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New Fluorinated Polymers Bearing Pendant Phosphonic Acid Groups. Proton Conducting Membranes for Fuel Cell

Russell Tayouo,[†] Ghislain David,*[,†] Bruno Améduri,[†] Jacques Rozière,[‡] and Stéphanie Roualdès[§]

[†]*Institut Charles Gerhardt UMR CNRS 5253 Equipe Ingénierie et Architecture Macromoléculaire, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier Cedex 05, France,* [‡]*Institut Charles Gerhardt UMR CNRS 5253 Equipe Agrégats, Interfaces et Matériaux pour l'Energie, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier Cedex 5, France, and* [§]*Institut Européen des Membranes UMR 5635 (ENSCM, UM2, CNRS), Université Montpellier 2, CC047, Place E. Bataillon, 34095 Montpellier Cedex 5, France*

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ABSTRACT: The synthesis and characterizations of original fluorinated copolymers bearing phosphonic acid side functions for novel membranes potentially involved in fuel cell applications are presented. These copolymers were obtained by chemical modifications of various poly(CTFE-*alt*-IEVE) and poly[(CTFE-*alt*-IEVE)-*co*-(CTFE-EVE)] terpolymers (where CTFE, IEVE, and EVE stand for chlorotrifluoroethylene, 2-iodoethyl vinyl ether, and ethyl vinyl ether) via the Arbuzov reaction. Then, the hydrolysis of the phosphonate moieties into phosphonic acid groups was carried out quantitatively in mild conditions, in the presence of bromotrimethylsilane. The ionic exchange capacities (IECs) determined by potentiometric titration were ranging from 2.9 to 6.8 mequiv/g. The thermal and electrochemical properties of the resulting membranes (processed by casting) were investigated. Whatever the phosphonic acid content, the main degradation started from 250 °C, showing a high thermo-oxidative stability of these copolymers. At 25 °C and 100% relative humidity (RH), the level of conductivity was found in the range 0.02−20 mS/cm and highly dependent on the IEC. Finally, moderate to good conductivity values (about 0.25 mS/cm) at higher temperature (120 °C) and lower RH (25%) were observed, which demonstrated a limited dependence toward both temperature and RH.

Introduction

A wide range of different polymer electrolyte membrane fuel cells (PEMFCs) are currently developed as future power sources for automotive, stationary, and portable applications.[1] Presently, one of the key challenges in advancing PEMFC technology lies in the development of new durable membranes that allow operation in a broad temperature window, typically from subzero degrees up to 120 °C, at low humidification with water vapor partial pressures below 0.5 bar or with no humidification at all. The background is the pressing need to reduce the complexity and the cost and to increase the efficiency of systems for especially automotive applications.[2] Fluorinated polymers exhibit remarkable properties such as chemical, thermal, and electrical stability, inertness to acids, solvents and oils, low dielectric constant, low refractive index, low or nonflammability, high resistance to aging and oxidation, and low surface tension.[3,4] These polymers show low friction coefficient and relative permittivity, and they are strongly hydrophobic. For application in a polymer electrolyte fuel cell, they must be functionalized,[1] and the choice of the protogenic group plays an important role in the proton conductivity of fuel cell separator materials. So far, the materials used for proton exchange membranes in fuel cell applications have relied on the presence of water as proton carrier.[5] Although practicable at lower temperatures, water management at temperatures higher than 100 °C has a significant impact on the viability of the membrane electrode assembly and on overall operation of the system. Commercially available perfluorosulfonic acid (PFSA) polymers, in particular Nafion, have their conductivity dependent on ambient relative humidity, and their glass transition temperature limits their use at temperatures < 130 °C.[5,6] Polymers functionalized with alternative protogenic groups, including phosphonic acids[7,8] and different heterocycles,[9] have been investigated with the aim of overcoming the shortcomings of Nafion membrane. Phosphonic acid derivatives in particular are considered suitable candidates as ionomers because of their efficient proton transport properties.[10−15] They are amphoteric and possess a relatively high dielectric constant. The combination of these properties leads to a high degree of autodissociation which favors the formation of a hydrogen-bonding network, and acid-functionalized polymers are able to perform even in anhydrous conditions.[10] In order to apply these ionomers in proton-exchanging membranes, they have to be incorporated into a polymer matrix, which is typically a high performance polymer such as polybenzimidazole. The main disadvantage of these systems is that water, which is formed during the operation of the cell, dilutes and washes out the acid. To overcome these problems, covalent bonding of the acid to a suitable polymer matrix is suggested. Several authors have shown the capability of phosphonic groups to form strong hydrogen bonds. For instance, compared to methanesulfonic acid where the length of hydrogen bonding is 2.72 Å, methanephosphonic acid shows a hydrogen bonding length of 2.62 Å.[15,16] However, Paddison et al.[15] have demonstrated that trifluoromethanephosphonic acid requires a higher energy barrier for efficient proton transfer compared to methanephosphonic acid. They concluded that electroattractive groups in the α-position of phosphonic acid would decrease the pK_a values and then temper the amphoteric behavior of phosphonic acid groups.

These studies of model systems suggest that polymer membranes should be highly flexible to enhance the formation of hydrogen bonds and, further, that the phosphonic acid groups

*Corresponding author. E-mail: ghislain.david@enscm.fr.

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should be chemically grafted to the polymeric backbone by using flexible spacers. These spacers should be also non-electron-attracting groups to allow the amphoteric behavior of phosphonic acid groups. The combination of these properties is an important requirement for membranes operating in a high-temperature regime. Several phosphonic acid-containing polymers have been developed for fuel cell applications, starting from poly(vinylphosphonic acid) (PVPA)[17] to less flexible polymers such as polysulfones.[7,18] The synthetic strategies are limited to two different pathways: postphosphonation of premade polymers and polymerization of phosphonate-containing monomers.[7,18−25] For instance, Kotov et al.[26] and Yamabe et al.[27] connected phosphonic acid groups to a flexible fluorinated polymeric backbone. These authors synthesized a new fluorinated monomer, bearing a phosphonic group, able to copolymerize with fluorinated olefins such as tetrafluoroethylene. However, poor conductivity values were reached due to the low content of incorporated phosphonic groups into the fluorinated backbone. On the other hand, the postphosphonation of premade polymers has been more generally employed since it requires fewer reaction steps and is mainly based on two chemical modification reactions, e.g., Friedel−Crafts with PCl_3 and Michaelis−Arbusov with $P(O)(OEt)_2$.[28,29] More recently, Lafitte and Jannasch[7] grafted phosphonic groups onto modified aromatic polysulfones by using a cross-coupling reaction. Polymers of low ion exchange capacity (IEC) were obtained (about 1.5 mequiv/g), resulting in low conductivity values at high temperature. These authors subsequently increased[30,31] both IEC and conductivity values by grafting PVPA as side chains onto aromatic polysulfones. To our knowledge, no study relates on the chemical grafting of phosphonic acid group onto flexible fluorinated polymer backbones. We suggest here another approach, comprising the chemical modification of a fluorinated polymer into ionomers bearing a high content of phosphonic acid groups. A recent article[32] reports a series of five fluorinated copolymers bearing a controlled amount of dangling iodine atoms tethered to the backbone. The iodine atoms were separated from the fluorinated backbone by an ethyl ether flexible group. This present work is aimed at providing a series of fluorinated copolymers bearing pendant phosphonic acid groups. The iodine groups were converted into phosphonic acid groups to afford original well-defined phosphonic acid-grafted fluorinated polymers. The controlled incorporation of iodine atoms as well as their modification into phosphonic acid groups allows obtaining a wide range of IEC values.

After investigation on the structural characterization of the copolymers, a further motivation deals with the preparation of original membranes and the assessment of the thermal stability, water uptake, and proton conductivity under both high and low relative humidities.

Experimental Section

Materials. *tert*-Butyl peroxypivalate (TBPPi, Trigonox 25-C75, 75 wt % solution in isododecane) was kindly provided by Akzo Nobel (Compiègne, France). Chlorotrifluoroethylene (CTFE) and 1,1,1,3,3-pentafluorobutane ($C_4F_5H_5$) were kindly provided by Solvay S.A. (Tavaux, France and Brussels, Belgium). Vinyl ethers such as 2-chloroethyl vinyl ether (CEVE) and ethyl vinyl ether (EVE), sodium iodide (NaI), triethyl phosphite ($P(OEt)_3$), bromotrimethylsilane ($BrSiMe_3$), sodium chloride (NaCl), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%), potassium carbonate (K_2CO_3), acetone, dimethyl sulfoxide, methanol, diethyl ether, and dichloromethane were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Deuterated solvents for NMR were purchased from Euriso-top (Grenoble, France) (purity > 99.8%). All reactants were used without further purification except for 1,1,1,3,3-pentafluorobutane and K_2CO_3, which were respectively distilled and dried overnight under vacuum oven at 60 °C prior to use.

Copolymer Characterization. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker AC 400 MHz instrument. ^1H and ^{31}P NMR spectra were recorded at room temperature at 400 and 160 MHz, respectively. The chemical shifts (δ) were given in ppm and were calibrated using the residual signal from the deuterated solvents $CDCl_3$ (δ = 7.27 for ^1H) or DMSO-d_6 (δ = 2.50 for ^1H). In the figures and discussion below, the letters s, d, t, q, and m stand for singlet, doublet, triplet, quintet, and multiplet, respectively.

Weight percentages of carbon, fluorine, chlorine, oxygen, hydrogen, iodine, and phosphorus atoms were assessed by elemental analysis at the CNRS-Service Central d'Analyze (Solaize, France) on a CH elemental analyzer equipped with a CO_2/H_2O infrared detector. Theoretical carbon and hydrogen compositions were calculated according to the copolymer compositions assessed by ^1H and ^{19}F NMR spectroscopy and considering that co- or terpolymers have alternating structures (with 50 mol % of fluorinated olefins and 50 mol % of vinyl ethers).

The thermal stability of the different copolymers was evaluated by thermogravimetric analysis (TGA) on a Q50 analyzer from TA Instruments. The data were collected from 100 to 600 °C after the samples were kept at 110 °C for 30 min. The samples were analyzed both under a nitrogen atmosphere at a heating rate of 10 °C/min and under air at a heating rate of 5 °C/min. Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer Pyris 1 apparatus. Scans were recorded at a heating/cooling rate of 20 °C min^{-1} from −100 to 150 °C. A second scan was required for the assessment of the T_g, defined as the inflection point in the heat capacity jump.

Grafting Phosphonic Acid Groups onto Fluorinated Polymers Bearing Iodine Atoms. The synthesis of fluorinated polymers bearing phosphonic acid groups proceeds in three steps, that is, the radical copolymerization of chlorotrifluoroethylene (CTFE) with vinyl ethers and especially 2-chloroethyl vinyl ether (CEVE), followed by the nucleophilic substitution of the chloride atom into iodine atom. The experimental procedure associated with these two steps was deeply described in previous papers.[32,33] The third step is the chemical modification of the iodine atoms into phosphonate groups, which are then hydrolyzed to reach to the corresponding phosphonic acid groups. We describe here the experimental procedure from step 3.

Nucleophilic Substitution of Iodine Atoms of Vinyl Ether to Phosphonate Unit by Michaelis−Arbuzov Reaction. In a 250 mL single-neck round-bottom flask supplied with a condenser and a magnetic stirrer, 20 g of $[(F:Cl)_{0.03}$-*co*-$(F:I)_{0.97}]$ was dissolved in 100 mL of triethyl phosphite. Then, the reaction was heated to 140 °C for 24 h. After completion of the reaction and upon cooling to room temperature, the side products (triethyl phosphite and diethyl ethylphosphonate) were removed by vacuum distillation (60 °C/5 mbar and 90 °C/5 mbar, respectively). The remaining viscous solution was diluted in 50 mL of acetone and then precipitated in distilled water. The dark red polymer $[(F:I)_{0.07}$-*co*-$(F:P)_{0.93}]$ was obtained after drying under vacuum at 90 °C for 12 h. The product was obtained in high yield (>90%). T_g = 5 °C. FTIR (CH_2Cl_2, cm^{-1}): 3000 (−C−H); 1270 (P═O); 1180 (C−O−C); 1100 (P−O−C); 990 (C−F). ^1H NMR (400 MHz, 297 K, $CDCl_3$, ppm) δ: 4.32 to 4.72 (m, $-CH_2-CH$); 4.04 (m, OCH_2CH_3); 3.93 (m, $O-CH_2CH_2-$); 2.31−3.09 (m, $CF-CH_2$); 2.08 (m, $-CH_2-P$); 1.26 (t, OCH_2-CH_3). ^{31}P NMR {^1H} (160 MHz, 297 K, $CDCl_3$, ppm) δ: 27.0 (s, $-CH_2-$**P**). ^{19}F NMR {^1H} (377 MHz, 297 K, $CDCl_3$, ppm) δ: −108 to −123 (m, $-CF_2CF$).

Hydrolysis of Phosphonate Groups. The hydrolysis of phosphonated polymer was carried out according to a procedure published by Bressy-Brondino et al.[34]

In a 250 mL three-neck round-bottom flask equipped with a condenser, a magnetic stirrer, and a dropping funnel, and under nitrogen flow, 15 g of $[(F:I)_{0.07}$-*co*-$(F:P)_{0.93}]$ and 50 mL of anhydrous dichloromethane were introduced. Then, 2.2 equiv

of bromotrimethylsilane $BrSi(CH_3)_3$ (8 mL) was added in a dropwise manner, and the mixture was stirred at 40 °C for 6 h. After the reaction, solvent and volatile residues were evaporated (40 °C/30 mbar). The alcoholysis of the silylated intermediate was performed by adding an excess of methanol (100 mL). The mixture was stirred at 30 °C for 4 h, and the solvent was evaporated. The remaining solution was precipitated in distilled water. The dark brown polymer $[(F:I)_{0.07}$-*co*-$(F:POH)_{0.93}]$ was quantitatively obtained (yield >95%) after drying under vacuum at 90 °C for 12 h. T_g = 76 °C. FTIR (CH_2Cl_2, cm^{-1}): 3600−2500 (−P−OH); 2985 (C−H); 1310 (P=O); 1180 (C−O−C); 1100 (P−O−C); 990 (C−F). ^{1}H NMR (400 MHz, 297 K, DMSO-d_6, ppm) δ: 7.55 (m, −PO**H**); 4.36−4.92 (m, $-CH_2-$C**H**); 3.87 (m, O**C**$\mathbf{H}_2$CH$_2$); 3.28 (m, O−CH$_2$C$\mathbf{H}_2$−I); 2.14−3.18 (m, CF−C$\mathbf{H}_2$); 1.91 (m, −C$\mathbf{H}_2$−P). ^{31}P NMR {^{1}H} (160 MHz, 297 K, $CDCl_3$, ppm) δ: 21.30 (s, $-CH_2-$**P**OH). ^{19}F NMR {^{1}H} (377 MHz, 297 K, $CDCl_3$, ppm) δ: −108 to −123 (m, −C**F**$_2$C**F**).

Membrane Preparation. Fluorinated polymers bearing pendant phosphonic acid group (27−40 wt %) were added to DMSO, leading to a suspension. After heating that suspension between 30 and 60 °C for 3 h, a dark brown solution was obtained, which was filtered to remove any insoluble material. The solution was cast into a film on a PTFE plate, using a doctor blade. Solvent was removed by drying at 60 °C for 1 h, then at 70 and 90 °C for 2 h, and finally at 120 °C for 24 h. The membrane was removed from the PTFE plate by immersion in distilled water. The 65−150 μm thick membranes were then dried in a vacuum oven at 70 °C for 24 h. To ensure that no residual impurities or solvent were present in the membranes, they were leached in Millipore water for at least 12 h and then dried again as described above.

Determination of Water Uptake. To assess the water uptake (W_{water}) at different temperatures (25−80 °C) and relative humidities (RH; 30−80%), the membranes (0.5 × 1 cm) were first dried under vacuum at 90 °C for 48 h to obtain their dry weights (W_{dry}) and then placed for 3 h in a climate chamber from a Binder APT.Line KBF equipped with an electronically controlled preheating chamber, a humidification and dehumidification system with capacitive humidity sensor suitable for stability tests according to ICH guideline Q1A (R2). The weights of the water-swollen membranes (W_{wet}) were obtained. The water uptake was then calculated as $W_{water} = [(W_{wet} - W_{dry})/W_{dry}] \times 100\%$, and the hydration number (λ) was calculated using $\lambda = n_{H_2O}/n_{-PO_3H_2}$. The experimental ionic exchange capacity was determined by titration at room temperature from the relationship $IEC_{exp} = [OH^-]V/W_{dry}$, where $[OH^-]$ and V are the concentration of the exchange solution in anions OH^- (mol L^{-1}) and the volume of the exchange solution (mL), respectively. Potentiometric pH titrations of membranes were carried out to study possible polyelectrolyte effects and to verify the theoretical IECs calculated from NMR data and assuming complete dissociation of phosphonic acid groups. In order to obtain pK_a values for each of both weak acidities, an automatic titrator (model TT-processor 2, Tacussel) fitted with extension glass and calomel electrodes was used for recording direct and differential titration curves. These titrations were conducted at room temperature, and the solution was prepared in water and titrated with 0.01 mol L^{-1} standard solution of HCl.

Proton Conductivity Measurements. The proton conductivity (σ) was assessed by electrochemical impedance spectroscopy (EIS) using a HP 4192. Membrane samples (1 × 4 cm) were clamped between two stainless steel electrodes of the temperature-controlled conductivity cell. In-plane (four-electrode) resistance measurements were also made over the temperature range to 120 °C and at RH values of 25, 50, 75, and 100%, and the conductivity was calculated from the relationship $\sigma = L/RdW$, where L, d, and W are the distance between the electrodes, the thickness, and the width of the sample strip, respectively. In all the cases, R was derived from the low intercept of the high-frequency semicircle on a complex impedance plane with the Re(Z) axis.

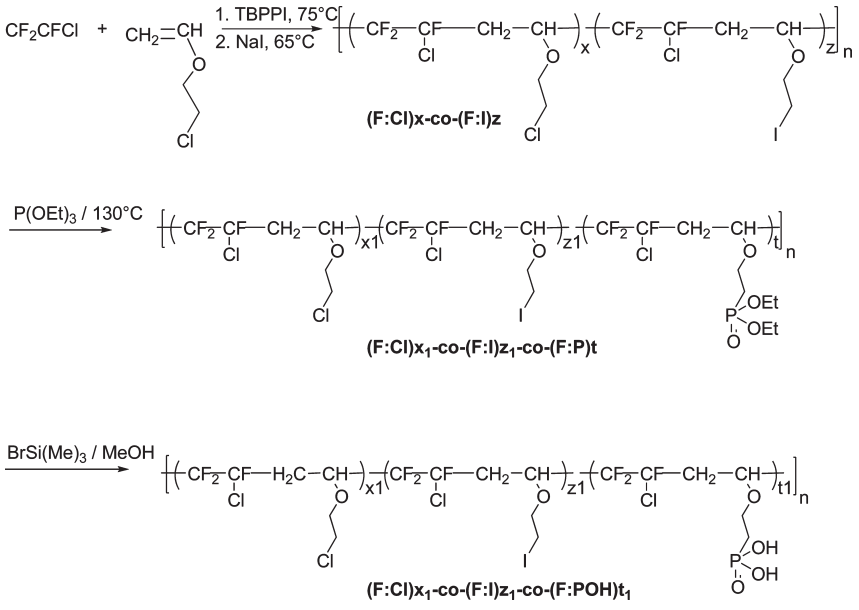
Results and Discussion

Copolymer Synthesis and Characterization. The synthesis of iodine atoms bearing fluorinated polymers was achieved by radical copolymerization of fluorinated olefins, such as chlorotrifluoroethylene (CTFE), with vinyl ethers (VE), such as 2-chloroethyl vinyl ether (CEVE). These radical copolymerizations usually lead to alternated copolymers,[35−38] which enable to incorporate a high amount of chlorine atoms (from CEVE) into the fluorinated backbone. These chlorine atoms can be easily modified into iodine atoms by nucleophilic substitution using NaI. Following the procedure reported by Valade et al.,[33] a series of five fluorinated copolymers with an iodine atom controlled amount were synthesized.[32] These copolymers were deeply characterized, and a special attention was devoted to the determination of the halogen atom content that governs the range of ionic exchange capacity (IEC) values. Two types of iodine bearing fluorinated copolymers were obtained: (i) the first one by radical copolymerization of CTFE with CEVE followed by chlorine substitution (Scheme 1); (ii) the second one concerned the radical terpolymerization of CTFE with CEVE and ethyl vinyl ether (EVE) followed by the chlorine substitution (Scheme 2).

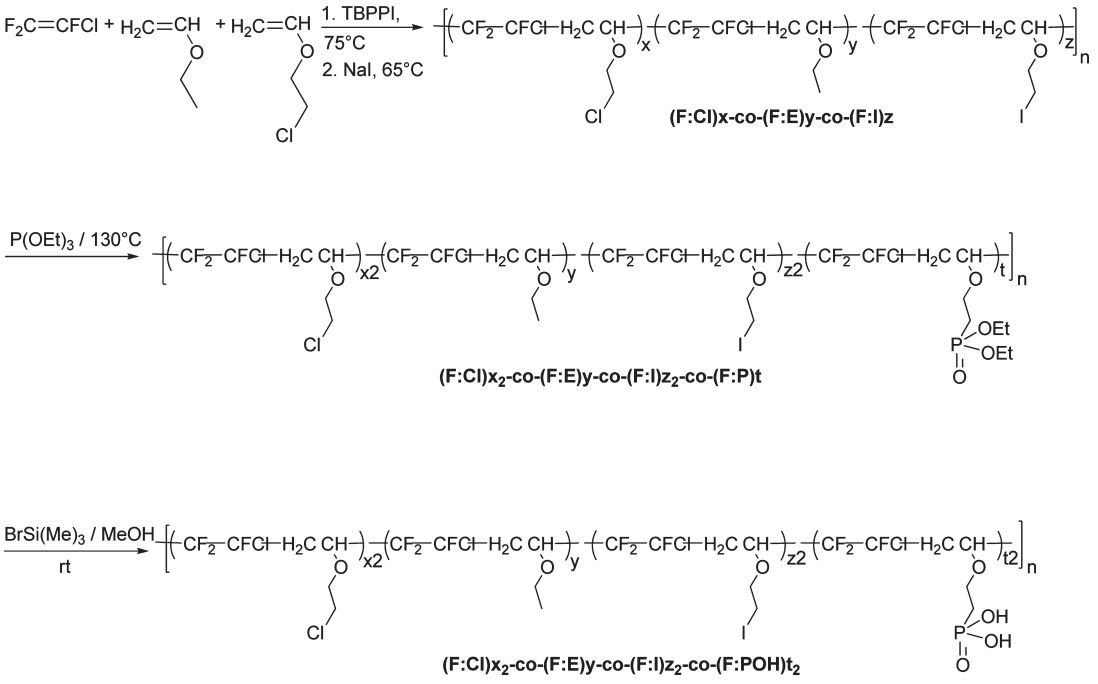
In a previous publication,[32] the alternated behavior of the radical copolymerizations was demonstrated. Then, the resulting copolymers could be written as $(F:Cl)_{x_1}$-*co*-$(F:I)_z$, where x_1 and z represent the contents in mol % of CTFE/CEVE units and CTFE/IEVE (IEVE stands for 2-iodoethyl vinyl ether and was obtained by nucleophilic substitution of CEVE) units, respectively. Similarly, $(F:Cl)_{x_2}$-*co*-$(F:E)_y$-*co*-$(F:I)_z$ was produced by radical terpolymerization of CTFE, CEVE, and EVE and x_2, y, and z stand for the contents of CTFE/CEVE units and CTFE/IEVE (IEVE is obtained by nucleophilic substitution of CEVE) units, respectively. $(F:Cl)_{x_1}$-*co*-$(F:I)_z$ and $(F:Cl)_{x_2}$-*co*-$(F:E)_y$-*co*-$(F:I)_z$ copolymers exhibited molecular weight values of about 25 000 g/mol. Then, for both types of copolymers, steps 2 and 3 were similar, i.e., substitution of iodine atom into phosphonate group through the Arbuzov reaction at 130 °C in the presence of triethylphosphite followed by the cleavage of the ester groups in the presence of $BrSi(Me)_3$. The nucleophilic substitution of halogenated alkyl compounds into phosphonate groups was extensively described in the literature[39−42] and was performed at high temperature (130 °C) in the presence of triethyl phosphite. This reaction usually required efficient leaving groups; i.e., iodine atom is a better living group than chlorine atom. The replacement of chlorine by iodine atom allowed to quantitatively perform the nucleophilic substitution into phosphonate as well as to decrease the reaction time. All these steps were monitored by NMR spectroscopy. Typical ^{1}H NMR spectra are given in Figures 1 and 2 for $[(F:Cl)_{0.23}$-*co*-$(F:I)_{0.19}$-*co*-$(F:P)_{0.58}]$ and $[(F:E)_{0.44}$-*co*-$(F:P)_{0.56}]$, respectively, the copolymers bearing phosphonic ester groups.

As seen in both spectra, the CH_2 and CH_3 protons of the diethylphosphonic ester were centered at δ = 4.04 and 1.26 ppm, respectively. The partial or total shift of the signal centered at δ = 3.20 ppm assigned to CH_2-I group into the new signal at δ = 2.08 ppm characteristic of CH_2-P confirms the efficient nucleophilic substitution. The integrals of both signals allow the determination of the phosphonate molar content, ranging from 15 to about 50 mol %. A typical ^{31}P NMR spectrum is given in Figure 3, where only one signal is

Scheme 1. Synthetic Pathway to Chemically Graft Phosphonic Acid Groups onto Fluorinated Copolymers Obtained by Radical Copolymerization of CTFE with CEVE



Scheme 2. Synthetic Pathway to Chemically Graft Phosphonic Acid Groups onto Fluorinated Copolymers Obtained by Radical Terpolymerization of CTFE with CEVE and EVE



observed at $\delta = 27$ ppm corresponding to the diethylphosphonic ester group.

Triethyl phosphite and ethyl diethylphosphonate (side product) were removed by vacuum distillation. Finally, fluorinated polymers bearing pendant phosphonic acid groups were obtained by silylation of the diethylphosphonic ester group.[43] The ^{31}P NMR spectrum of [(F:Cl)$_{0.23}$-*co*-(F:I)$_{0.19}$-*co*-(F:POH)$_{0.58}$] copolymer is given in Figure 3, showing a main signal at $\delta = 21$ ppm characteristic of the phosphonic acid group. The ester cleavage was carried out almost quantitatively as the signal of the diethylphosphonic ester group totally disappeared. The ^{31}P NMR spectrum also exhibits another signal centered at $\delta = 23$ ppm for the monophosphonic acid group,[44] obtained in a very low molar content (about 4 mol %, according to NMR data). ^{19}F NMR spectra of these phosphonic acid containing copolymers were similar to those of the copolymers precursors bearing iodine or chlorine atoms. This synthetic pathway allowed obtaining five fluorinated copolymers bearing different molar contents of phosphonic acid groups, ranging from 15 to 47 mol %. The main characteristic data, i.e., molecular weights, PDIs, and phosphonic acid contents, of the five copolymers are given in Table 1.

Thermal Stability. The copolymers were characterized by thermogravimetry analysis (TGA) under air at a heating rate of 10 °C/min. Figure 4 represents the TGA thermograms of [(F:Cl)$_{0.07}$-*co*-(F:POH)$_{0.93}$] copolymer in both its ester and acid forms. The main degradation of the copolymer in its

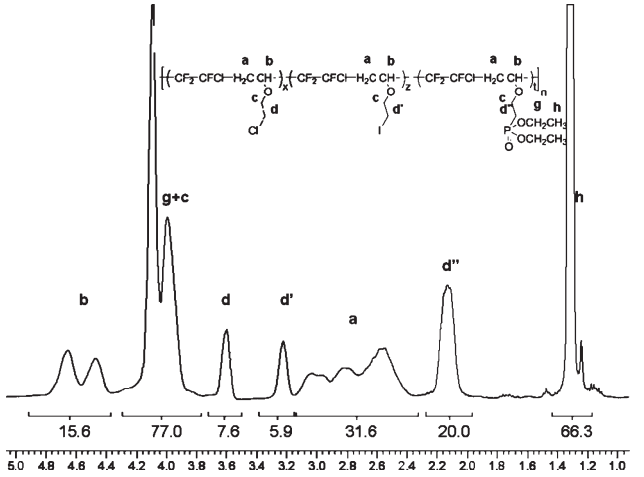


Figure 1. ^{1}H NMR spectrum of [(F:Cl)$_{0.23}$-*co*-(F:I)$_{0.19}$-*co*-(F:P)$_{0.58}$] (ester form).

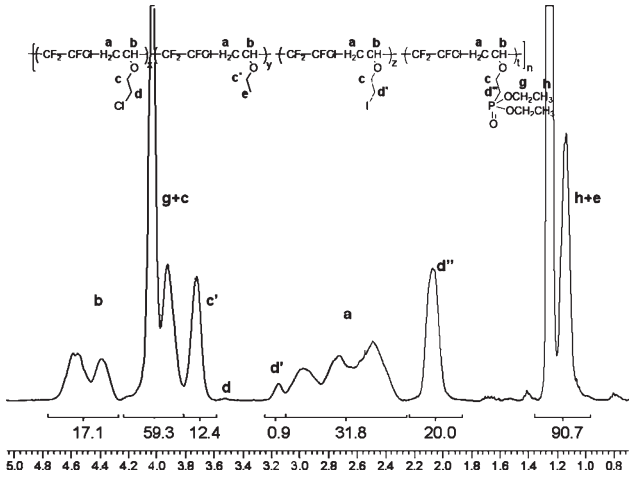


Figure 2. ^{1}H NMR spectrum of [(F:E)$_{0.44}$-*co*-(F:P)$_{0.56}$] (ester form).

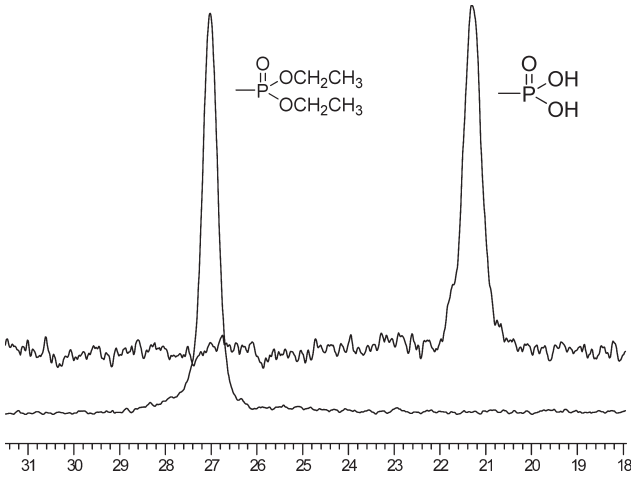


Figure 3. ^{31}P NMR spectra of [(F:Cl)$_{0.23}$-*co*-(F:I)$_{0.19}$-*co*-(F:P)$_{0.58}$] (ester form) and [(F:Cl)$_{0.23}$-*co*-(F:I)$_{0.19}$-*co*-(F:POH)$_{0.58}$] (acid form).

ester form shows a first degradation step ranging between 300 and 400 °C, corresponding to about 70% of weight loss.

The very low degradation observed between 250 and 300 °C may be ascribed to the loss of diethyl ester group. Then, the cleavage of the C−P bond[30,31] (bond dissociation energy (BDE) of about 260 kJ/mol)[45] followed by the degradation of the fluorinated backbone is probably responsible of the main degradation. Fluoropolymers are known to exhibit a high thermostability linked to the strong C−F bond (its BDE is ca. 485 kJ/mol).[46] The copolymer in its acid form showed an initial weight loss of about 5% from 100 °C due to desorption of water. These water molecules are ascribed either to the adsorption from phosphonic acid group or to self-condensation. Then, the main degradation is observed between 250 and 350 °C with a magnitude almost similar to that observed for the ester form. A third degradation occurs after 400 °C and arises from self-condensation reactions which form water molecules as well as anhydride bonds between phosphonic groups.[47,48] Figure 5 shows TGA thermograms of fluorinated copolymers with different phosphonic acid contents, i.e., 15, 25, and 47 mol %.

Whatever the phosphonic acid content, the main degradation starts from 250 °C, showing a high thermo-oxidative stability of these copolymers. Table 1 gathers the starting degradation temperature observed for both 5 and 10% weight losses for the five copolymers. The third degradation occurring from 400 °C differs with the phosphonic acid content. Indeed, [(F:Cl)$_{0.07}$-*co*-(F:POH)$_{0.93}$] copolymer, with the highest phosphonic acid content, shows the slowest thermal degradation. This behavior evidence the high stability of these copolymers by the anhydride bond formation. Sustained fuel cell operation of PEMFC membranes requires high thermal stability at high temperature. Isotherms at 130 °C for several days would definitively assess the good thermal stability of these fluorinated copolymers. Hence, TGA thermograms were recorded at 130 °C under air for 72 h for the five copolymers and only 5% of degradation was observed, ascribed to the loss of water molecules (as already mentioned above).

Differential scanning calorimetry (DSC) heating traces were recorded at low temperature for the five copolymers, and their glass transition temperatures (T_g) are given in Table 1. Interestingly, only one glass transition is observed for each copolymer. This result shows that no phosphonic acid proper phase is observed due to the alternated structure of the fluorinated copolymers. The registered values range from about 50 to 75 °C, depending on the phosphonic acid POH content, and the higher the POH content, the higher the T_g value. These values increased compared to the iodine groups bearing fluorinated copolymers as well as to the copolymers in the ester form (about 15 °C), which evidence the hydrogen bonding between the phosphonic acid groups.

Water Uptake. Potentiometric titration of the present fluorinated copolymers was carried out to study possible polyelectrolyte effects. The curves indicated a pK_{a1} value ranging from 3.5 to 3.8 and a pK_{a2} value ranging from 8.2 to 8.9 (Table 2).

These values are in good agreement with those obtained for conventional alkylphosphonic acid groups.[49] The potentiometric curves show two distinct steps for the five fluorinated copolymers, corresponding to the addition of 1 and 2 equiv of base, which enhances the behavior of a diprotic acid. Interestingly, this result differs from that of Bingöl et al.[17] and Parvole et al.[31] on poly(vinylphosphonic acid) (PVPA). Indeed, these authors observed only one step corresponding to 1 equiv of base and ascribed this result to the close proximity of phosphonic acid units allowing the dissociation of a single proton. For the fluorinated copolymers, the phosphonic acid groups are separated by at least one CTFE unit (Scheme 3), which may explain the dissociation of both protons.

Parvole et al. have shown that when PVPA chains are grafted along a polysulfone backbone, aggregation into

Table 1. Preparation and Characterization of Fluorinated Copolymers Bearing Phosphonic Acid Groups[a]

copolymers	ratios of the reactants [CTFE]:[CEVE]:[EVE] (mol %)	PO_3H_2 content (mol %)	M_n (g/mol)	PDI	TGA under air $T_{d,5\%}$ (°C)	TGA under air $T_{d,10\%}$ (°C)	$T_{g,exp}$ (°C)
$[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$	50:50:00	47	26 000	2.7	195	260	76
$[(F:Cl)_{0.23}$-*co*-$(F:I)_{0.19}$-*co*-$(F:POH)_{0.58}]$	50:50:00	29	25 500	2.6	245	270	65
$[(F:Cl)_{0.26}$-*co*-$(F:I)_{0.24}$-*co*-$(F:POH)_{0.50}]$	50:50:00	25	25 500	2.6	248	275	63
$[(F:E)_{0.44}$-*co*-$(F:POH)_{0.56}]$	50:30:20	28	23 000	3.0	207	268	68
$[(F:E)_{0.64}$-*co*-$(F:POH)_{0.36}]$	50:20:30	18	20 000	3.1	230	270	53

[a] $T_{d,5\%}$ and $T_{d,10\%}$ stand for the temperatures at which the membrane lost 5 and 10 wt %, respectively.

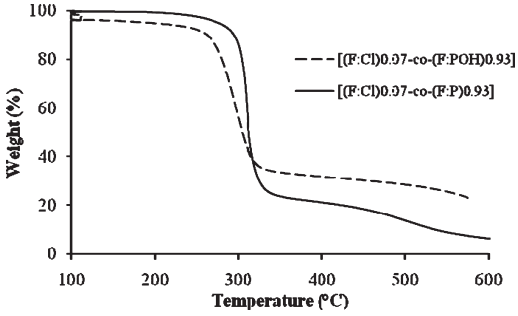


Figure 4. TGA traces of $[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$ and $[(F:Cl)_{0.07}$-*co*-$(F:P)_{0.93}]$ (ester form) recorded under air at 10 °C/min.

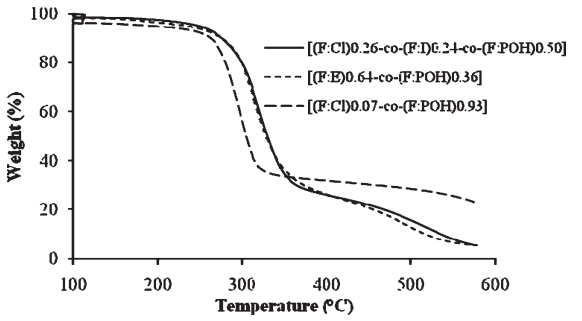


Figure 5. TGA thermograms of $[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$, $[(F:Cl)_{0.26}$-*co*-$(F:I)_{0.24}$-*co*-$(F:POH)_{0.50}]$, and $[(F:E)_{0.64}$-*co*-$(F:POH)_{0.36}]$ recorded under air at 10 °C/min.

phosphonic acid dense regions occurs, which favors proton conductivity. In the work of Bingol et al., however, condensation of closely neighboring groups forming P−O−P bonds decreased the ionic conductivity of PVPA. This is not observed in poly(*m*-phenylenephosphonic acid), which shows a diprotic behavior attributed to a larger phosphonic acid group separation. As shown in Scheme 3, the alternating character of the copolymerization may explain this result although the flexible ether bridge may favor phosphonic acid linkage. IEC values were derived from the titration curves and were compared to those calculated from ^{1}H NMR data considering two acid protons (Table 2). These values show very good agreement in a wide range (from 2.9 to 6.8 mequiv/g), corresponding to $[(F:E)_{0.64}$-*co*-$(F:POH)_{0.30}]$ and $[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$, respectively. The five fluorinated copolymers bearing phosphonic acid groups were solubilized in DMSO and cast from the DMSO solution at high temperature (90 °C) under a nitrogen atmosphere. Five flexible and transparent membranes were obtained and labeled M*x*, where *x* represents the mol % content of phosphonic acid unit (Table 2).

Water uptake properties of phosphonic acid polymer membranes are critical in determining their intrinsic proton conductivity and their dimensional stability. The water uptake of the membranes is directly related to the IEC. In the case of sulfonated membranes, where proton transport is water-assisted, a high water uptake is generally required. For sulfonated membranes, the number of water molecules per sulfonic acid group (λ) is usually high (about 15).[50] For phosphonic acid-functionalized polymer membranes, the higher degree of hydrogen bonding as well as the lower acidity may limit the membrane swelling. Figure 6 displays the plots of hydration number (λ) against IEC determined in two experimental conditions: at 25 °C and 100% relative humidity (RH) and at 80 °C and 30% RH.

Water uptake of the membranes at low temperature and 100% RH is similar in a wide range of IEC values: from 2.9 to 4.6 mequiv/g, λ is about 6 (ca. 20% of water uptake). For higher IEC, i.e., for M47, the trend diverges to reach a λ value of almost 11.

For membrane M47, showing the highest phosphonic acid content, the morphology has probably evolved from one having hydrophobic−hydrophilic separated domains into a structure having continuous hydrophilic regions, giving rise to a significantly increase in the water uptake, so ensuring high conductivity ($> 10^{-2}$ S cm^{-1}). This phenomenon was already observed for polysulfone-*g*-PVPA membranes when IEC was higher than 5 mequiv/g.[31] Kaltbeitzel et al.[51] also studied the water sorption of PVPA and noted that water uptake strongly decreased at decreasing RH. At 80 °C and 30% RH, λ values lower than 1 were also observed. They attributed this behavior mainly to self-condensation reactions, i.e., formation of inter- and intramolecular anhydrides, and showed that about 17% water uptake is required at room temperature to avoid self-condensation, corresponding to ∼0.8 water molecules per phosphonic acid group. Furthermore, it was suggested that the presence of self-condensation at higher water uptakes proves that self-condensation and water coexist in the sample. Noteworthy, self-condensation also produces water molecules, which may be involved in the conduction mechanism. In the case of PVPA, the self-condensation has a negative effect on proton conductivity. In the last part of this paper, proton conductivity is evaluated in different conditions and especially at high temperature and low RH, where self-condensation takes place.

Proton Conductivity. The proton conductivity is highly significant for the performance of the PEMFC. First, the dependence of the conductivity on IEC was investigated at room temperature and 95% RH (Figure 7). The level of conductivity was found in the range of 0.02−20 mS/cm, which is comparable to the value found with Nafion 115 (about 50 mS/cm).[52] The conductivity is strongly dependent on the IEC: the conductivities of $[(F:E)_{0.64}$-*co*-$(F:POH)_{0.36}]$ (IEC of 2.9 mequiv/g) and $[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$ (IEC of 7.0 mequiv/g) differ by almost 3 orders of magnitude. Comparison of Figures 6 and 7 indicates that in the range of IEC value between 2.9 and 4.6 mequiv/g λ does not change whereas the conductivity gains almost 2 orders of magnitude. This indicates that at low temperature and high RH the conductivity of fluorinated phosphonic acid membranes is mainly governed by the content of acidic protons. However, a minimum water content is required. When the content of

Table 2. Ionic Exchange Capacity (IEC), Water Uptake (W_{water}), and Hydration Number (λ) Values for Membranes Based on Fluorophosphonic Acid Copolymers

copolymers	membrane	POH content (mol %)	IEC (mequiv/g) theor[a]	IEC (mequiv/g) expt[b]	pK_{a1}[b]	pK_{a2}[b]	W_{water} (wt %)[c]	λ[c]
$[(F:Cl)_{0.07}$-*co*-$(F:POH)_{0.93}]$	M47	47	6.7	8.4	3.5	8.4	65	10.6
$[(F:Cl)_{0.23}$-*co*-$(F:I)_{0.19}$-*co*-$(F:POH)_{0.58}]$	M29	29	4.5	4.0	3.8	8.9	25	6.2
$[(F:Cl)_{0.26}$-*co*-$(F:I)_{0.24}$-*co*-$(F:POH)_{0.50}]$	M25	25	3.9	3.3	3.8	8.5	15	5.6
$[(F:E)_{0.44}$-*co*-$(F:POH)_{0.56}]$	M28	28	4.6	3.9	3.7	8.6	26	6.4
$[(F:E)_{0.64}$-*co*-$(F:POH)_{0.36}]$	M18	18	2.9	2.7	3.6	8.2	17	5.6

[a] Calculated from ^{1}H NMR considering two acidic protons. [b] Obtained from potentiometric titration. [c] Measured at 25 °C and 100% RH.

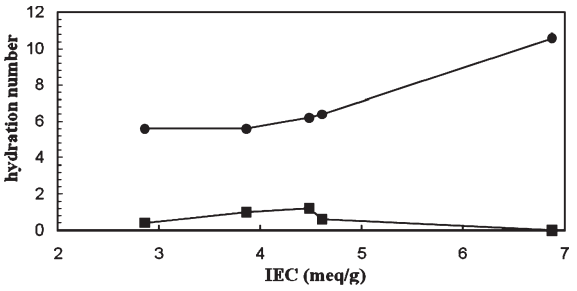


Figure 6. Dependence of hydration number of phosphonic acid grafted fluorinated membranes on ionic exchange capacity (IEC) at 25 °C/100% RH (●) and at 80 °C/30% RH (■).

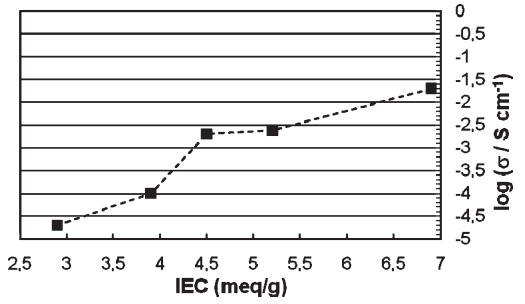
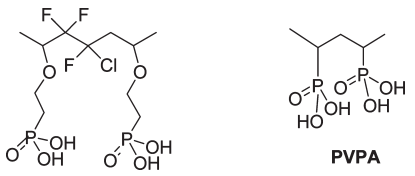


Figure 7. Proton conductivity of phoshonic acid grafted fluorinated membranes as a function of Ionic Exchange Capacity (IEC) at 25 °C/95% RH.

Scheme 3. Schematic Proximity of Phosphonic Acid Groups for PVPA and for Fluorinated Copolymers



phosphonic acid groups becomes higher, e.g. for M47, a change in membrane morphology is obtained and hydrophilic domains are assumed to be preponderant. The conductivity is then mainly governed by water-assisted proton transfer, and high conductivity is reached. At 20 °C and 95% HR, M47 displays similar or even higher conductivity values than that of polysulfone-*g*-PVPA membranes recently synthesized by Parvole et al.,[31] by using anionic polymerization of diethylvinylphosphonate monomer.

Finally, the proton conductivity of phosphonic acid grafted fluorinated membrane M47 was evaluated in a wide range of RH (from 25 to 95%) at both 90 and 120 °C (Figure 8). There is an almost linear relation between RH and the logarithm of the conductivity at both temperatures. When increasing RH from 25 to 95% the proton conductivity increased by about 1

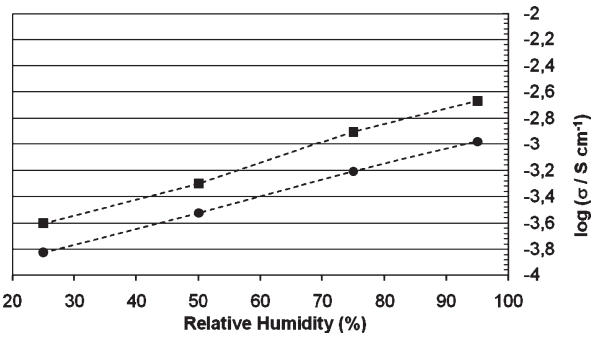


Figure 8. Proton conductivity of phosphonic acid grafted fluorinated membrane M47 as a function of relative humidity at 90 °C (●) and 120 °C (■).

order of magnitude. However, the increase of the temperature induced twice higher conductivity in the whole range of RH. The increase in temperature may likely favor the phosphonic acid interconnections. These connections would lead to strong hydrogen bonding and also to self-condensation (thus generating water). This behavior can be related to the alternating structure of the fluorinated copolymers cumulated with the high content of phosphonic acid groups. Indeed, as explained above, the alternating structure certainly limits the formation of P−O−P groups, and the high content of phosphonic acid allows hydrophilic domains to form. This combination affords only moderate to good conductivity values (about 0.25 mS/cm) at high temperature (120 °C) and low RH (25%), corresponding to conditions close to those in a fuel cell in quasi-dry conditions. Finally, the dependence of both the temperature and RH is relatively limited for these membranes since the conductivity only decreases by less than 2 orders of magnitude from 20 °C/100% RH to 120 °C/25% RH. It can be concluded that the IEC of the fluorinated membranes is the main parameter governing both the structure of the membrane and the conduction mechanism.

Conclusion

Fluorinated copolymers were successfully functionalized with phosphonic acid groups. Five copolymers were thus synthesized with different phosphonic acid content by radical copolymerization of CTFE with vinyl ethers. Interestingly, these copolymers were produced by using commercially low-cost reagents and remained soluble in DMSO, allowing film forming from the solution. The membranes resulted in phase separation due to the hydrophobic fluorinated backbone and to the hydrophilic phosphonic acid side groups. The thermal stability of these membranes was good enough for fuel cell applications with $T_{d5\%}$ at about 200 °C whatever the phosphonic acid content. The determination of the hydration number vs the phosphonic acid content, i.e. IEC, revealed two behaviors; at RH 100%, when IEC becomes high, the morphology of the membrane changes to increase the water uptake. At low RH, however, water soprtion is very low even at high IEC, and self-condensation takes place.

This typical hydration behavior for phosphonic acid polymeric membranes caused a decrease of the protonc conductivity. Indeed, when decreasing RH from 95 to 25%, the conductivity values decrease of about 1 order of magnitude. However, an increase of the temperature (from 90 to 120 °C) leads to an increase of the proton conductivity by twice in the same range of RH. This result indicates that water molecules and phosphonic acid hydrogen bonding are involved in the proton conduction mechanism. Finally, the proton conductivity increases by 3 orders of magnitude by increasing IEC (from 2.5 to 7 mequiv/g) to reach 20 mS/cm at 25 °C and 95% RH. It can be concluded that the high IEC is the key factor to significantly change the water sorption and, as a consequence, to increase the proton conductivity. Noteworthy, these fluorinated membranes allowed to better understand the behavior of the phosphonic acid groups chemically linked to a fluorinated backbone. In further work, these membranes will be cross-linked in order to increase their mechanical stability and to reduce the content of halogen atoms that could be detrimental for fuel cell operations.

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