T) was determined at 67 °C and 75 °C by O'Brien and Gornick's method⁵². Figure 3 plots the evolution of $\ln \frac{[T]_0}{[T]}$ versus $\ln \frac{[M]_0}{[M]}$, where [T] and [M] represent the concentrations in mercaptan and monomer at t time, respectively, at 67 °C and 75 °C with $R_o=0.2$, and shows a linear relationship. The slopes of the straight lines led to the C_T value. It is well known that the value of a transfer constant depends on several factors (temperature, solvent, pH, reactivity of monomer, etc...) ^{45,53}. Concerning the telomerization of styrene with mercaptans, Bechkok *et al.*⁴⁹ showed that it proceeded in two main steps: multiadducts were produced first (in the presence of a high amount of monoadduct), and when all the thiol was consumed, radical polymerization of styrene took place. These same authors⁴⁹ deduced that the C_T values of thioglycolic acid and 2-perfluorohexylethanethiol for styrene telomerization were 7.5 and 12.3 at 80 °C, respectively. Boyer *et al.*⁴⁵ reported that the transfer constant value for a mercaptoethylamine hydrochloride with methyl methacrylate in DMF varied from 0.23 to 0.34 versus the pH value, at 70 °C.

Insert Figure 2

From O'Brien and Gornick's method⁵² (Figure 3), the transfer constant values for mercaptoethylamine hydrochloride were 3.4 and 5.0 at 67 and 75 °C, respectively. As expected, it is observed that the C_T value increases with the temperature, showing that the higher the temperature, the more efficient the transfer of mercaptans. Moreover, those values are low enough to obtain mono and multiadducts, and to form polystyrene sodium sulfonate even when mercaptan was still present in the mixture.

To conclude on the study of $R_o < 1$, the telomerization of styrene sodium sulfonate (SNaS) in excess with a mercaptan yielded mono-, multi adducts and homopolymer PSNaS. This result

shows that mercaptoethylamine hydrochloride is a transfer agent having a fair efficiency when involved with styrene sodium sulfonate.

Insert Figure 3

1.2. With $R_o \geq 1$

1.2.1. ^1H and ^{13}C NMR spectroscopy

After work up and purification, the telomer (1) was characterized by ^1H and ^{13}C NMR spectroscopy^{43,54-56}, and all spectra are given in the Supporting Information section.

Both ^1H and ^{13}C NMR spectra of the telomer of Experiment I support the formation of the monoadduct shown in Scheme 2.

Insert Scheme 2

1.2.2. Mass spectrometry

This technique permits the molecular weight determination of the telomer by separating molecular ions according to their mass-to-charge ratio (m/z).

The mass spectra of the telomer of experiment I are given in the Supporting Information. They exhibit the most intense fragments at $m/z=260$ for the deprotonation, and $m/z=262$ for the protonation. Hence, the molecule that exhibits a molecular weight of 261 g/mol is a zwitterion⁵⁷ (Scheme 3).

Insert Scheme 3

To avoid the zwitterion, the telomer was chemically neutralized into a sulfonate salt in the presence of a base (Scheme 4).

Insert Scheme 4

Before reaction with NaOH, the zwitterion was insoluble in water at low temperature (5 °C). After its chemical neutralization, the resulting amino sodium sulfonate telomer became soluble in water even at room temperature, hence supplying the good evidence that the reaction with NaOH was successful.

1.2.3. Thermostability of the monoadduct telomer by thermogravimetry (TGA)

Figure 4 shows both TGA thermograms of the $^+\text{H}_3\text{N}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{C}_6\text{H}_4-\text{SO}_3^-$ (zwitterion-product before reaction with NaOH), and $\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$ (**1**) (salt-product after reaction with NaOH) performed under air atmosphere. It is observed that both thermograms exhibit a good thermostability under air: up to 280 °C for the zwitterion and until 200 °C for the salt. The thermogram of the zwitterion is composed of three main parts: (A) from 30 to 350 °C, (B) from 350 to 550 °C and (C) from 550 °C. Part (C) is assigned to NaCl residue (11.3% of the product) residue that does not decompose even at 700 °C^{58,59}. Parts (A) and (B) correspond to the zwitterion telomer. Table 2 explains the assignments of both of these parts.

Insert Figure 4

Insert Table 2

Hence, the first part (A) of the product corresponds to a loss of $\text{C}_6\text{H}_4\text{-SO}_3^-$ that decomposed from 280 to 350 °C, while the second part (B) deals with the loss of the $^+\text{H}_3\text{NCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2-$ chain that decomposed from 460 °C⁵⁹. This result shows that in the case of the zwitterion, the “weak point” of the $^+\text{H}_3\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3^-$ molecule is not SO_3^- group as it could be expected, but rather the $\text{C}_6\text{H}_4\text{-SO}_3^-$ group that starts to decomposes at 280 °C.

The thermostability of $\text{H}_2\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}$ is lower than that of $^+\text{H}_3\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3^-$. In the case of $\text{H}_2\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}$, a first mass decrease under 100 °C is from water release. Indeed, the telomer salt is highly hygroscopic. In contrast to the thermogram of $^+\text{H}_3\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3^-$, the less thermostable behavior of $\text{H}_2\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}$ from 200 °C certainly arises from the decomposition of the SO_3Na group⁵⁹.

To conclude on the study of the reaction where $\text{Ro} \geq 1$, the telomerization of styrene sodium sulfonate with an excess of mercaptan led to the monoadduct only. The synthesis of this amino sulfonate telomer is simple, environmentally friendly and selectively produces the expected telomer, and in high yield. Furthermore, as the starting material (styrene sodium sulfonate) already contains the sulfonated group, no further sulfonation by oleum is required. This amine bearing sulfonated aromatic ring can be grafted onto poly(VDF-co-HFP) copolymers.

2. Grafting of $\text{H}_2\text{N-C}_2\text{H}_4\text{-S-C}_2\text{H}_4\text{-C}_6\text{H}_4\text{-SO}_3\text{Na}$ (1) onto poly(VDF-co-HFP) copolymers

2.1. Mechanism of grafting of amines onto poly(VDF-co-HFP) copolymer

Grafting of $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$ (**1**) onto poly(VDF-co-HFP) copolymer is shown in Scheme 5.

Insert Scheme 5

The sites of amine grafting onto poly(VDF-co-HFP) copolymers were identified to be first VDF units between two HFP units (i.e., HFP/VDF/HFP triad), and then the VDF adjacent to HFP^{5,17}. Grafting occurs onto the CF_2 groups of VDF units^{5,17,36} and several rearrangements are possible leading to an imine⁶⁰.

Three different copolymers were grafted with different amounts of that amino-sulfonated telomer. The molar percentage of initial telomer was calculated *via* the molar percentage of HFP in the copolymer. The reaction was carried out in different solvents, at different temperatures and times.

^1H NMR spectroscopy enabled us to assess the molar percentage of telomer grafted onto copolymer.

2.2. Rate of grafting of telomer

The mol. % of grafted telomer onto poly(VDF-co-HFP) copolymer is reported in section 2.2. of the experimental part. Table 3 summarizes the copolymers used, the initial percentages of telomer, and the percentages of grafted telomer measured by NMR and by elemental analysis, and the average of both.

Insert Table 3

Table 3 shows that for a same copolymer, the higher the initial percentage of telomer, the higher the molar percentage of grafted telomer. Indeed, grafting Kynar[®] copolymer starting from 50 mol.% of initial telomer gave an average of 3.1 mol.% of grafted telomer (samples M2), whereas starting from 150 mol.% of initial telomer (1), 10.6 mol.% was grafted (samples M4). The maximum rate of telomer grafted onto the copolymers was almost 12 %, and was reached when using a copolymer containing 20 mol. % of HFP.

2.3. Properties of membranes M1 to M6b in water and in methanol

Membranes were performed from M1 to M6b samples. The extractible fraction and swelling rates were measured in water, and in methanol (5 mol.L⁻¹). Table 4 summarizes the copolymers, the mol. % of grafted telomer, the weight % of extractible, and water and methanol uptakes.

Insert Table 4

A grafting rate higher than 10 mol. % can induce poor performances of the membrane in terms of resistance to oxidation in water at 100 °C such as for M6a membrane that decomposed in water and seemed to partly dissolve in water. Such an observation can be explained by the high molar percentage of grafted telomer, which induces a high amount of SO₃H groups. The sulfonic acid groups are known to be hydrophilic and thus increase the water solubility of the membrane. To improve the resistance in water membranes were crosslinked with diamine such as 2,4,4-trimethyl-1,6-hexanediamine⁶¹ yielding, for example, the M6b membrane. This crosslinking agent improves the resistance of the membrane in water at 100 °C. However, the amount of diamine has to be low enough not to react with SO₃H

groups, and hence to avoid any decrease of the ionic conductivity. M6b membrane contains 50 mol.% of 2,4,4-trimethyl-1,6-hexanediamine.

It is noted that M1 membrane decomposed in water at 100 °C after 48 hrs. Indeed, the synthesized copolymer decomposed because it has a much lower molecular weight than that of the commercially available copolymers, the molecular weights of which are higher than 400,000 g.mol⁻¹.

The swelling behavior of fluorinated ionomer membranes has been a frequent topic of study because of its relationship to membrane properties such as ionic conductivity and because water is required to enable the proton conductivity. The pre-treatment of these polymers have a marked impact on their swelling and solubility properties⁶². Because of this observation, the swelling rates in water and methanol are higher for membranes in this present study than that of perfluorinated Nafion[®] 115.

Moreover, membrane swelling (Table 4) results from a complex interplay between the affinity of the polymer and ionic sites for polar solvents⁶²⁻⁶³, and thus the swelling rates are different (and higher) in water than in methanol.

2.4. Ion exchange capacity (IEC) and protonic conductivity

The main application of these grafted membranes is devoted to fuel cells. Several properties must be assessed to evaluate the efficiency of those membranes. Theoretical ion exchange capacities (IEC, in mmol equivalent per gram of copolymer) were first assessed from the molar percentages of grafted telomer. After treatment in deionized water (100 °C for 2 hrs), the conductivities of the membranes were measured at room temperature and at 100 % relative humidity. Finally, the relationship of swelling rates in water was compared to that of

proton conductivities.

Insert Table 5

First, it is mentioned that the thickness and the conductivity of M6a membrane could not have been measured because, as shown in Table 5, the membrane decomposed in water. Second, the IEC of M6b membrane was not determined because the crosslinking by aliphatic diamine can occur on SO₃H groups.

The conductivity of Nafion117[®] at room temperature and under 100 % humidity was 54 mS/cm and the best conductivity of telomer-grafted copolymer, (that is 0.4 mS/cm for M4 and M5) is 100 times lower than that of the Nafion[®] membrane.

Conductivities were much lower than that of Nafion117[®], and this may arise from various parameters: micro-organization and morphology of the clusters of SO₃H groups, swelling, diffusion of water, mobility of protons and H₃O⁺, etc...

Moreover, conductivity is strongly dependant on the content of hydration⁶⁴, and hydration of membranes may vary from M2 to M6.

Figure 5 presents the conductivities *versus* IEC of membranes M2 to M6b, it is observed that, except for membrane M6, the higher the amount of SO₃H per gram of copolymer (IEC), the higher the conductivity^{62,65}.

Insert Figure 5

In fact, it is well-known that other parameters such as hydration, microstructure, or organization of the SO₃H ionic clusters in fluorinated polymer matrix have an influence on the

transfer of the H^+ from the anode to the cathode, and so on the conductivity, and especially in the Nafion[®] membrane⁶⁶. Moreover, ionic conductivity is closely related to the mobility of the water molecules in the membranes⁶⁵.

As water is needed as the mobile phase to favor the proton conductivity, it was of interest to evaluate the water uptake, and swelling rate in methanol for the application in DMFC (Table 4) were evaluated.

Conductivities values were compared to swelling rates in water (Figure 6).

Insert Figure 6

There is a tendency for the water uptake with increasing with the conductivity values. The microstructure of the ionomer changes with the swelling in water⁶⁷. A model was proposed, showing that the dry membrane was considered to contain isolated and spherical ionic clusters. It can be assumed that with the absorption of water, the clusters swell and percolation was achieved by the formation of connecting cylinders of water between the swollen, spherical clusters^{67,68}. In addition, the accessible SO_3H sites for proton exchange were water swollen to ensure the good proton transport from one cluster to one another. Thus, it is obvious that the higher the swelling, the higher the conductivity.

2.5. Thermal stability of the membranes

Usually, a fuel cell operates at a temperature of almost 80 °C, though nowadays, the tendency is for medium temperature membranes (operating at ca. 120 °C). The thermal behaviors of M2 to M6 membranes were evaluated by thermogravimetric analysis and by applying an isotherm at 120 °C. Figure 7 represents the thermograms of the grafted membranes based on

Kynar[®] or FC-2230[®] copolymer, and grafted at different amounts (from 5 to 13 %).

Insert Figure 7

As expected, all membranes were less thermally stable than the virgin copolymer, and all of them started to decompose starting from 170 °C. The higher the rate of grafted sulfonated amine, the higher the weight loss. Indeed, the imine bonds C=N, created in the last step of grafting mechanism induced weak bonds, hence leading to a decomposition from 170 °C⁶⁰.

The isotherms at 120 °C in air atmosphere of M2 and M6 membranes are shown in Figure 8. M2 and M6 membranes were thermally stable at 120 °C under air, since only 0.8 and 1.2 wt % was lost after 6 hrs, respectively. Nevertheless, it must be noted that M2 and M6 membranes contained 5 and 13 mol. % of the grafted telomer, respectively, (measured by ¹H NMR spectroscopy) and the higher the grafted telomer, the lower the thermostability. Then, considering the thermal stability, these membranes (M2 to M6) can be utilized as proton exchange membranes.

2.6. Energy Dispersive X-Ray Spectrometer

Several samples were analyzed by a scanning electron microscope (SEM) coupled with an energy dispersive X-Ray analyzer (EDX) to investigate the structure of the membrane (homogeneity, porosity, etc...), and to get a qualitative data in terms of the different elements (C, O, F, Na and S atoms). Figure 9 represents the SEM picture of a cross section of the M4 membrane, and the EDX analysis.

Insert Figure 8

The M4 Membrane and all the other membranes were homogeneous. Indeed, the detection of secondary electrons characterizes the topography of the sample, and Figure 9 shows only one main color for sample M4, thus indicating one main topography.

All elements present in the grafted copolymer can be observed in the EDX spectrum, except nitrogen that might be overlapping with the peak of carbon. Interestingly, it is noted that the signal assigned to element Na (at 1.0 keV) is absent, and proves that all SO_3Na groups of the telomer were chemically modified into SO_3H functionality, after acid treatment. This proton exchange is essential for protonic conductivity. Thus, these grafted membranes exhibit a good structure at micrometer scale to find potential applications as proton exchange membranes in fuel cells.

Insert Figure 9

Hence, it was shown that the successful grafting requires an excess of telomer as the starting material (150 mol. %) as the starting material and the grafted amount of telomer can not exceed 13 mol % with a copolymer containing 20 mol. % of HFP. This limitation arises from the specific sites of grafting that are mainly VDF located between two HFP units, and VDF adjacent to HFP. A limit was reached close to 11% when the membrane started to decompose in water at 120 °C. Indeed, oxidative and hydrolytic stabilities can be improved by crosslinking with a diamine. Hence, the best membrane seems to be a commercially available copolymer grafted with 13 mol % of amine, crosslinked with a low amount of 2,4,4-hexamethylene-1,6-diamine. Protonic conductivity behaves reasonably with the increasing of the IEC of the membrane.

CONCLUSION

This study deals with the synthesis of a new amino sulfonated aromatic telomer and its grafting onto poly(VDF-*co*-HFP) copolymer for proton exchange membrane for fuel cells. First, the assessment of the transfer constant of 2-mercaptoethylamine hydrochloride showed a fair efficiency with styrene sodium sulfonate. Hence, the telomerization of styrene sodium sulfonate in excess ($R_o < 1$) with mercaptoethylamine hydrochloride yielded monoadduct, multiadducts and homopolymers. For $R_o \geq 1$, only the monoadduct was obtained, and the zwitterions can be chemically exchanged into the sodium salt form.

Second, the synthesized amine bearing sulfonated aromatic ring was grafted onto poly(VDF-*co*-HFP) copolymers with a maximum grafting molar percentage of 100 %. Even at this grafting rate, the thermal stability was very high. The protonic conductivity increased with the water uptake of the membrane. Nevertheless, although the ion exchange capacity (based on the molar percentage of grafted amine) is high, the conductivity of membranes is 100 times lower than that of Nafion[®]. This low conductivity can be explained by many factors. Indeed, protonic conductivity is related to the transport of H^+ or H_3O^+ move (of by SO_3H groups) from the anode to the cathode, and this transfer can be slowed down by the micro-organization or morphology of the clusters of the SO_3H groups, swelling, diffusion of water, mobility of protons and H_3O^+ .

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Supporting Information Available: Additional data in the experimental and the “results and discussion” sections are given: the evolution of the molar percentage of monomer, mercaptan, monoadduct, monomer units, and polymer noted in the radical telomerization of styrene sodium sulfonate with mercaptoethylamine hydrochloride; ¹H NMR spectrum of styrene sodium sulfonate monomer; ¹H and ¹³C NMR spectra and mass spectra of H₂N-C₂H₄-S-C₂H₄-C₆H₄-SO₃Na telomer and its corresponding zwitterions isomer; the elementary analyses of the telomer; results from the elementary analyses of the grafted telomer onto poly(VDF-co-HFP) copolymers, assessments of the mol. % of grafted telomer; and the determination of σ conductivities of the membranes from the impedance diagrams.

5. References

- (1) Scheirs, J. Modern Fluoropolymers; Wiley: New York, 1997.
- (2) Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T. Fluoropolymers 2: Properties; Kluwer, Plenum: New York, 1999.
- (3) Imae, T. Current Opinion in Colloid & Interface Science 2003, 8, 307-314.
- (4) Ameduri, B.; Boutevin, B. Well-Architected Fluoropolymers: Synthesis, Properties and Applications; Elsevier: Amsterdam, 2004.
- (5) Schmiegel, W. W. Angew Makromol Chem 1979, 76/77, 39-65.
- (6) Logothetis, A. L. In Organofluorine Chemistry: Principles and Commercial Applications; Banks, R. E., Tatlow, J. C., Eds; Wiley: New York, 1994; chap 16.

- (7) Arcella, V.; Brinati, G.; Apostolo, M. *Chem Ind* April 1997, p 490.
- (8) Arcella, V.; Ferro, R. In *Modern Fluoropolymers*; Scheirs J., ed; Wiley: New York, 1997; Chap2, p71.
- (9) Van Cleeff, A. In *Modern Fluoropolymers*; Scheirs J., ed; Wiley: New York, 1997; Chap 32, p 597.
- (10) Ameduri, B.; Boutevin, B.; Kostov, G. K.; Petrova, P. *Design Mono Polym* 1999, 2, 267-285.
- (11) Banik, I.; Bhowmick, A. K. *J Mat Sci* 2000, 35, 3579-3582.
- (12) Ameduri, B.; Boutevin, B.; Kostov, G. *Prog Polym Sci* 2001, 26, 105-187.
- (13) Schmiegel, W. W. (DuPont Dow Elastomers). US Patent 2,003,065,132, 2002.
- (14) Nasef, M. M.; Dahlan, K. Z. M. *Nuclear Instruments & Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms* 2003, 201, 604-614.
- (15) Soresi, B.; Quartarone, E.; Mustarelli, P.; Magistris, A.; Chiodelli, G. *Solid State Ionics* 2004, 166, 383-389.
- (16) Coggio, W. D.; Scott, P. J.; Hintzer, K.; Hare, E. D. US Patent 2,004,014,900, 2004.
- (17) Taguet, A.; Ameduri, B.; Boutevin, B. *Adv Polym Sci* 2005, 184, 127-211.
- (18) Logothetis, A. L. *Prog Polym Sci* 1989, 14, 251-296.
- (19) Florin, R. E. In *Fluoropolymers*; Wall, L. A., ed.; Wiley: New York, 1972; Chap 11, p 317.
- (20) Singh, A.; Silverman, J. In *Progress in Polymer Processing*; Hansen: Munich, 1992; vol 3, p375.
- (21) Gupta, B.; Scherer, G. G. *Chimia* 1994, 48, 127-137.
- (22) Lyons, B. J. In *Modern Fluoropolymers*; Scheirs, J., Ed; Wiley: New York, 1997; chap. 18, p 335.
- (23) Uyama, Y.; Kato, K.; Ikada, Y. *Adv Polym Sci* 1998, 137, 1-39.

- (24) Dargaville, T. R.; George, G. A.; Hill, D. J. T.; Whittaker, A. K. *Prog Polym Sci* 2003, 28, 1355-1376.
- (25) Holmberg, S.; Lehtinen, T.; Naesman, J.; Ostrovskii, D.; Paronen, M.; Serimaa, R.; Sundholm, F.; Sundholm, G.; Torell, L.; Torkkeli, M. *J Mat Chem* 1996, 6, 1309-1317.
- (26) Hietala, S.; Holmberg, S.; Karjalainen, M.; Nasman, J.; Paronen, M.; Serimaa, R.; Sundholm, F.; Vahvaselka, S. *J Mat Chem* 1997, 7, 721-726.
- (27) Ennari, J.; Hietala, S.; Paronen, M.; Sundholm, F.; Walsby, N.; Karjalainen, M.; Serimaa, R.; Lehtinen, T.; Sundholm, G. *Macromol Symp* 1999, 146, 41-45.
- (28) Jokela, K.; Serimaa, R.; Torkkeli, M.; Sundholm, F.; Kallio, T.; Sundholm, G. *J Polym Sci, Part B: Polym Phys* 2002, 40, 1539-1555.
- (29) Gode, P.; Ihonen, J.; Strandroth, A.; Ericson, H.; Lindbergh, G.; Paronen, M.; Sundholm, F.; Sundholm, G.; Walsby, N. *Fuel Cells* 2003, 3, 21-27.
- (30) Paronen, M.; Sundholm, F.; Ostrovskii, D.; Jacobsson, P.; Jeschke, G.; Rauhala, E.; Tikkanen, P. *Chem Mat* 2003, 15, 4447-4455.
- (31) Kallio, T.; Jokela, K.; Ericson, H.; Serimaa, R.; Sundholm, G.; Jacobsson, P.; Sundholm, F. *J Appl Electrochem* 2003, 33, 505-514.
- (32) Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587-4611.
- (33) Pruett, R. L.; Barr, J. T.; Rapp, K. E.; Bahner, C. T.; Gibson, J. D.; Lafferty, R. H. *J. Am Chem Soc* 1950, 72, 3646-3650.
- (34) Arnold, R. G.; Barney, A. L.; Thompson, D. C. *Rubb Chem Technol* 1973, 46, 619-652.
- (35) Schmiegel, W. W. (DuPont). US Patent 4,496,682, 1985.
- (36) Taguet, A.; Ameduri, B.; Boutevin, B. *J Polym Sci, Part A: Polym Chem* 2006, 44, 1855-1868.

- (37) Paciorek, K. L.; Mitchell, L. C.; Lenk, C. T. *J Polym Sci* 1960, 45, 405-413.
- (38) Smith, J. F. *J Appl Polym Sci* 1961, 5, 460.
- (39) Thomas, D. K. *J Appl Polym Sci* 1964, 8, 1415-1427.
- (40) Wright, W. W. *Br Polym J* 1974, 6, 147-164.
- (41) Bryan, C. J. *Rubb Chem Techn* 1977, 50, 83-89.
- (42) Ikada, Y.; Iwata, H.; Nagaoka, S. *Macromolecules* 1977, 10, 1364-1371.
- (43) Ameduri, B.; Berrada, K.; Boutevin, B.; Bowden, R. D. *Polym Bull* 1992, 28, 531-537.
- (44) Shefer, A.; Grodzinsky, A. J.; Prime, K. L.; Busnel, J. P. *Macromolecules* 1993, 26, 2240-2245.
- (45) Boyer, C.; Loubat, C.; Robin, J. J.; Boutevin, B. *J Polym Sci, Part A: Polym Chem* 2004, 42, 5146-5160.
- (46) Nair, C. P. R.; Richou, M. C.; Chaumont, P.; Clouet, G. *Eur Polym J* 1990, 26, 811-815.
- (47) Tanaka, M.; Mori, A.; Imanishi, Y.; Bamford, C. H. *Int. J Bio Macromol* 1985, 7, 173-181.
- (48) Gregg, R. A.; Alderman, D. M.; Mayo, F. R. *J Am Chem Soc* 1948, 70, 3740-3743.
- (49) Bechkok, A.; Belbachir, M.; Guyot, B.; Boutevin, B. *Eur Polym J* 1998, 35, 413-421.
- (50) Pianca, M.; Bonardelli, P.; Tato, M.; Cirillo, G.; Moggi, G. *Polymer* 1987, 28, 224-230.
- (51) Gelin, M.-P.; Ameduri, B. *J Fluorine Chem* 2005, 126, 575-583.
- (52) O'Brien, J. L.; Gornick, F. *J Am Chem Soc* 1955, 77, 4757-4763.
- (53) Loubat, C.; Boutevin, B. *Polym Int* 2001, 50, 375-380.

- (54) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. Tables of Spectral Data for Structure Determination of Organic Compounds: ¹³C-NMR, ¹H-NMR, IR, MS, UV/VIS. Chemical Laboratory Practice; Springer-Verlag: Berlin, 1983.
- (55) Ameduri, B.; Boutevin, B.; Khamlichi, M.; Robin, J.-J. *Macromol Chem Phys* 1994, 195, 3425-3443.
- (56) Boutevin, B.; Rigal, G.; El Asri, M.; Lakhlifi, T. *Eur Polym J* 1997, 33, 277-284.
- (57) a) Kanetani, F. *Chem. Lett.* **1980**, 965-968; b) Charlier, P.; Jerome, R.; Teyssie, P. *Polym Networks Blends* 1992, 2, 107-112.
- (58) Fuertes, A. B.; Fernandez, M. J. *Thermochim Acta* 1996, 276, 257-269.
- (59) a) Yao, Q.; Wilkie, C. A. *Polym. Deg. Stab.* 1999, 66, 379-384; b) Jiang, D. D.; Yao, Q.; McKinney, M. A.; Wilkie, C. A. *Polym Deg Stab* 1999, 66, 423-434.
- (60) Mitra, S.; Ghanbari-Siahkali, A.; Kingshott, P.; Almdal, K.; Kem Rehmeier, H.; Christensen, A. G. *Polym Deg Stab* 2004, 83, 195-206.
- (61) Taguet, A.; Ameduri, B.; Dufresne, A. *Eur Polym J* 2006, 42, 2549-2561.
- (62) Doyle, M.; Rajendram, G., In *Handbook of Fuel Cells-Fundamentals, Technology, and Applications*; Vielstich, W., Ed.; Wiley: New York, 2003; Chap. 30, Vol. 3.
- (63) a) Yeo, R. S.; Cheng, C. H. *J Appl Polym Sci* 1986, 32, 5733-5741; b) Nandan, D.; Mohan, H.; Iyer, R. M. *J Membr Sci* 1992, 71, 69-80; c) Ren, X.; Springer, T. E.; Gottesfeld, S. *J Electrochem Soc* 2000, 147, 92-98; d) Geiger, A. B.; Newman, J.; Prausnitz, J. M. *AIChE J* 2001, 47, 445-452.
- (64) a) Zawodzinski, T. A., Jr.; Davey, J.; Valerio, J.; Gottesfeld, S. *Polymer Mat Sci Eng* 1993, 68, 115-116; b) Zawodzinski, T. A., Jr.; Derouin, C.; Radzinski, S.; Sherman, R. J.; Smith, V. T.; Springer, T. E.; Gottesfeld, S. *J Electrochem Soc* 1993, 140, 1041-1047; c) Zawodzinski, T. A., Jr.; Springer, T. E.; Davey, J.; Jestel, R.; Lopez, C.; Valerio, J.

Gottesfeld, S. J Electrochem Soc 1993, 140, 1981-1985; d) Baradie, B.; Poinsignon, C.; Sanchez, J. Y.; Piffard, Y. Macromol Symp 1999, 138, 85-91.

(65) Saito, M.; Arimura, N.; Hayamizu, K.; Okada, T. J Phys Chem B 2004, 108, 16064-16070.

(66) a) Porat, Z. E.; Fryer, J. R.; Huxham, M.; Rubinstein, I. J Phys Chem 1995, 99, 4667-4671; b) Gruger, A.; Regis, A.; Schmatko, T.; Colomban, P. Vibrational Spectroscopy 2001, 26, 215-225.

(67) Gebel, G. Polymer 2000, 41, 5829-5838.

(68) Mauritz, K. A.; Moore, R. B. Chem Rev 2004, 104, 4535-4585.

FIGURE CAPTIONS

Figure 1: ^1H NMR spectra of the poly(VDF-*co*-HFP) copolymer (containing 17 mol % of HFP) grafted by the sulfonated amine containing an aromatic ring (M1) (spectrum 1), and of the sulfonic telomer (spectrum 2). Spectra 1 and 2 were recorded in acetone d_6 and in D_2O , respectively.

Figure 2: ^1H NMR spectra (all recorded in deuterated water) of the transfer agent (spectrum a), of the monoadduct (spectrum b), of total product of Experiment IIb after 135 min at 75°C (spectrum c), and of the polystyrene sodium sulfonate (spectrum d).

Figure 3: $\ln[\text{T}]_0/[\text{T}]$ *versus* $\ln[\text{M}]_0/[\text{M}]$ for the evaluation of the C_T value from O'Brien and Gornick's method⁵² for radical telomerization of styrene sodium sulfonate with mercaptoethylamine hydrochloride at 67 and 75°C . T and M stand for transfer agent and monomer, respectively.

Figure 4: TGA thermograms of $^+\text{H}_3\text{N}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{C}_6\text{H}_4-\text{SO}_3^-$ (zwitterion-product; full line) (experiment I) and of $\text{H}_2\text{N}-\text{C}_2\text{H}_4-\text{S}-\text{C}_2\text{H}_4-\text{C}_6\text{H}_4-\text{SO}_3\text{Na}$ (**1**) (salt-product; dotted line).

Figure 5: Conductivity σ (in mS/cm) *versus* ion exchange capacity (in meq per gram of copolymer) at room temperature for 100% relative humidity.

Figure 6: Ionic conductivities of membranes M2 to M6b (Table 4) *versus* swelling rate measured in water, at room temperature, under 100% relative humidity.

Figure 7: Thermogram of virgin poly(VDF-*co*-HFP) copolymers and M2 to M6 membranes (the type of copolymer and the molar percentage of grafted telomer (Table 3)).

Figure 8: Isotherm at 120 °C under air of M2 membrane (Kynar[®] poly(VDF-*co*-HFP) copolymer grafted by 5 mol.% of telomer, thick curve) and M6 (FC-2230[®] poly(VDF-*co*-HFP) copolymer grafted by 13 mol.% of telomer, thin curve).

Figure 9: Scanning electron microscope image (secondary electrons for topographical resolution) of the cross section (after cryofracture) of M4 membrane and energy dispersive X-ray analysis showing the different elements (C, O, F, S) of the rectangle zone.

SCHEME CAPTIONS

Scheme 1: Radical telomerization of styrene sodium sulfonate with 2-mercaptoethylamine hydrochloride

Scheme 2: Chemical structure of the monoadduct, product of experiment I.

Scheme 3: Equilibrium reaction between the zwitterion and the unionized telomer.

Scheme 4: Chemical ion exchange of the zwitterion telomer into aromatic containing amino sodium sulfonate product by neutralization with base.

Scheme 5: Mechanism of grafting of an amino aromatic telomer onto poly(VDF-*co*-HFP) copolymer.

Graphical Abstract

Synthesis of Original Para-sulfonic Acid Aromatic Derivative Bearing the New Compound Amino group *p*-Aminoethylthioethylbenzenesulfonic by Telomerization, and its Grafting onto Poly(VDF-*co*-HFP) Copolymers for Proton Exchange Membrane for Fuel Cell

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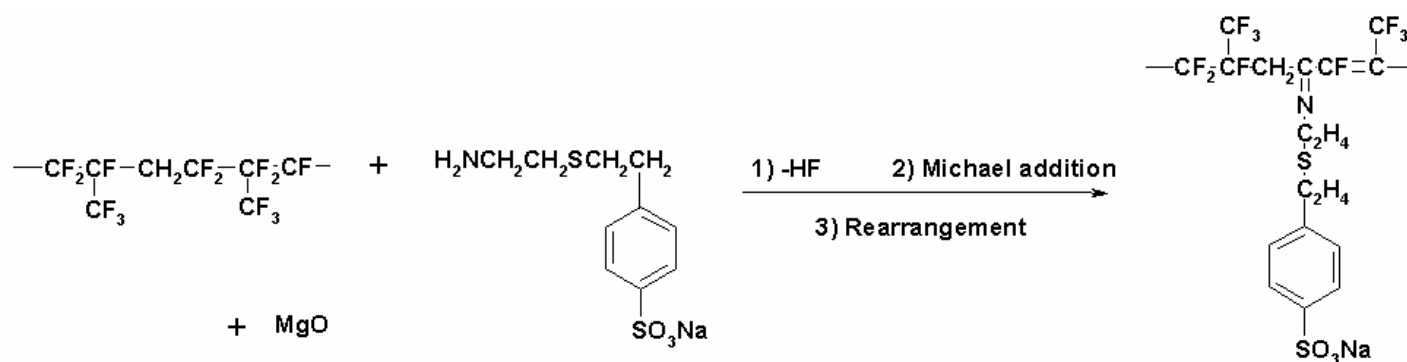
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Commercially available poly(VDF-*co*-HFP) copolymers are grafted with a novel amine bearing para-sulfonic acid aromatic group. The grafting mechanism includes first a dehydrofluorination of the fluorinated backbone, then the addition of the amine onto dehydrofluorinated macromolecules, and finally a rearrangement leading to an imine.