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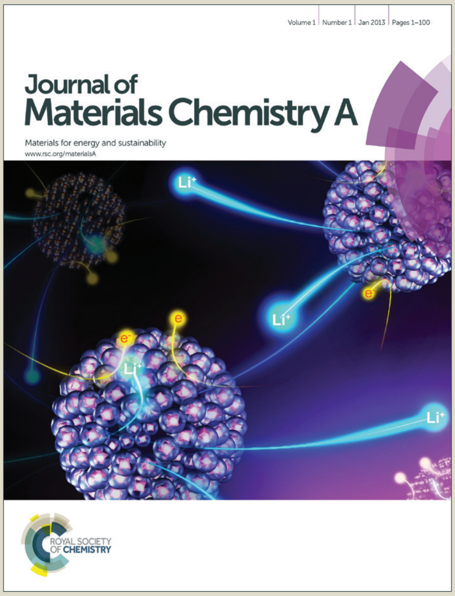

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Use of new cross-linking method to obtain semi-IPN membranes with phosphonic acid groups for a PEMFC application

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The synthesis of new semi-IPN membrane was performed from a commercial fluorinated copolymer and a fluoro-phosphonated copolymer with pendant phosphonic acid groups. The crosslinking of the fluoro-phosphonated was done from the presence of sulfonated groups by a simple heat treatment. Several membranes are casted with a crosslinking rate range from 5 to 20% and a molar percent of phosphonic acid range from 38 to 12%. These kinds of PEMFC show proton conductivity in a reach magnitude of 10^{-3} S.cm^{-1} in humidified conditions. All the membranes possess a high thermal stability. The mechanical behavior of all membrane was determined by DMA in function of the temperature and the relative humidity.

Introduction

During recent years, many research works have been carried out on the new technology development in order to use fuel cell as a new energy source. One of the main subjects of research was the amelioration of the proton exchange membrane performance, which is the heart of the fuel cell. Nowadays, the most used membranes are perfuorosulfonic polymers (Nafion®, Aquavion®…), which allow to reach the best performances in moderate range of temperatures between 25 and 80°C and high level of hydration with a required high relative humidity (more than 50% RH).

Nevertheless, in the automotive sector, fuel cell specifications were defined to be used nominally at 120°C with 30% RH and low pressure. Under these conditions, perfuorosulfonic membrane performances fall drastically due to loss of water. This implies the necessity to develop membranes with novel protogenic groups able to give proton conduction in low hydration condition and at 120°C. In these conditions, membranes bearing phosphonic acid groups seem to be a good potential candidate[1, 2]. Indeed, the proton conductivity of phosphonic acid polyelectrolytes was better than sulfonated polymer at elevated temperatures and in a dry state. This higher proton conductivity demonstrates the amphoteric character of the acid phosphonic groups associated to a proton transport by a Gröthuss mechanism[3]. Furthermore, phosphonic acid-functionalized polyelectrolytes permit to obtain material with low water swelling, which improve the mechanical stability during cycle of use. Then, during this last years different works were carried out on the synthesis of different polyarylphosphonic acid functionalized[4-9] or polystyrene derivative carrying phosphonic acid groups[10, 11].

Previous works perform by our team[12-14] involved the synthesis of partially fluorinated copolymer bearing phosphonic acid groups. Thanks to the acceptor/donor character of monomers used for the polymerization, the polymer obtained showed an alternated structure[15] between fluorinated and phosphonic acid units, which allows the presence of phosphonic acid groups distributed along the polymer. Interestingly, this polymer was used as PEMFC and showed a very good thermal stability (up to 200°C). Furthermore, when decreasing RH from 95 to 25%, the conductivity values decreased of only 1 order of magnitude, while the nafion® conductivity drops of about 3 orders of magnitude in the same range. Furthermore, 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. However, the molar mass of the polymer obtained was about 20,000 g.mol^{-1}, this implies that resulting membranes exhibit very poor mechanical properties, as they were very brittle. These low mechanical properties are greatly limiting their use in dry conditions, as well as decreasing life time of the membrane.

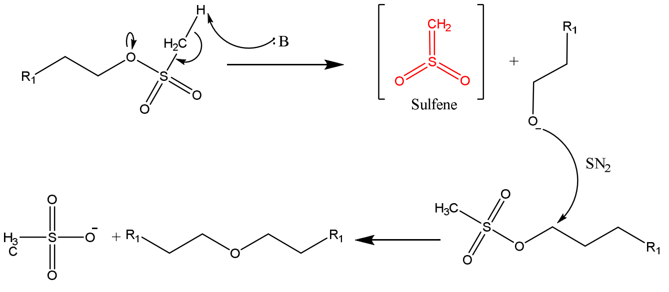
So, in order to improve the mechanical properties of the PEMFC a blend strategy was used [16]. To do this, the copolymer carrying phosphonic group (under the ester phosphonate form) was blended with a highly fluorinated copolymer. Indeed, polymer blending is gaining ground as a promising methodology for the development of PEMs. Nevertheless, during the acidification reaction of the phosphonate groups, membranes breakdown were observed. Indeed, the conditions of the acidification reaction are drastic (hydrochloric acid solution concentrated at 12N, at a temperature of 90°C and during 3 days). Furthermore, the strong hydrophilic/hydrophobic balance between the two polymers resulted in only partial miscibility. In order to use all the potential of these kinds of membranes, an improvement of two crucial points (i.e. the acid degradation and the partial miscibility) is required. In order to solve these problems, the most suitable method consists in crosslinking of the phosphonated copolymer. However, the conditions of PEMFC are quite extreme, high concentration of acid, high temperature, presence of radicals. It is thus necessary to perform the crosslinking through formation of strong covalent bonding that will able the membrane to resist to this hostile environment. In this framework, the formation of ether bonds between the polymer chains appears to realize all these requirements. The objective of this work is to develop a strategy to achieve crosslinking through thermal activation without addition of catalyst or initiator.

In this work we evaluate the feasibility of semi-interpenetrated networks (SIPN) obtained by blending poly(VDF-*co*-CTFE) (inert matrix, mechanical support phase) with covalently crosslinked phosphonated polyelectrolyte (proton conducting phase) as potential PEM materials candidate. To perform the crosslink of the phosphonated copolymer a new chemical method based on the sulfonated groups will be used [17]. So, the first part of this work is concentrated on the feasibility of the crosslinking reaction. Then, thermal and mechanical properties are examined for a wide range of membranes. Especially, the impact of the crosslinking ratio on the membranes properties is studied. Proton conductivity of membranes which possess the higher IEC were assessed.

Results and discussion

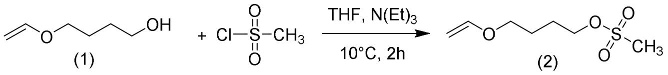
Study of crosslinking reaction

The crosslinking technique is based on the reactivity mesylate functional groups, allowed to cross-link the copolymer via inter-chain ether bonds. To do this, we relied on the work of Neal W. et al.[18] which perform the synthesis of aryl ethers from primary and secondary alcohols and aryl mesylates. The reaction proceeds via a sulfonyl transfer mechanism. A proposed mechanism of this reaction is shown in Scheme 1. The first step of this mechanism is the formation of the sulfene via an E2 elimination of the alcoholate. This reaction is thermally promoted, so at high temperature, the sulfene formation can be expected without the presence of based.



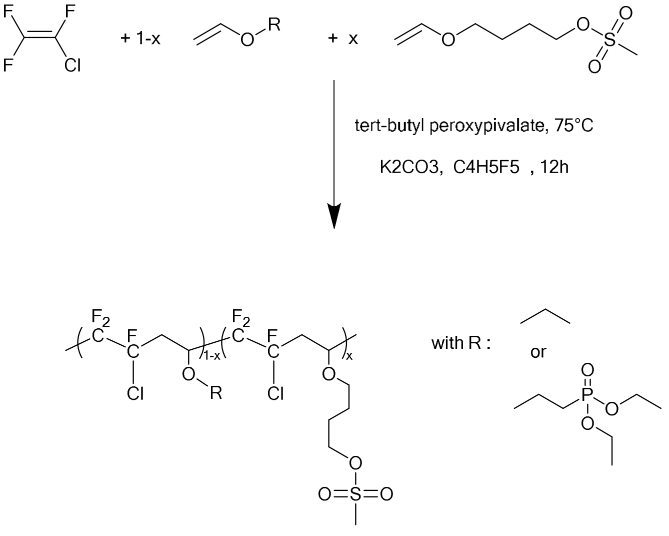
Scheme 1 Synthesis of ether bond from the sulfonate groups [18]

To demonstrate the validity of the cross-linking reaction described above, a model copolymer was synthesized from the polymerization of CTFE and ethyl vinyl ether (EVE) and 4-(vinyloxy) butyl methanesulfonate (VBMS) (Scheme 2). The synthetic route for VBMS (2) is shown in Scheme 2. Monomer 2 was easily synthesized from 4-(vinyloxy)butan-1-ol (monomer 1) and methanesulfonyl chloride by a Williamson reaction with high yield. The structure of monomer 2 was confirmed by ^{1}H NMR (supporting information)



Scheme 2 Synthesis of 4-(vinyloxy)butyl methanesulfonate (VBMS)

The copolymer synthesis is performed by radical terpolymerization between chlorotrifluoroethylene (CTFE), ethyl vinyl ether (EVE) and VBMS as indicated in Scheme 3 (where “x” is the molar percentage of VBMS in the feed).



Scheme 3 Radical terpolymerizations

The model study will be conducted without phosphonated group on the terpolymer, i.e. without using DEVEP. Indeed, the presence of this group could influence the crosslinking mechanism. To limit the amount of monomer carrying the reactive function, the synthesis will be carried out from a mixture of CTFE, ethyl vinyl ether (EVE) and VBMS in the molar proportions 50/45/5 respectively.

The copolymer obtained, i.e. the poly[(CTFE-*alt*-EVE)$_{0.9}$-co-(CTFE-*alt*-VBMS)$_{0.1}$], was characterized by ^{1}H NMR (Figure 1) to confirm the good incorporation of VBMS in the polymer chain. Based on the previous works[15] carried out on the alternated copolymerization of chlorotrifluoroethylene with vinyl ethers various significant signals of the methyl and methylene groups were clearly identified. The presence of groups signals: -O-$\underline{\mathbf{CH_2}}$-$CH_2$-$CH_2$-$CH_2$-O-S(O)$_2$-$CH_3$ (*e*), -O-CH_2-$\underline{\mathbf{CH_2}}$-$\underline{\mathbf{CH_2}}$-$CH_2$-O-S(O)$_2$-$CH_3$ (f, f'), -O-CH_2-CH_2-CH_2-$\underline{\mathbf{CH_2}}$-O-S(O)$_2$-$CH_3$(g); -O-$CH_2$-$CH_2$-$CH_2$-$CH_2$-O-S(O)$_2$-$\underline{\mathbf{CH_3}}$(h) respectively centered at 3.79, 1.71, 1.84, 4.25 and 3.02 ppm allows to confirm the incorporation of VBMS in the terpolymer chain. The ^{19}F NMR spectrum of the product, available in supporting information, allows to confirm the alternated character of the copolymer.

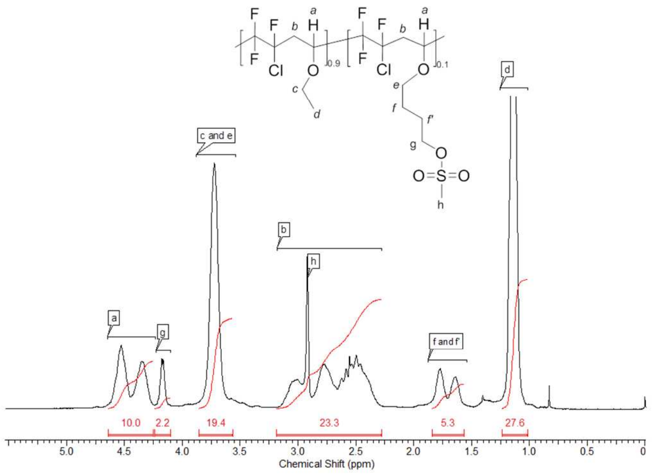


Figure 1 : ^{1}H NMR spectrum of poly(CTFE-alt-EVE)$_{0.9}$-co-(CTFE-alt-VBMS)$_{0.1}$ performed in $CDCl_3$.

In order to determine the efficiency of the crosslinking reaction, different analyses have been performed on the membrane before and after the cross-linking reaction. To perform the cross-linking reaction, the terpolymer solution was cast onto glass plate, and then dried at 80°C during 12h to eliminate the solvent and obtain the uncross-linked membrane, then at 150°C to perform the crosslink reaction to obtain the resulting membrane.

Thermal analyses

The thermal stability of the membrane has been assessed by Thermogravimetric analysis (TGA) before and after the crosslinking reaction. Figure 2 shows the thermogram obtained by TGA analyses of the membrane cast from the poly[(CTFE-*alt*-EVE)$_{0.9}$-co-(CTFE-*alt*-VBMS)$_{0.1}$] before (-) and after (-) crosslinking. The derivative curves are also given.

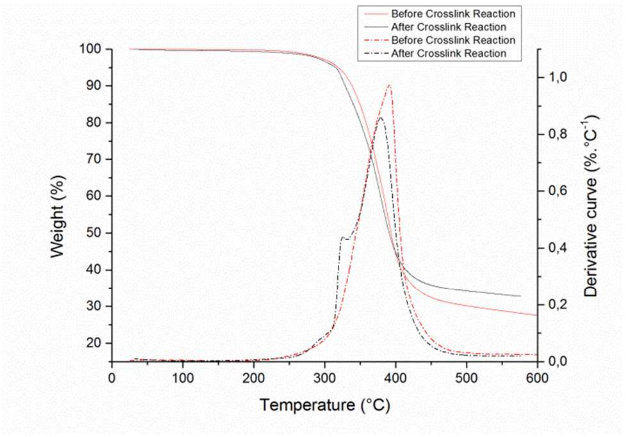


Figure 2 TGA analyses of poly[(CTFE-*alt*-EVE)$_{0.9}$-co-(CTFE-*alt*-VBMS)$_{0.1}$] before and after the crosslinking reaction.

Before crosslinking, we can note two main decompositions between 270 and 500°C. The first degradation occurs between 270 and 330°C. The bond energy dissociation (–O-S) of C-**O-S(O$_2$)-CH$_3$** groups is weaker than the bond energy (-O-C) of -C-**O-CH$_2$CH$_3$** groups, so we can attribute this weight loss to the dissociation of the -O-S- bond of VBMS units. Then from 350°C, the degradation of all pending polymer chains can be observed. After crosslinking, only one single decomposition was observed ranging from 270 to 500°C. Indeed, between 270 and 330°C on the derivative curve, the peak attributed to the -O-S-bond dissociation of VBMS units is no longer observed. Thus, during the crosslinking reaction, it seems that all mesylate groups are consumed. We also note that the crosslinked membrane has a slightly higher thermal stability than the non-crosslinked membrane. This increase of the thermal stability resulted in a slight increase of both $Td_{5\%}$ and $Td_{10\%}$ (Table 1). Indeed, after crosslinking, the temperature corresponding to 10% weight loss ($Td_{10\%}$) is 338°C, whereas for the non-crosslinked membrane, the $Td_{10\%}$ is 328°C.

Table 1 : Degradation temperatures and glass transition temperatures of poly[(CTFE-*alt*-EVE)$_{0.9}$-co-(CTFE-*alt*-VBMS)$_{0.1}$] before and after crosslinking obtained respectively by TGA under nitrogen at 20°C.min^{-1} and DSC at 20°C.min^{-1}.

Membranes	$Td_{5\%}$(°C)	$Td_{10\%}$(°C)	Tg(°C)[a]
Before Crosslinking	314	328	10
After Crosslinking	319	338	90

a : Uncertainty about the glass transition temperature determined by DSC : ±2°C

The glass transition temperatures of the terpolymers before and after crosslinking reaction were determined by DSC. The results obtained are listed in the Table 1. Tg value is 10°C before crosslinking, and increases to reach 90°C after crosslinking. This increase of the glass transition temperature characterizes a significant polymer network rigidification due to the formation of inter-chain bridges during the second heat treatment at 150°C.

Terpolymer solubility

The crosslinking reaction of the terpolymer leads to a three-dimensional network due to the formation of inter-chain bonds. This will directly impact the solubility of the polymer in various organic solvents, even resulting in total insolubility of the polymer for a sufficient degree of crosslinking. Thus, in order to confirm the crosslinking of membranes, solubility tests were carried out in different solvents. The test consists of immersing the membrane in the solvent for a period of 72 hours with weak stirring. The tests were conducted at both room temperatures 50°C (Table 2).

Table 2: Solubility tests at RT and 50°C of poly[(CTFE-*alt*-EVE)$_{0.9}$-co-(CTFE-*alt*-VBMS)$_{0.1}$] before and after crosslinking

Solvent	**Before Crosslinking**	**After Crosslinking**	
		T=RT	T=50°C
Methanol	+	x	x
Acetone	+	x	x
MEK	+	x	x
THF	+	x	x
DMSO	+	x	x
DMF	+	x	x

+ = soluble

X = insoluble

From Table 2, we note that the thermal treatment allows membranes to become totally insoluble in most organic solvents after crosslinking, at room temperature but also at 50°C. The insolubility of the membranes, especially in the solvents used for the casting, confirms the success of the crosslinking reaction of the membrane during heat treatment.

FTIR analyses

Fourier transform infrared spectroscopy (FTIR) analyses have been performed on terpolymer before and after the crosslinking reaction (Figure 3).From FTIR, the sulfonate groups are characterized by the presence of two bands around 1150 and 1350 cm^{-1}. Although the TGA results show a total consumption of mesylate groups after heat treatment, we observe a slight decrease of the characteristic band. But, the band characteristic of ether bonds significantly increases. The emergence of a new band between 1700 and 1800 cm^{-1} can be observed. This band is characteristic of carbonyl bonds. In view of the required thermal crosslinking of the terpolymer (>150°C), this band cannot be characteristic to the formation of ester or aldehyde groups. This band probably corresponds to the formation of a ketone group during the crosslinking reaction. Further investigations are nevertheless necessary to fully understand this reaction.

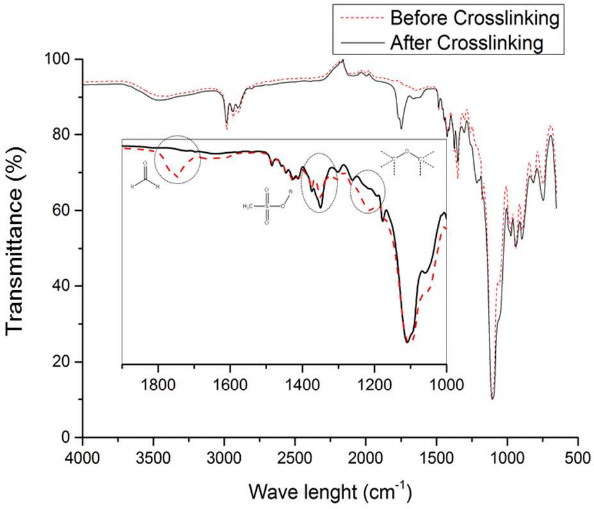


Figure 3 : FTIR spectrum of poly[(CTFE-alt-EVE)$_{0.9}$-co-(CTFE-alt-VBMS)$_{0.1}$] before and after crosslinking.

The crosslinking reaction probably occurs via the formation of ether and ketone bonds. During the reaction, the denser polymer network thereby reduces the mobility of the remaining sulfonate groups. In addition, we did not find any mechanism that could explain the formation of ketones groups. A model study from the coupling molecule with a mesylate or tosylate group will be carried out to obtain more insight about the reaction occurring during the crosslinking of the copolymer.

Preparation of semi-IPN membranes

The copolymer synthesis was performed by radical terpolymerization between chlorotrifluoroethylene (CTFE), diethyl vinyl ether phosphonated (DEVEP) and VBMS as indicated in Scheme 3. The structure of poly[(CTFE-alt-DEVEP)$_{1-x}$-co-(CTFE-alt-VBMS)$_x$] was confirmed by ^{1}H NMR, as shown in Figure 4. The integral ratio of signals between 1.6 and 1.9 ppm (H$_h$) and between 4.35 and 4.75 ppm (H$_a$) was calculated to confirm that the terpolymer composition corresponds to the initial stoichiometric proportion. In order to study the effect of the cross-link density onto physico-chemical properties of the membranes, we have synthesized fluorophosphonate terpolymer with a VBMS content of 5, 10 and 20 mol% respectively P$_5$, P$_{10}$ and P$_{20}$. The molar content of VBMS, DEVEP and CTFE is ascribed in Table 3 for each terpolymer.

Table 3 terpolymers composition

Terpolymers	Molar ratio of monomers into the terpolymer (%)^a		
	CTFE	DEVEP	VBMS
P$_5$	50	43	7
P$_{10}$	50	39	11
P$_{20}$	50	31	19

a: determined by ^{1}H NMR

Table 4 Composition, degradation temperatures at 5 and 10% weight loss, glass transition temperature and theoretical and experimental IEC of the all semi-IPN membranes obtained respectively by TGA in dynamic mode at 20°C.min^{-1} and obtained from DSC at 20°C.min^{-1}, and by acido-basic titration.

Membranes	Rate of fluorophosphonate terpolymer (wt%)	Rate of Poly(VDF-*co*-CTFE) (wt%)	Rate of phosphonic acid (mol %)	Td$_{5\%}$(°C)	Td$_{10\%}$(°C)	Tg(°C)^{d}	Tg(°C)^{e}	IEC$_{theo}$ (meq.g^{-1})	IEC$_{exp}$ (meq.g^{-1})
M$_5$-80^{a}	80	20	38	285	310	11	92	5.32	2.1
M$_5$-60^{a}	60	40	28.5	295	318	10.5	95.5	3.99	0.44
M$_5$-50^{a}	50	50	23.75	287	304	12	108	3.15	0.8
M$_5$-30^{a}	30	70	14.25	316	333	-5	85.8	2	0.4
M$_{10}$-80^{b}	80	20	36	283	308	31	92.5	5.04	1
M$_{10}$-60^{b}	60	40	27	286	311	54	98	3.78	0.3
M$_{10}$-50^{b}	50	50	22.5	288	313	55	105	3.15	0.4
M$_{10}$-30^{b}	30	70	13.5	310	330	1	101.4	1.89	0.52
M$_{20}$-80^{c}	80	20	32	284	305	54	92	4.48	0.9
M$_{20}$-60^{c}	60	40	24	295	314	90	98	3.36	0.5
M$_{20}$-50^{c}	50	50	20	300	322	80	115	2.8	0.8
M$_{20}$-30^{c}	30	70	12	311	334	76	90.8	1.68	0.9

a: Terpolymer P$_5$; b: Terpolymer P$_{10}$; c: Terpolymer P$_{20}$; d: before acidification reaction; e: after acidification reaction

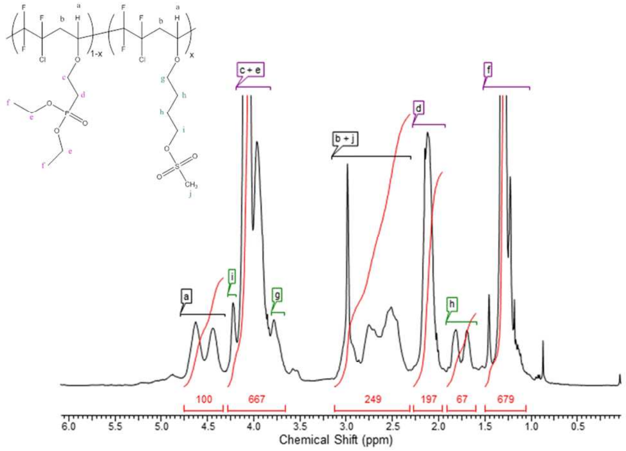


Figure 4 ^{1}H NMR spectrum of poly[(CTFE-alt-DEVEP)-co-(CTFE-alt-VBMS)] (realized in $CDCl_3$)

The membranes were prepared from film casting of a polymeric solution of poly(VDF-*co*-CTFE) and poly[(CTFE-*alt*-DEVEP)$_{1-x}$-*co*-(CTFE-*alt*-VBMS)$_x$] (Figure 5). After the evaporation of the cast solvent, membrane were heats at 150°C to perform the crosslinking reaction. Cleavage of the ester groups from the phosphonate was then performed in 12N HCl solution at 90°C during 3 days. No coloration was observed during the acidification process, which proves that cross-linking allows the polymer stabilization. Indeed, in the previous work[16], the acidification of the poly(CTFE-*alt*-DEVEP) by the same method result in a coloration of the acid solution. From the three synthesized terpolymers, a range of membranes was synthesized by varying the content of poly(VDF-*co*-CTFE). The membranes have been noted M$_x$-Y, where x is the molar content of VBMS into the copolymer and Y is the mass content of poly[(CTFE-*alt*-DEVEP)-*co*-(CTFE-*alt*-VBMS)]. For instance M$_5$-80 was obtained from 80w% of poly[(CTFE-*alt*-DEVEP)-*co*-(CTFE-*alt*-VBMS)], which contains 5 mol% of VBMS. The different membranes performed for this study are gathered inTable 4. The minimum rate of fluorophosphonate terpolymer was 30 wt% in order to get sufficient values of IECs into the semi-IPN membranes. Moreover, the minimum rate of poly(VDF-co-CTFE) was assessed to 20 wt% to afford sufficient mechanical properties for fuel cell applications.

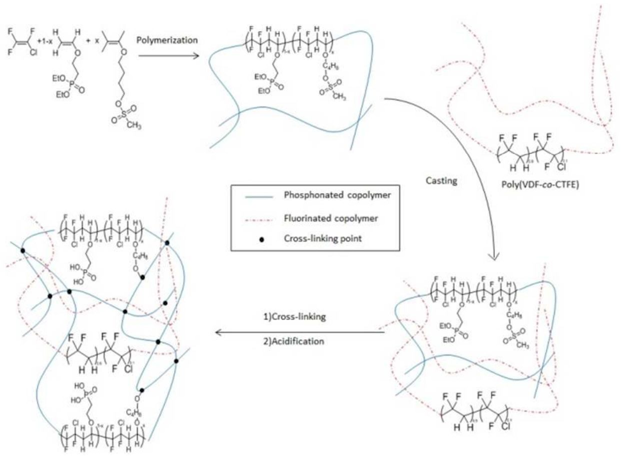


Figure 5 Schematic representation of procedure to obtain pseudo semi-IPN membrane comprising crosslinked poly[(CTFE-alt-DEVEP)-co-(CTFE-alt-VBMS)] and poly(VDF-co-CTFE).

Thermal properties of the membranes

The thermal properties of the different membranes were assessed after the crosslinking reaction and acidification step. The temperature corresponding to a weight loss of 5 and 10 % (respectively Td$_{5\%}$ and Td$_{10\%}$) and the temperature of glass transition temperature (Tg) values for all membranes are gathered in Table 4 (respectively determined by ATG and DSC). For all the membranes, the Td$_{5\%}$ is highest at 250°C. So, the thermal stability of this kind of membrane is clearly sufficient for PEMFC applications.

The glass transition temperatures were determined for each membrane before and after acidification. The T$_g$ values clearly increase for all membranes after acidification reaction, which proves that the phosphonic acid groups undergo hydrogen bonding between them. Thus more energy is then required to go from the viscous to the glassy state. In Figure 6, we have plotted the evolution of the T_g values vs the content of fluorophosphonate terpolymer for the membranes M_5, M_{10} and M_{20} after acidification.

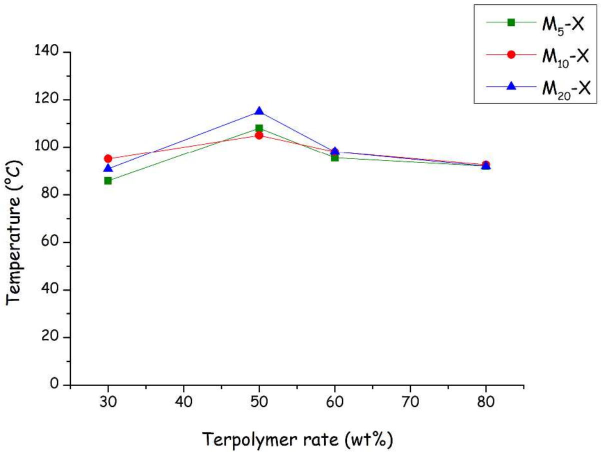


Figure 6 : Evolution of Tg vs the content of flurophosphonate terpolymer for the membranes M_5, M_{10} and M_{20} after acidification

For membranes M_5, M_{10} and M_{20} T_g values increase with a decrease of fluorophosphonate terpolymer content until reaching a maximum for 50% of terpolymer, below this content the T_g values slightly decrease. The decrease of fluorophosphonate terpolymer content, to 80 at 50%, in the membranes probably allows the phosphonic acid groups been closer to each other and then an increase of hydrogen bonding[16]. But when the content of fluorophosphonate terpolymer becomes too low, i.e. 30 wt%, this effect is no more predominant and thus the T_g values decrease. Finally, we can note that the content of cross-linking agent does not really impact the T_g values of the membranes.

Water uptake and swelling ratio

Water uptake of the membranes is a key parameter for the electro-chemical performances of the PEMFC as well as for the mechanical properties. Indeed, water is essential for the proton transport through a vehicular mechanism. Even if membranes made from fluorophosphonate polymers aim to be used at high temperature (from 90 to 130°C) and at low relative humidity (RH< 50%), these membranes have to show sufficient water uptake to undergo proton transport at low temperature and high RH as well. Nevertheless, too high water uptake will therefore lead to a sharp decrease of the mechanical properties of the membrane during the fuel cell operation. We have determined the water uptake for all the membranes at room temperature and at 100% RH (Figure 7).

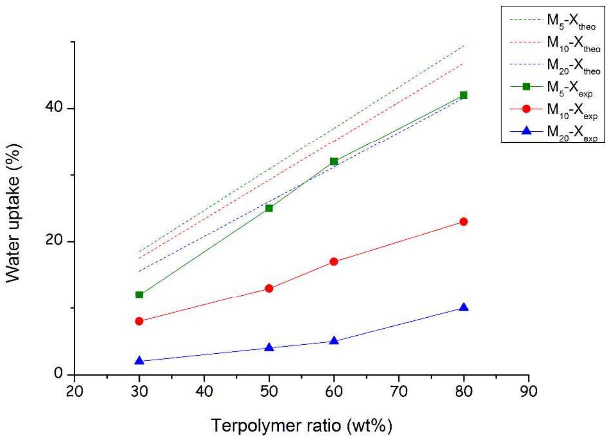


Figure 7: Evolution of the water uptake vs the content of fluorophosphonate terpolymer for the M_5-X, M_{10}-X and M_{20}-X membranes.

The experimental water uptakes (WUs) were compared to the theoretical ones, calculated from the WUs of poly(CTFE-*alt*-VEPA) been about 65% at 100% RH and room temperature[14] (Figure 7). Concerning first the M_5 membranes, both experimental and theoretical WU values are very close, which means that all the phosphonic acid groups can be easily accessible in the membrane. But, when the membranes are more densely cross-linked, i.e. M_{10} and M_{20} membranes, the accessibility to the phosphonic acid groups remains limited; this is the reason why we note a discrepancy between the experimental and theoretical WU values for M_{10} and M_{20} membranes. We can remark that both M_{10}-80 and M_{10}-60 show WU of about 20%, which should be enough for reaching good proton conductivity. For M_{20}-X membranes, the WU remains lower than 10%, which seems to be detrimental for the proton conductivity.

The swelling rate of the membranes is also a key parameter to take into account for PEMFC use. The swelling is characterized by an increase of the membrane thickness due to water uptake. During the fuel cell operation, cycles of swelling/un-swelling of the membrane are observed. If the membrane swelling is too high, a loss of the mechanical properties occurs during these cycles. Figure 8 shows the evolution of the swelling rate for the M_5-X, M_{10}-x and M_{20}-x membranes *vs* the content of fluorophosphonate terpolymer.

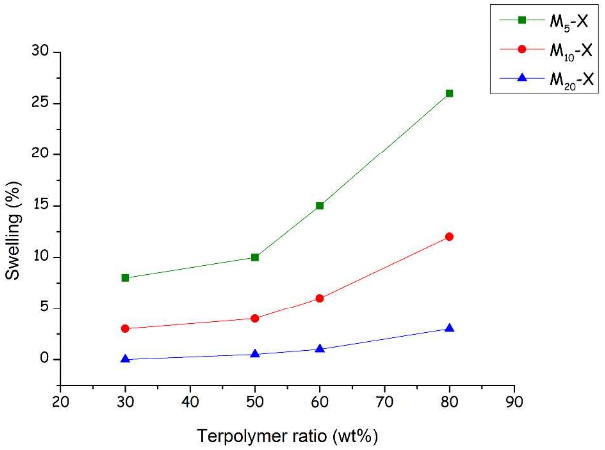


Figure 8 Evolution of the swelling rate (%) vs the content of fluorophosphonate terpolymer for the M_5, M_{10} and M_{20} membranes.

We can observe that the swelling rate of the M_{20} membranes is very low, which can be connected to the low water uptake for these membranes. Furthermore, even for a lower content of VBMS, i.e. lower cross-linking rate, the swelling rate remains lower than 30%. The cross-linking reaction of the terpolymer in the membrane leads to a network stiffness, which limits the polymer expansion due to the water uptake. The swelling rates showed in Figure 8 are nevertheless acceptable and in the same order than that of Nafion112®[19]. Thus, we except that the swelling cycles during the fuel cell operation should not lead to a loss of the mechanical properties of the membranes.

Evaluation of the Ionic Exchange Capacity (IEC)

Since poly(CTFE-*alt*-VEPA) shows an alternated structure, the IEC is rather high. Thus the IEC_{theo} values in the case of pseudo semi-IPN membranes are expected to be high. The values are gathered in and range from 5.32 for M_5-80 membrane to 1.68 for M_{20}-30 membrane.

We can see in the Table 4 that the IEC_{theo} values are much lower than the IEC_{exp} values. As a reminder, the principle of this method is based on the transformation of phosphonic acid of the membranes in a sodium phosphonate groups. In order to realize the transformation of the phosphonic acid functions from phosphonate groups, it is necessary that the Na^+ cation migrate through the membrane. However, the membrane crosslinking results in an increase of the density of the polymer network, therefore the accessibility of phosphonic acid groups is much reduced. Indeed, we have already observed that the water uptake values, for membranes M_{10}-X and M_{20}-X, are below than the theoretical values, so that the phosphonic acid groups are much less accessible. On the other hand, the experimental M_5-X water uptake values are in the same order of magnitude than the theoretical values. But, the IEC_{exp} values concerning the M_5-X membranes remain lower than the IEC_{theo}. In this case, the polymer network densification allows the migration of water molecule to create the hydration sphere around the phosphonic groups, but for the Na^+ cation, the access of the phosphonic acid groups is more difficult in particular when the solvation effect is considered. However, the proton being much smaller than the cation Na^+, transport through the membrane should be achievable. The measurement of the membranes proton conductivity will allow to confirm this assumption.

Proton Conductivity

The performance of a membrane for PEMFC is closely dependent to the proton conductivity, which directly influences the ohmic losses and finally the power densities. Proton conductivity measurements of M_5-80, M_{10}-80 and M_{20}-80 membranes were performed from 20 to 90 °C in water immersed conditions in order to characterize fully hydrated membrane properties (Figure 9). These results were compared to previous work, obtained for the M-100 membrane (cast only from phosphonate terpolymer)[14]. These membranes have been chosen because they show the best results due to their higher phosphonated terpolymer rate.

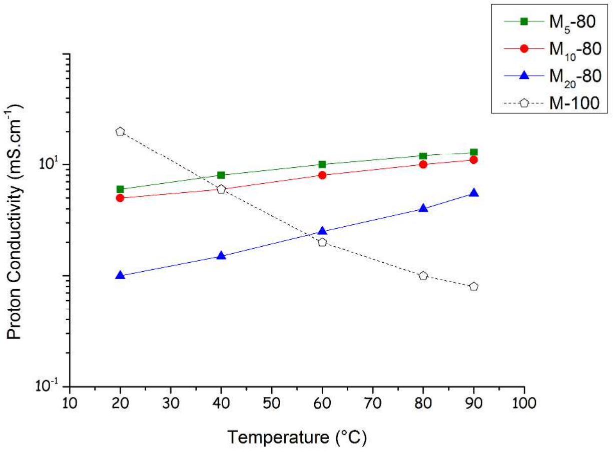


Figure 9 Average Conductivity versus temperature in immersed conditions for the M100, M_5-80, M_{10}-80 and M_{20}-80 membranes

Firstly, the evolution of the proton conductivity versus temperature is very different between the M-100 membrane and the M_5-80, M_{10}-80 and M_{20}-80 membranes. Indeed, concerning the M-100 membrane, a decrease of the proton conductivity versus temperature is observed. At 20°C, proton conductivity is around 20 mS.cm^{-1} and at 80°C is around 1 mS.cm^{-1}. In the previous works [13, 14], a diminution of the swelling was demonstrated when the temperature increases, which may explain this behaviour. Concerning the crosslinked membranes, an increase of the proton conductivity versus temperature was observed. In this case, the increase of the proton conductivity can be connected to a better structuration of the membranes. However, the performances of the crosslinked membranes are lower than that of blend membranes[16]. Indeed, the mobility of phosphonic groups was decreased by the crosslinking reaction. So, the macroscopic organisation of the crosslinked membrane is not the same that the blend membrane. This decrease of the proton conductivity can also be attributed to the decrease of the phosphonic acid accessibility, due to the higher crosslinking rate.

Mechanical properties

Dynamic mechanical analysis (DMA) was used to study the mechanical properties of the membranes and in this way, assess the contribution of poly(VDF-co-CTFE) on the mechanical properties of blend semi-IPN membranes. Before performing the mechanical study of different semi-IPN membranes, it is necessary to look at the mechanical properties of poly(VDF-*co*-CTFE). For this, the M-0 membrane (cast from only poly(VDF-*co*-CTFE)) was analysed by DMA. The result is shown in Figure 10.

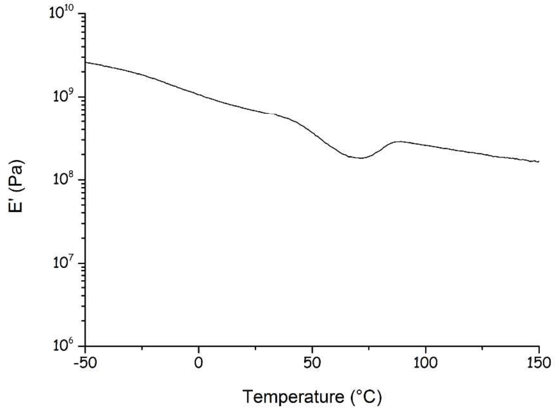


Figure 10: Storage modulus versus temperature of M-0 performed at 1Hz and 2°C.min^{-1}.

The variation of storage modulus (E') for a temperature ranging from -50 to 150°C was shown Figure 10. We observe that the storage modulus of the membrane cast only from poly(VDF-*co*-CTFE) is high throughout the temperature range studied. Indeed, it is 2.5 x 10^9 Pa at a temperature of -50°C, and then decreased steadily to 2.2 x 10^8 Pa at a temperature of 120°C. Around 70°C, we observe a slight decrease followed by an increase of the storage modulus. This variation of the modulus corresponds to a change of crystallographic state of poly(VDF-*co*-CTFE). Although, the Tg of the polymer is -30°C (determined by DSC), we do not see a drastic drop in the storage modulus, this is due to the semi-crystalline nature of poly(VDF-*co*-CTFE). This semi-crystalline character will bring stability throughout the temperature range used. On the other hand, the DMA analysis of the M-100 membrane (i.e. cast only from the poly(CTFE-*alt*-DEVEP) without crosslinking agent) is impossible, since the membrane is too brittle.

Semi-IPN membranes were then analyzed by DMA. Two parameters may vary during the analysis: temperature and relative humidity of the measuring chamber. The mechanical behavior of membranes was measured on temperature ranging from -50 to 150°C.

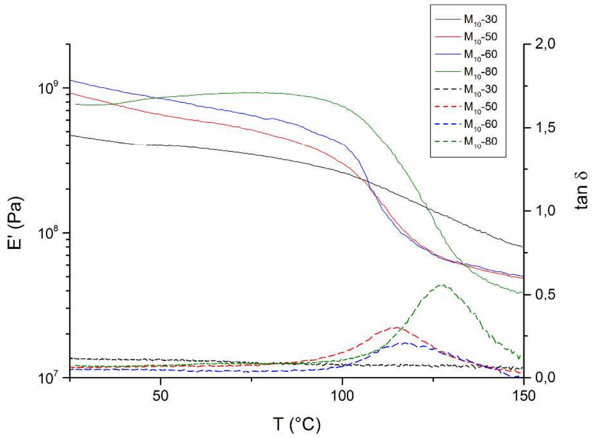


Figure 11 Storage modulus (-) and tanδ (---) evolution versus temperature for the M_{10}-30, M_{10}-50, M_{10}-60 and M_{10}-80 membranes.

The evolution of the storage modulus for the M_{10}-30, M_{10}-50, M_{10}-60 and M_{10}-80 for a temperature range from 25 to 150°C was shown Figure 11. At low temperature (<0°C) (Table 5), the mechanical behavior is the same than that of M-0 membrane (cast only from poly(VDF-*co*-CTFE)). Then, the storage modulus gradually decreases with temperature. From 80°C, we observed that the storage modulus starts to decrease more significantly, reaching a plateau of 5 x 10^7Pa. Indeed, for T>Tg, the storage modulus of an amorphous polymer drastically drops, reaching several decades. In our case, the drop of the storage modulus is limited by the presence of poly(VDF-*co*-CTFE) which possesses a storage modulus about 2 x 10^8Pa at this temperature. However, we note that there are slight differences according to the rate of phosphonated polymer. Indeed, for the membrane M_{10}-80, which has the highest rate of phosphonated polymer, the storage modulus is slightly higher, especially for temperatures above 50°C. However for T> Tg (Tg of phosphonated copolymer), M_{10}-80 membrane shows the lowest modulus values. In contrast, for the M_{10}-30 membrane, which has the lowest rate of phosphonated copolymer, for T<Tg, it has the lowest storage modulus and for T>Tg, it has the highest modulus values. From the curves Figure 11, we can determine an approximation of the Tg values of the phosphonated copolymer. To do this, we consider the temperature where the storage modulus starts to sharply decrease. Results are listed in Table 5, where we can see that the Tg obtained by DMA are similar to that determined by DSC. However, for the membrane M_{10}-30, the influence of the phosphonated copolymer on the mechanical properties is too low in order to perform the determination of Tg from DMA. From the observation of tanδ, we can see the presence of one maximum around 120°C (except for the M_{10}-30 membrane). The presence of this maximum signifies a change in the mechanical behavior of the membranes. However, the mechanical stability was insured by the presence of the fluorinated copolymer.

Table 5 : Storage modulus of M_{10}-30, M_{10}-50, M_{10}-60 and M_{10}-80 membranes compared to the M0 membrane (100% poly(VDF-co-CTFE)).

Membrane	Storage Modulus (Pa)			Tg(°C)[1]	Tg(°C)[2]
	-50°C	25°C	150°C		
M_{10}-80	$2.6*10^9$	$8.6*10^8$	$4*10^7$	92.5	102
M_{10}-60	$2.4*10^9$	$8.5*10^8$	$5*10^7$	98	100
M_{10}-50	$2.3*10^9$	$6.5*10^8$	$5*10^7$	105	98
M_{10}-30	$2.2*10^9$	$4*10^8$	$8*10^7$	101.4	nd
M0	$2.2*10^9$	$3.5*10^8$	$2*10^8$	nd	nd

[1] : Determined by DSC

[2] : Determined by DMA

From the Figure 12, we can observe that for a temperature of -50°C the composition of membranes has little influence on the values of storage modulus. At this temperature, the mechanical properties were dominated by the poly(CTFE-*co*-VDF). However, at temperatures above the Tg of poly(VDF-*co*-CTFE) some variations are observed. For a temperature of 25°C, the membranes with the highest rate of phosphonated terpolymer (M_5-80, M_{10}-80 and M_{20}-80) show the highest storage modulus values. This behavior is due to the rigidity of the phosphonated copolymer when the temperature is below its Tg. And for a temperature of 150°C, we observe the opposite behavior, ie, the lowest storage modulus corresponds to membranes having the highest rate of phosphonated copolymer.

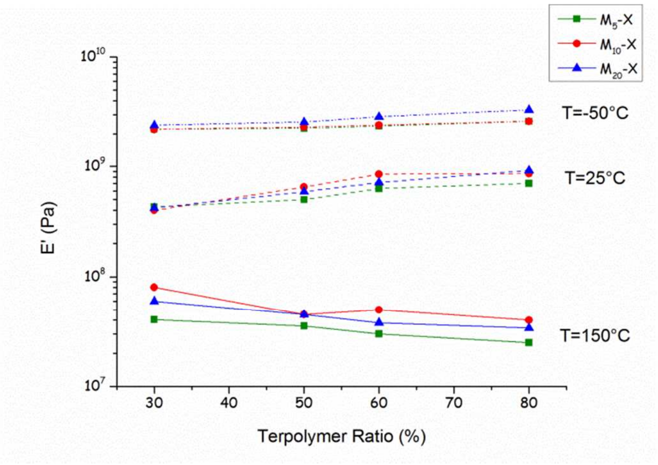


Figure 12 : Storage modulus evolution versus the content of phosphonate terpolymer at -50, 25 and 150°C for the M_5-X, M_{10}-X and M_{20}-X membranes.

In order to analyze the behavior of the membranes in humid condition, the DMA analysis can be performed with a regulation of the RH during the analysis. To do this, the measuring chamber is crossed by the flow of neutral gas (nitrogen or argon) more or less charged with water molecules. Thus, we can observe the mechanical behavior for RH ranging from 0 to about 80% and a temperature of 30°C. The membranes used are very thin (about 40µm), so it is necessary that the membranes have a significant capacity of water uptake to see an influence of RH on the mechanical behavior. Tests conducted on the M_{20}-X and M_{10}-X membranes were not conclusive, due to too low amount of water recovery and swelling (see Figure 7 and Figure 8). The most interesting results were obtained for the M_5-X membranes, thanks to their high values of water uptake and swelling (see Figure 7 and Figure 8). The results obtained are showed in Table 6.

Table 6 : Storage modulus evolution (in Pa) versus RH for the M_5-30, M_5-50, M_5-60 and M_5-80 semi-IPN membranes at RT

RH	M_5-80	M_5-60	M_5-50	M_5-30
0%	8.1×10^8	7.2×10^8	6×10^8	6.4×10^8
35%	7.1×10^8	6.4×10^8	5.2×10^8	3×10^8
70%	6.3×10^8	5.1×10^8	4.3×10^8	1.6×10^8

Table 6 shows the values obtained at 0, 35 and 70% of relative humidity for M_5-80, M_5-60, M_5-30, M_5-50 membranes. From this table, two trends are distinguishable. Indeed, when the RH is low, we can observe that a high rate of phosphonated terpolymer implies a high storage modulus. Indeed, when the RH is reduced the phosphonated terpolymer becomes more rigid, so the storage modulus is higher and the mechanical behaviour is dominated by the phosphonated terpolymer. However, at high RH, the effect is reversed. Indeed, the mechanical behaviour of the membrane is then dominated by the poly(VDF-co-CTFE), except for the M -80 membrane which possess a high rate of phosphonated terpolymer. We find the same trend in the temperature study, i.e. a high rate of poly(VDF-co-CTFE) leads to a lower storage modulus. We can nevertheless conclude that, in the operating cycles of the fuel cell, the mechanical properties of membranes remain high and ensure their role as a gas barrier between two electrodes.

Experimental

Materials

Diethyl vinyl ether phosphonated was purchased from Specific Polymers (Montpellier, France). *Tert*-Butylperoxypivalate (TBPPI) 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 Honeywell (Buffalo, USA) and Solvay S.A. (Tavaux, France and Bruxelles, Belgium), respectively and were used as received. The poly(VDF-*co*-CTFE) grade was Solef 31508 supplied by Solvay. 2-chloro ethyl vinyl ether, sodium iodide, triethyl phosphite, acetone (analytical grade), methanol (analytical grade), carbonate potassium (K_2CO_3), ethyl vinyle ether, hydroxyl butyl vinyl ether, mesyl chloride, triethylamine, tetrahydrofuran (THF, analytical grade), ethyl acetate (analytical grade), hexane (analytical grade), were purchased from Sigma-Aldrich (Saint Quentin-Fallavier, France). Deuterated solvents for NMR spectroscopy were purchased from Euroiso-top (Grenoble, France) (purity> 99.8%)

Synthesis of 4-(vinyloxy) butyl methanesulfonate (VBMS)

As an example, in a 250mL single-neck round bottom flask equipped with a magnetic stirrer, one equivalent hydroxide butyl vinyl ether (10g, 86.2 mmol), 1 equivalent of mesyl chloride were introduced (9.85g, 86.2mmol) and 1 equivalent of triethylamine (9.6g, 94.9mmol) were introduced in THF (100mL). After 2h, the produced salts were filtered. Two liqudi/liquid (water/ethyl acetate) extractions have been realized and the product was obtained in high masse yield (80%).

Radical copolymerization of CTFE with vinyl ethers

All copolymerization reactions were carried out in a 100mL Parr autoclave equipped with a rupture disk (3000psi), a manometer, inlet and outlet valves and a mechanical stirrer. Prior to the reaction, potassium carbonate (3 mol% about the overall molar amount of vinyl ether(s)) was inserted in the autoclave, which was then tightly closed and pressurized with 20 bar of nitrogen to check for eventual leaks. The autoclave was then put under vacuum (10-2 mbar) for 2 hours to remove oxygen. The liquid phase (*i.e.* vinyl ether(s), initiator and solvent) was introduced via a funnel, and CTFE was transferred by double weighing (*i.e.* the difference of weight before and after gas insertion). The reaction mixture was then stirred mechanically and progressively heated at 75°C for 8 hours. During this step, a slight increase (*i.e.* lower than 5 bars) and decrease of pressure were observed together with a strong rise of the temperature that reached about 35°C. After reaction completed, the autoclave was cooled in ice and degased to release unreacted CTFE After opening the autoclave, the product was dissolved in acetone, concentrated with a rotary evaporator, precipitated from cold methanol and filtered. The product was then dried under vacuum (10mbar) at 60°C for 123 hours.

Preparation of semi-IPN membranes

A specific amount of poly(CTFE-*alt*-PEVE) was dissolved in DMSO (20-25 wt%), then poly(VDF-*co*-CTFE) powder was added into the poly(CTEF-*alt*-PEVE) solution, which was stirred several hours at 50°C. After the poly(VDF-*co*-CTFE) was fully dissolved, the solution was cast onto glass plate, and then dried at 80°C during 12h to eliminate the solvent, then at 150°C to perform the crosslink reaction.

To obtain the phosphonic acid groups, membranes were immerged in an HCl concentrated solution (12N) at 90°C during 3 days. After reaction, membranes were washed by distilled water, and then dried under vacuum at 80°C during one night.

Nuclear Magnetic Resonance

The nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform, d_7-N,Ndimethylsulfoxide as the solvents. Chemical shifts are given in part per million (ppm). The experimental conditions for recording 1H NMR specta were as follows: flip angle 90°, acquisition time 4.5s, pulse delay 2s, number of scans 128.

Thermogravimetric analyses.

Thermogravimetric analyses were carried out on a TGA 51 apparatus from TA Instruments, from room temperature to 600°C, at a heating rate of 20°C.min^{-1}, under air and nitrogen.

Differential scanning calorimetry

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 Tg, defined as the inflection point in the heat capacity jump.

The ion exchange capacity (IEC)

The ion exchange capacity (IEC) of the different blend membranes was determined from back titration. The sample were immersed and stirred in an aqueous solution of NaOH (0.1N, 2.5mL) and NaCl (2N, 50mL). This solution was back titrated with 0.01N HCl aqueous solution. The IEC value (meq.g^{-1}) of the blended membranes was calculated using the equation 1, where V_{eq} is the volume of 0.01 HCl aqueous solutions for the volumetric titration, [OH$^-$] the OH$^-$ concentration of the initial aqueous solution and m_d the dry weight of the membrane.

$$\mathbf{IEC(meq.g^{-1})} = \frac{\mathbf{[OH^-]*V_{eq}}}{\mathbf{m_d}} \quad (1)$$

The IEC_{theo} was calculated by using the IEC of poly(CTFE-*alt*-VEPA) equal to 7 meq.g^{-1}. For each fluorophosphonate terpolymer, the IEC_{theo} was calculated according to equation:

$$\mathbf{IEC_{theo}} = \left(\mathbf{7} \times (\mathbf{1} - \boldsymbol{\tau}_{\mathbf{CL}})\right) \times \boldsymbol{\tau}_{\mathbf{ter}} \quad (2)$$

Were τ_{CL} is the content of cross-linking agent VBMS into the terpolymer and τ_{ter} is the content of terpolymer in the membrane.Water uptake and swelling measurements

Water uptake was assessed from the wet and dry states of the materials according to the following protocol: the membranes were immersed in distilled water for 24 hours and then removed. The membranes were wiped with a tissue paper, and then both the mass and thickness of the blend membranes were determined in these wet conditions. The membranes were dried at 70-80°C for 72 h to determine the dry weight and the dry film thickness. The water uptake was determined by the following equation:

$$\mathbf{Water\ uptake}\ (\%) = \frac{\mathbf{m_w - m_d}}{\mathbf{m_d}} * \mathbf{100} \quad (3)$$

Where, m_w is the wet mass of the blend membranes.

The theoretical water uptake was calculated by using the WU of poly(CTFE-*alt*-VEPA) equal to 65% at 100%R.. For each fluorophosphonate terpolymer, the WU_{theo} was calculated according to equation:

$$\mathbf{WU_{theo}} = (\mathbf{65} \times (\mathbf{1} - \boldsymbol{\tau}_{\mathbf{CL}})) \times \boldsymbol{\tau}_{\mathbf{ter}} \quad (4)$$

The swelling of the membranes was determined by the following equation:

$$\textbf{Swelling}\ (\%) = \frac{t_w - t_d}{t_d} * \mathbf{100} \tag{5}$$

Were t_w and t_d are the wet and dry thickness of the blend membranes, respectively.

Mechanical properties

Dynamic-mechanical analysis (DMA) was conducted with a METRAVIB DMA 25. Uniaxial stretching of samples were performed while heating at a rate of 2°C/min from -100 to 150°C, keeping frequency at 1 Hz (viscoelastic region) and a constant deformation rates. The glass transition temperature was obtained from tanδ determination. It has been shown that tanδ maximum relates much better to the value obtained by DSC[20]. Furthermore, the mechanical comportment was studied versus the RH range between 0 and 100% and in the temperature range between 25 and 70°C

Proton conductivity.

The impedance of the membranes was determined by the two-point probe ac impedance spectroscopy using Mates 7260 impedance analyzer. The impedance measurement was carried out at various temperatures in deionized water (relative humidity 100%). Then, the proton conductivity (σ) was obtained from the following equation:

$$\boldsymbol{\sigma} = \frac{l}{R * S} \tag{6}$$

Where σ is the proton conductivity ($S.cm^{-1}$), R is the ohmic resistance of the membrane sample (omh), *l* is the thickness of blend membrane (cm) and S is the cross-sectional area of the membrane sample (cm^2).

Conclusion

New polymer electrolyte membranes have been synthesized from a semi-IPN strategy between a crosslinkable fluoro-phosphonated copolymer and a commercially available fluorinated copolymer. One crucial point of interest of this work concerns the synthesis of new crosslinkable polymer by a simple heat treatment. Indeed, to the author's knowledge, this work is the first one reporting the use of the mesylate groups to perform a crosslinkable polymer. More investigations are nevertheless required to determine the exact crosslinking mechanism.

The use of crosslinking fluoro-phosphonated copolymer to cast PEMFC allows to increase the chemical stability of the membranes versus acid and oxidative environments. The presence of the fluorinated copolymer allows to obtain a material with good mechanical properties, even at high crosslinking ratio.

However, in order to obtain membrane with high values of proton conductivity, it is necessary to use fluoro-phosphonated copolymer with a crosslinking rate around 5wt%. In these conditions, the proton conductivity ($10 mS.cm^{-1}$ at 90°C) allows to use this material as membrane for PEMFC.

In order to enhance the proton conductivity of these membranes, it could be interesting to perform the synthesis of the terpolymer with only 2 or 3 percent of crosslinkable monomer in the composition of the poly[(CTFE-*alt*-DEVEP)-*co*-(CTFE-*alt*- VBMS)], in order of a better access to the phosphonic acid groups.

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Notes and references

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