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# LE RAYONNEMENT $\gamma$ COMME METHODE DE MODIFICATION DES PROPRIETES MACROSCOPIQUES.



# INTRODUCTION

Après avoir étudié la radiolyse des matrices à travers l'étude des espèces radicalaires formées et leur impact sur la formation d'un réseau, cette partie se consacre à apporter une réponse "Matériaux" à la problématique initialement posée qui consiste à limiter le gonflement des matrices PVDF par un électrolyte tout en conservant de bonnes affinités physico-chimiques avec celui-ci.

Une première section vise ainsi à déterminer l'impact du rayonnement  $\gamma$  sur les propriétés macroscopiques du PVDF et des deux copolymères p(VDF-co-HFP) et p(VDF-co-CTFE). Une stratégie de réticulation ayant été retenue dans un premier temps pour limiter le gonflement, la caractérisation du réseau formé lors de l'irradiation constitue une part importante du travail effectué. La tenue mécanique, critère important pour le procédé d'élaboration des supercapacités, est aussi étudiée. L'influence de la dose d'irradiation et de la nature de la matrice polymère est présentée. Enfin, une attention particulière est accordée à l'amélioration de la densité de réticulation. Nous verrons comment, à travers l'incorporation d'un agent réticulant, le triallyl isocyanurate (TAIC) nous avons pu atteindre une partie des objectifs initiaux (Partie I).

Dans la seconde section, une approche différente relative à la modulation des propriétés de surfaces du PVDF sera présentée. Les polymères fluorés étant connus pour leur résistance chimique élevée, le radiogreffage d'un monomère permettant une modification ultérieure sans toutefois diminuer la stabilité électrochimique du PVDF est envisagée. Ainsi, cette stratégie vise à allier les bénéfices liés à la réticulation sous rayonnement de la matrice et la possibilité de moduler les interactions de surface polymère/électrolyte. Nous décrirons alors les procédés de radiogreffage d'un monomère fluoré, le 2,3,4,5,6-pentafluorostyrene (PFS) et la post-modification mis en œuvre à travers une réaction chimiosélective avec un mercaptoalcool. En particulier, les moyens de caractérisation associés aux deux étapes de modification seront présentés. Enfin, les propriétés de surface seront discutées à travers l'étude de la mouillabilité avec différents liquides sondes, tels que l'eau et l'acétonitrile, ce dernier constituant le milieu de référence en tant que solvant utilisé dans les applications supercapacités (Partie II).

## I. $\gamma$ -IRRADIATED VINYLIDENEFLUORIDE BASED POLYMERS IN SITU REINFORCED BY A CROSSLINKING AGENT.

Polyvinylidene fluoride and its copolymers containing either hexafluoropropene or chlorotrifluoroethylene were subjected to  $\gamma$ -radiation in argon up to doses of 500 kGy. The macroscopic behavior of the irradiated materials was investigated and correlated to the ability of the polymers to form crosslinks. The network formation was revealed by swelling tests while crosslinking density was evaluated from rheological measurements. The influence of polymer matrix was compared and a part of the study was then focused on the increase of crosslinking efficiency. For this purpose, a chemical crosslinker, namely triallyl isocyanurate (TAIC) which is sensitive to free radical reactions was incorporated into the polymer matrix. The effect of crosslinker concentration for a given dose was studied with the 3 different fluorinated matrix. Significant increases of both mechanical properties and gel content, as well as a relevant decrease of solvent uptake as determined with using two solvents, dimethylformamide and acetonitrile, have been observed until the rate of TAIC reaches 10 wt%. This improvement is especially noticeable in the case of copolymers. Studies of the effect of radiation dose for a given TAIC rate have shown that the properties reach a threshold value from 300 kGy and that the major influent parameter is the crosslinker concentration.

### INTRODUCTION

Owing to their exceptional chemical and thermal resistance combined with their low surface energy poly(vinylidene fluoride) (PVDF) based polymers were applied in a wide range of applications, from the medical field to the energy one.<sup>1</sup> Thus the use of fluorinated polymers was considered as microporous membranes for conventional batteries or supercapacitor according to their excellent mechanical properties and electrical stabilities. In such application affinity with the liquid medium is also required as well as a conservation of the dimensional integrity. Indeed, the compromise between a good wetting of the polymer membrane and a limited swelling without any dissolution is one of the most important parameters needed in electrical separators.<sup>2</sup> These antagonist properties could be partially reached with PVDF or PVDF copolymers since crystalline regions can provide sufficient mechanical integrity to the membrane.<sup>3</sup>

Another strategy consist in using polymers blend in which one of the component is not soluble in the electrolyte medium as polystyrene (PS) in the case of p(VDF-co-HFP) /PS blends.<sup>4</sup> Crosslinking the membranes was also reported as a relevant strategy to fulfill the aforementioned requirements, by

using either a crosslinking agent such as polyethylene glycol dimethacrylate (PEGDMA)<sup>5</sup> or by submitting a p(VDF-co-HFP) copolymer to the irradiation of Li ion.<sup>6</sup> The latter approach can be applied on materials already processed and does not need a pre-modification of the matrix or addition of further initiator.

Despite such advantages, and to the best of our knowledge, no other work upon the crosslinking of PVDF-based materials induced by irradiation has been mentioned in the literature, while the use of ionizing radiation applied on polymers has been intensively studied since the 1960s and reviewed several times.<sup>7,8</sup> Radiation involves the generation and reaction of radical species and can be summarized as a competition of mechanisms of crosslinking and chain scission. Based on numerous reported works related to many fluoro-based polymers irradiated in different conditions, Lyons et al.<sup>7</sup> have ordered fluoropolymers with increasing crosslink efficiency, and PVDF homopolymer turns out to be comprised between poly(vinylidene fluoride – co – chlorotrifluoroethylene) p(VDF-co-CTFE), the presence of a chlorine atom reducing the crosslinkability and the poly(vinylidene fluoride – co – hexafluoropropene) p(VDF-co-HFP). However with radiation doses commonly envisioned in industrial field (< 100 kGy), the solvent uptake factor, *i.e.* the weight fraction of solvent contained in polymer gel, remains higher than 1000 % whatever the VDF-based polymers.<sup>9</sup> Obviously, if the crosslink density were increased, the solvent uptake would decrease. One way to proceed is by thermal control: as an example, it has been reported that when temperature rises from 0 to 120 °C, PVDF samples lead to higher gel content, from 20% to 60 % when irradiated at a given dose of 150 kGy.<sup>10, 11</sup> However this method is limited because the temperature has to be controlled and tunable during the irradiation step. By the way, the most common method to promote the radiation crosslinking is the use of additional polyfunctional monomers incorporated in the matrix prior to irradiation. Crosslinking efficiency depends on both their miscibility with the polymer and their functionality as shown by Makuuchi et al.<sup>10</sup> for a series of acrylate monomers. The latter are generally di- and tri-functional vinyl compounds but allyl functions are in some cases more suitable due to their lower reactivity with temperature.<sup>7</sup>

Surprisingly the triallylisocyanurate or TAIC, commonly used to crosslink VDF-based polymers with the use of free radical initiators such as peroxides,<sup>12</sup> has scarcely been employed in combination with  $\gamma$ -radiation. Only few patents<sup>13-16</sup> claim the crosslinking of VDF-based polymers containing CTFE and HFP units whereas the works of Forsythe et al.<sup>17</sup> proposed a mechanism of crosslinking fluoroelastomers. Herein we present a detailed comparison of the  $\gamma$ -radiation crosslinking of three different fluoropolymers: PVDF, p(VDF-co-HFP) and p(VDF-co-CTFE) and the impact of the introduction of TAIC at various concentrations. In particular, the mechanical properties as well as the uptake of solvent were investigated in depth in relation with the crosslinking density.

## I.1. EXPERIMENTAL SECTION

### I.1.1. MATERIALS

Commercially granulated PVDF homopolymer Kynar 740, poly(vinylidene fluoride – co – hexafluoropropene) SEPBATT 2740 and poly(vinylidene fluoride – co – chlorotrifluoroethylene) SEPBATT 2734 were provided by Arkema, France. Comonomer contents are about 6 wt% and 8 wt% for S2740 and S2734, respectively. All polymers were tested as H2-type dumbbell-shaped specimen formed by an extrusion-injection process. Triallyl isocyanurate (TAIC) was supplied from Sigma-Aldrich and used as received without any further purification treatment. Dimethylformamide (DMF) and acetonitrile used in sol-gel analysis were supplied from Carlo Erba.

### I.1.2 METHODS

The extrusion process was performed using a twin screw DSM microcompounder. Pristine polymers were sheared with at 100 rpm speed, at 200 °C for the homopolymer and 190 °C for the copolymers, and injected in a 1.5 cm<sup>3</sup> mold at 25 °C to obtain dumbbell-shaped specimens. TAIC was pre-incorporated in the polymer matrix using a dissolution process to avoid excessive loss of TAIC during the extrusion process. Granulated polymers and TAIC with percentage of 3, 7, 10, and 13 wt% were extruded at 190 °C and 180 °C for the homopolymer and the copolymers respectively. The mixtures were sheared during 3 min and the rate of TAIC was verified using a thermogravimetric analysis. Samples were stocked at -18 °C to prevent any diffusion and exudation of TAIC.

Specimens were placed into Schlenk tubes, vacuumed at ambient temperature, purged with argon several times and finally kept under argon atmosphere. The tubes were then placed into a vacuum bell jar under argon to avoid any oxygen contamination. Irradiations were carried out using an industrial <sup>60</sup>Co gamma source at room temperature with dose rate of 0.7 kGy.h<sup>-1</sup>. An annealing at 100 °C under argon was performed after the irradiation in order to favor the reaction of remaining radicals.<sup>18-20</sup>

DSC measurements were carried out by using Q20 (TA instruments). Samples were heated from -80 °C to 200 °C under nitrogen flow (50 mL.min<sup>-1</sup>) with a rate of 10 °C.min<sup>-1</sup>, held at 200 °C for one minute and cooled to -80 °C at the same rate before a second heating run. Crystallinity yields were calculated with using the enthalpy change of melting as measured during the second heating run, corrected to the weight fraction of polymer contained in the sample, and compared to the enthalpy change of melting of a 100% crystalline PVDF homopolymer  $\Delta H_f^0$  (104.7 J.g<sup>-1</sup>).

Stress-strain curves in tension were obtained using an MTS 2/M electromechanical testing system at  $22 \pm 1$  °C and  $50 \pm 5\%$  relative humidity at cross-head speed of  $10 \text{ mm.min}^{-1}$  corresponding to a  $\dot{\epsilon}$  of  $8.33 \cdot 10^{-3} \text{ s}^{-1}$ .

Sol-gel analyses were performed with two different solvents, i.e. DMF and acetonitrile. About 1 g was taken from dumbbell specimen then introduced in a closeable flask. After determining with accuracy the weight ( $w_i$ ) a large excess (60 mL) of solvent was introduced. Solutions were heated at 80 °C (with DMF) or 60 °C (with acetonitrile) for 48 h to allow complete extraction of the soluble part. Swollen samples were carefully wiped with a tissue and weighted ( $w_g$ ). The solvent was then evaporated under vacuum 24 h at 100 °C to determine the weight of dried gel ( $w_{dg}$ ) i.e. the weight of insoluble. The gel content (% gel) and the solvent uptake in the gel (% sol) were obtained by following equations:

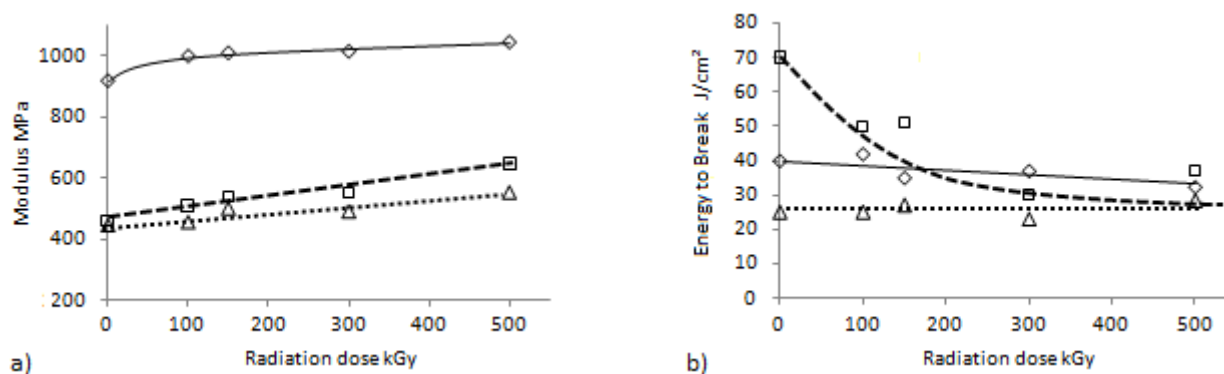
$$\% \text{ gel} = \frac{w_{dg}}{w_i} \times 100 \quad \text{and} \quad \% \text{ sol} = \frac{w_g - w_{dg}}{w_{dg}} \times 100$$

Dynamic mechanical properties were evaluated using a Rheometric Scientific Rheometer ARES. Sample with cross section of about  $2 \times 4 \text{ mm}^2$  and a length comprised between 10 and 15 mm were cut from the central part of dumbbell-shaped specimens. Measurements were carried out using a 2000 g.cm transducer and a low torque transducer (200 g.cm with a lower resolution limit of 0.2 g.cm) over a frequency of  $6.28 \text{ rad.s}^{-1}$  (1Hz) from -80 °C to 200 °C. The heating rate was set at  $5 \text{ °C.min}^{-1}$  and the 1% applied strain was taken in the linear domain.

## I.2. RESULTS AND DISCUSSION

### I.2.1 COMPARISON OF PVDF, p(VDF-CO-HFP) AND p(VDF-CO-CTFE) UPON $\gamma$ -IRRADIATION

The three PVDF based polymers and copolymers: PVDF (K740), p(VDF-co-HFP) (S2740) and p(VDF-co-CTFE) (S2734) were irradiated at different dose ranging from 0 to 500 KGy. As illustrated in Figure 1a, an increase of modulus with dose is observed whatever the polymer is. Gains in modulus are respectively about 15 %, 45 % and 25 % when dose reaches 500 kGy indicating a more pronounced sensitivity of copolymers toward  $\gamma$ -radiation. In contrast, stress and strain at yield and stress at break are not affected by the radiation upon the range studied (not presented), while energy to break decreases slightly for PVDF but remains constant for the two copolymers (Figure 1b). However, for the p(VDF-co-HFP) copolymers, results present a wider dispersion as the necking propagates more or less along the sample.



**Figure 1.** Evolution of modulus (a) and energy to break (b) as a function of radiation doses for pristine PVDF based polymers.  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE).

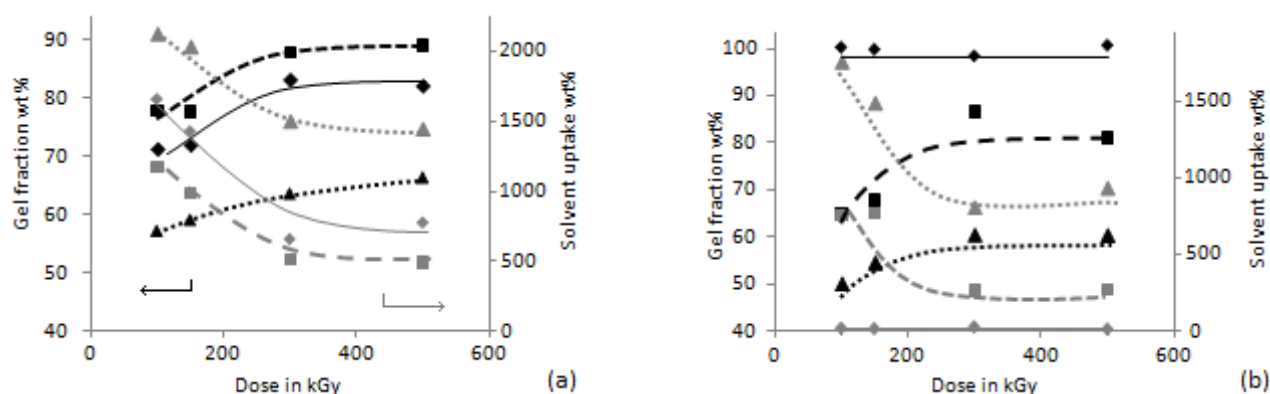
In the literature, an increase of the PVDF modulus between 10 and 20 % correlated to the decrease of both tensile strength and elongation to break was already reported when irradiation doses ranged from 100 to 1 000 kGy.<sup>21</sup> However such results have to be considered with care since radiation and post-treatment conditions were not clearly provided. Indeed other references showed that tensile modulus, stress and strain at break are not drastically modified on this range of radiation dose.<sup>22-24</sup> In our study, the experimental conditions are the same whatever the polymer is (homopolymer or copolymer), and thus our results are comparable with each other. Additional thermal analysis were attempted in order to investigate the evolution of the crystallinity with the dose. Indeed crystallinity could reinforce the material and therefore have an impact on the modulus level. The results (Figure S1) show an increase of crystallinity rate up to the dose of 150 kGy followed by a further decrease with a stabilization around the initial rate. These results are similar to those reported by Zhudi et al.<sup>25</sup> who attributed the increase of crystallinity at low dose to the formation of small crystallites in amorphous regions, an all the more favored process that the chain mobility is increased due to chain scissions, while for higher dose, crystallites are damaged. However this behavior cannot explain the evolution of the modulus and therefore the increase can be ascribed to the change in crosslinking rate when submitted to ionizing radiation.<sup>9,25</sup>

The crosslinking level can generally be estimated by swelling tests in good solvent. In our work we have used DMF, due to its affinity with VDF based polymers, as well as acetonitrile, a common solvent having a high dielectric constant and being able to dissolve electrolyte salts.<sup>26</sup> The gel fraction and solvent uptake are presented in Figure 2a for DMF and in Figure 2b for acetonitrile. As illustrated, the gel fraction increases when the dose is increased whatever the polymer is, except for PVDF in acetonitrile (Figure 2b) which apparent gel content is 100 wt% whatever the dose. The gel fractions of p(VDF-co-HFP) are higher than those of p(VDF-co-CTFE) whatever the dose is. The same trends are observed in DMF and acetonitrile and are in agreement with both the results



reported by several authors<sup>7, 9, 25, 27</sup> when using other solvents, and with the ranking previously established by Lyons et al.<sup>7</sup> However these previous studies have not involved the same solvents as us and moreover our study shows that the gel fraction and the solvent uptake reached a threshold value at 300 kGy. Thus one can confirm that the presence of HFP unit and CTFE respectively increases and decreases the crosslinking of VDF based copolymers.

It should have been interesting to calculate the average molecular weight between crosslinks ( $M_c$ ) using solvent uptake according to traditional Flory's theory.<sup>28</sup> However this is not advised since the crosslinking process occurs heterogeneously with a preference to amorphous phase and since the solubility parameters for VDF copolymers are not well-known. Indeed the changes in  $M_c$  values when  $\chi$  parameter varies in the range of 0 to 0.4 are too large to be neglected.



**Figure 2.** Evolution of gel fraction (in black) and solvent uptake (in grey) vs. radiation dose in DMF (a) and acetonitrile (b).  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE).

Another well-suited technique to calculate directly  $M_c$  consists in performing torsional rheology. Indeed, the formation of chemical crosslink nodes gives rise to a change of the storage modulus which is revealed at high temperature (Figure S2). While for non-irradiated pristine specimens, polymer chains can totally flow at a temperature higher than the melting one, for irradiated samples the crosslink nodes maintain polymer chains in the liquid state even after melting of the crystalline phase. Thus the theory of rubber elasticity<sup>29</sup> can be applied and the  $M_c$ <sup>30</sup> can be calculated according to the following equation  $G' = \rho RT/M_c$  where  $R$  is the noble gas constant,  $T$  the temperature and  $\rho$  the density of polymer which is taken as the one of the amorphous PVDF homopolymer *i.e.*  $1.68 \text{ g.cm}^{-3}$ .<sup>31</sup>

**Table 1.**  $M_c$  of irradiated polymers calculated from the storage modulus  $G'$  taken at 180°C according to the rubber elasticity theory.  $M_c$  are given in  $\text{g.mol}^{-1}$ .

Dose kGy	100	150	300	500
PVDF	19 600	9 900	3 600	3 080
p(VDF-co-HFP)	24 100	12 700	3 700	3 380
p(VDF-co-CTFE)	33 500	31 300	11 400	12 900

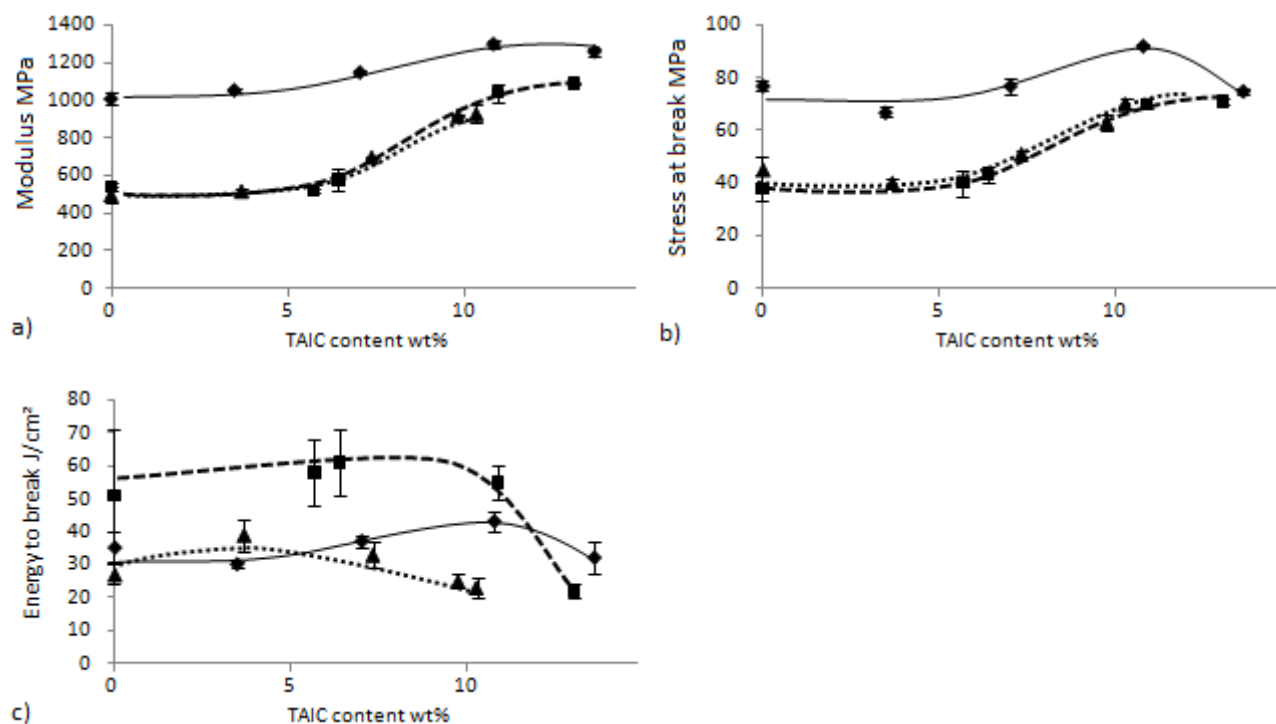
The  $M_c$  of the three VDF-based (co)polymer samples irradiated at different doses are gathered in Table 1. As expected the  $M_c$  values decrease when the dose increases highlighting a densification of the network. Surprisingly the density is more pronounced with PVDF than with the two other copolymers, in contradiction with the aforementioned swelling experiments conducted in DMF and the crosslinking ranking reported by Lyons et al.<sup>7</sup> but in agreement with the swelling experiments performed in acetonitrile. Moreover, both  $M_c$  of PVDF and p(VDF-co-HFP) are in the same order of magnitude for high doses, while chlorinated copolymer distinguishes itself by a much higher average molecular weight between nodes (around three times higher).

Nevertheless our results point out that for high doses, the impact of radiation diminishes as the network becomes tighter and therefore further significant gain becomes more difficult as observed with the swelling data obtained in DMF. Also, it can be noted that glass transition temperatures are found unchanged whatever the irradiation dose (Figure S3) indicating that the number of carbon atom between two crosslink is higher than 20 which is the threshold value below which the  $T_g$  may be changing.

### 1.2.2. EFFECT OF ADDITION OF CROSSLINKING AGENT (TAIC)

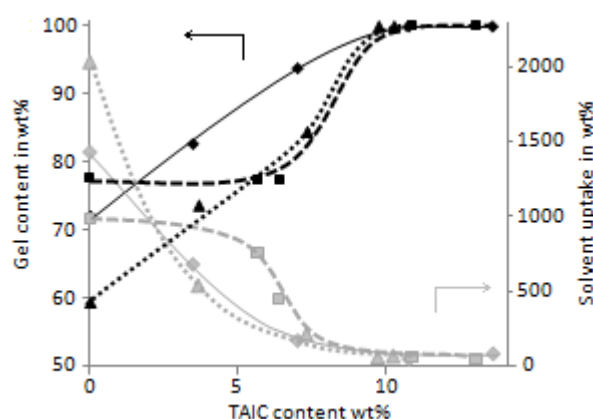
TAIC was blended with fluorinated polymer and copolymers through a two steps protocol: (i) dissolution in acetone and (ii) extrusion at the lowest possible temperature, in order to minimize its loss during the extrusion process. According to the thermogravimetric analysis, more than 90% of introduced TAIC was still present in the dope, the protocol being reproducible even if minor variations could be detected. By the way, no thermal polymerization occurred during the extrusion process, since polymers remains soluble in both DMF and acetonitrile. However the tensile modulus and the stress at break of the blends both decrease while the energy to break increases with the presence of TAIC (Figure S4). This could be explained by the fact that TAIC acts as a plasticizer,<sup>17, 32</sup> as it is only located in amorphous phase, as suggested by the absence of modification of degrees of crystallinity (Figure S5) and melting temperatures.

First, the results obtained for samples with different rates of TAIC and subsequently irradiated at a given dose, i.e. 150 kGy, are discussed. Mechanical properties as measured by tensile tests are first compared. Surprisingly no variation of the tensile modulus (Figure 3a) and stress at break (Figure 3b) was observed for any polymer when the TAIC rate was lower than 5 wt%. Then, up to a TAIC percentage of 10 wt%, both these values gradually increases whereas a drop is observed for 13 wt%. Thus, the maximum values are obtained for 10 wt% of TAIC, and the increase in modulus was respectively 30 %, 100% and 85 % for PVDF, p(VDF-co-HFP) and p(VDF-co-HFP) and 20%, 85% and 55% in the case of the stress at break. These tensile results suggest an enhancement of crosslinking when the content of TAIC is increased and reveal an optimal content at around 10%, higher TAIC content leading to an embrittlement of the material. While the mechanical properties of pristine p(VDF-co-HFP) and p(VDF-co-CTFE) are much lower than the ones of PVDF – being irradiated or not-, it is interesting to notice that such optimized TAIC content brings the mechanical properties of the copolymers up to the level of pristine PVDF. Thus, adding TAIC to VDF-based (co)polymers not only facilitates the processability but also improves a lot the mechanical properties of copolymers.



**Figure 3.** Evolution of modulus (a) stress at break (b) and Energy to break (c) of  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE) samples with increasing rate of TAIC and subsequently irradiated at 150 kGy under argon.

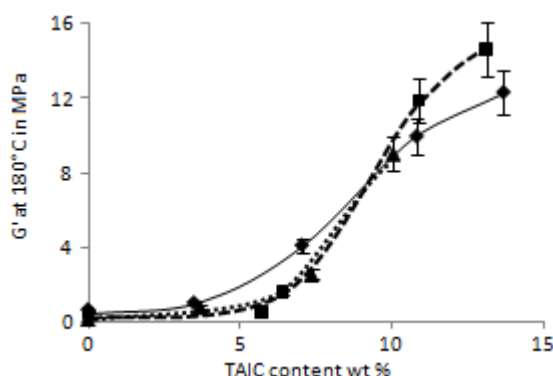
Evolutions of gel content and solvent uptake were also investigated in DMF with the same blends as aforementioned (Figure 4). These results reveal that the presence of TAIC gives rise to an increase of the gel content with in parallel a decrease of swelling. It is worth noting that the optimum concentration of TAIC is the same (10 wt%) as the one determined with mechanical properties. Moreover, while some differences exist between the pristine three (co)polymers when irradiated at 150 kGy (see Figure 2a), both the gel fraction and solvent uptake are similar whatever the polymer matrix is when 10 wt% of TAIC is introduced. For higher TAIC content, no further improvement is observed.



**Figure 4.** Evolution of gel fraction (in black) and solvent uptake with DMF (in grey) of  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE) samples with increasing TAIC content and subsequently irradiated at 150 kGy under argon.

Figure 5 shows the increase of the storage modulus at 180 °C with respect to TAIC content for the three (co)polymers after an irradiation at 150 kGy. (Curves of storage modulus for PVDF are depicted in Figure S6). Effect of TAIC is clearly highlighted by this method but the average molecular weight between crosslinks cannot be evaluated using the rubber elasticity theory since the network nodes are not punctual anymore, as TAIC is a triallyl derivative. In addition, drift from rubber elasticity law may be explained by the heterogeneity of crosslinks as the crystalline domains do not contain any crosslinking agent. Hence higher local concentration of TAIC surrounding crystal part may be expected since the crosslinker is expelled from crystal part during the crystallization process, and since the TAIC diffusion is low. (Differences of TAIC solubility into the 3 polymers for different temperatures is illustrated in Figure S7) Concept of hard cluster and their influence on rubber elasticity have been previously reported for other kind of polymers<sup>33</sup> but no further investigations were made on this way. However, the increase of storage modulus as measured at 180°C is clearly significant, and is related to a higher crosslinking density which cannot be numerically estimated.  $G'$  is multiplied by a factor 20 and 30 for PVDF and p(VDF-co-HFP) respectively when the TAIC concentration reaches 13 wt% when compared to their respective

references irradiated at the same dose, but without crosslinker. For the p(VDF-co-HFP) copolymer, the gain factor was about 40 times for 10 wt% of TAIC. This increase of storage modulus for both copolymers starts to be significant when TAIC concentration reaches nearly 6 wt% while it is not that pronounced for the homopolymer.



**Figure 5.** Storage modulus  $G'$  measured at 180 °C for  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE) with increasing TAIC content and subsequently irradiated at 150 kGy under argon.

### 1.2.3. EFFECT OF RADIATION DOSE.

The impact of radiation dose was studied on samples containing around 7 wt % of TAIC, a lower rate than the one at which the mechanical properties and gel fraction are the highest ones as measured at 150 kGy. Samples were irradiated at 4 different doses: 100, 150, 300 and 500 kGy and their properties were compared to the ones obtained with non-irradiated samples on the one hand, and to the ones obtained for pristine irradiated samples on the other hand (Table 2).

As expected, the irradiations lead to an increase of the tensile modulus whatever the polymer is. Moreover the same value of modulus was obtained whatever the dose at which the polymer was irradiated, highlighting the high reactivity of TAIC toward  $\gamma$ -irradiation. Thus, the increase of modulus is respectively 200, 250 and 280 % for PVDF, p(VDF-co-HFP) and p(VDF-co-HFP). Such improvement clearly shows that crosslinking reaction occurred in the presence of TAIC. It is noteworthy that these gains are still relevant, but to a lesser extent, if one compares the values obtained for  $\gamma$ -irradiated polymers containing 7 wt% of TAIC to those for non-irradiated polymers. Indeed the gains become respectively 20, 45 and 55 % for PVDF, p(VDF-co-HFP) and p(VDF-co-HFP). The reason for the moderate gains is due to the aforementioned plasticizing effect of TAIC.

**Table 2.** Modulus, stress at break and energy to break of PVDF, p(VDF-co-HFP) and p(VDF-co-CTFE) all containing around 7 wt% of TAIC and irradiated at different dose.

Dose (kGy)	0	100	150	300	500	Reference*
<i>Modulus of Elasticity E in MPa</i>						
PVDF (7%)	38	1150	1150	1120	1130	920
p(VDF-co-HFP) (6.4%)	19	700	580	700	710	460
p(VDF-co-CTFE) (7.4%)	17	590	700	660	690	445
<i>Stress at break <math>\sigma_R</math> in MPa</i>						
PVDF (7%)	42	75	77	79	77	85
p(VDF-co-HFP) (6.4%)	25	48	43	50	49	33
p(VDF-co-CTFE) (7.4%)	24	50	51	52	51	48
<i>Energy to break <math>J.cm^{-2}</math></i>						
PVDF (7%)	56	37	37	36	36	40
p(VDF-co-HFP) (6.4%)	15	55	61	46	49	70
p(VDF-co-CTFE) (7.4%)	90	32	33	27	28	25

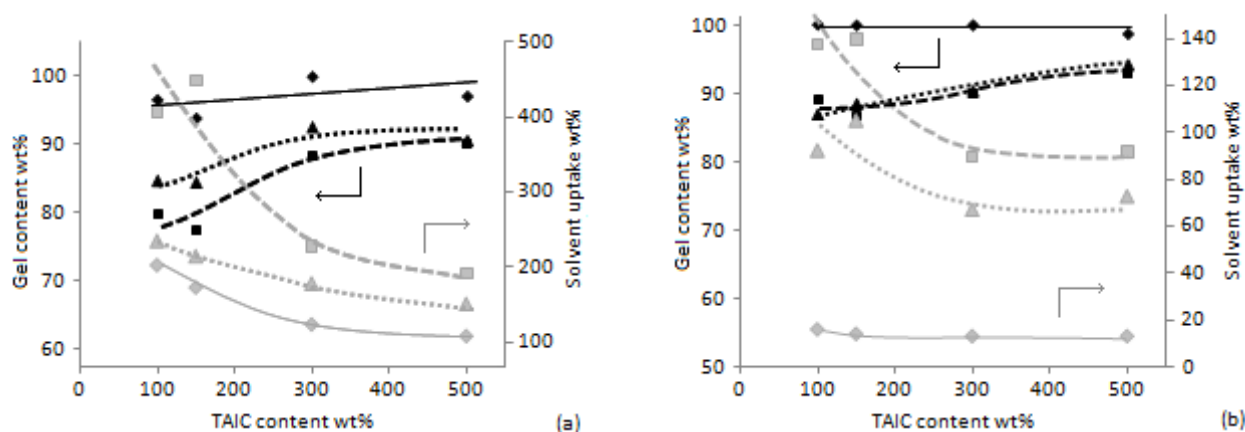
\* Values obtained with non-irradiated polymer without crosslinker.

The comparison of other mechanical properties determined at different dose: evolution of stress at break and energy to break confirm the same result, which states that increasing irradiation dose has no further impact. This kind of behavior is surprising even if Lambert et al.<sup>16</sup> already reported the same trend for a p(VDF-co-CTFE) copolymer containing 3 wt% of TAIC irradiated in the 0-100 kGy dose range. One can explain these results by the role of the crystalline part which may “mask” the possible contribution of the crosslinking part.

Another way to characterize the networks is to examine the swelling properties. Gel content and solvent uptake were determined with using both DMF (Figure 6a) and acetonitrile (Figure 6b). When compared to results obtained for pristine samples irradiated at different dose (Figure 2), the first conclusion is that the gel content has dramatically increased and solvent uptake has decreased whatever the matrix is, with the addition of 7wt% of TAIC. Focusing on results depicted in Figure 6, the gel content increases when doses increases, but for PVDF in either DMF or acetonitrile which gel content is already maximum at 100 kGy. Clearly this effect is more pronounced with p(VDF-co-HFP) and p(VDF-co-CTFE) than with PVDF; indeed, for both copolymers, the gel content as determined in DMF increases when the dose rises from 100 to 300 kGy, then a pseudo-plateau is obtained. For irradiation doses higher than 300 kGy a threshold is attained with maximum values of 95, 92 and 90 wt% for PVDF, p(VDF-co-HFP) and p(VDF-co-CTFE) respectively. From these results it can be inferred that the crosslinking reactions imply both the crosslinking agent and the polymer, the structure of the latter being responsible for the sensitivity of the {crosslinker/polymer} blend towards the radiation. The literature has also reported that the threshold dose is closely related to the functionality of the crosslinking agent<sup>10, 27</sup> with a threshold value found close to 250 kGy for

triacylate crosslinking agents. Our results are in good agreement with these values, as TAIC being also a trifunctional reagent.

This threshold for a dose around 300 kGy was also observed with the solvent uptake as determined with using either DMF (Figure 6a) or acetonitrile (Figure 6b). One can deduce that the gel content and the solvent uptake are much more sensitive to the crosslink rate than mechanical properties are, mostly because the crystalline part is solubilized. Additional experiments using torsional rheology analysis over a large range of temperature were attempted. The storage modulus at 180 °C clearly increases with radiation dose (Figure 7). Comparable variations were observed with the three fluorinated polymers with also the presence of a threshold at around 300 kGy as detected with sol-gel analysis.

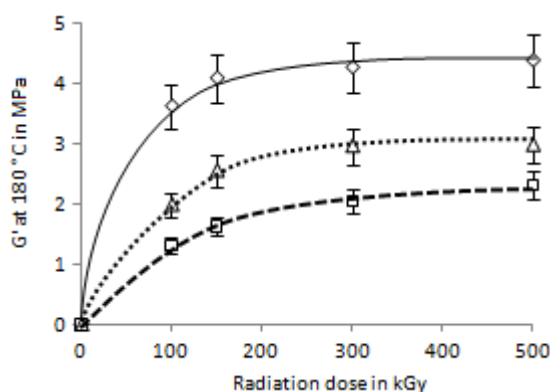


**Figure 6.** Evolution of gel content (in black) and solvent uptake (in grey) in DMF (a) and acetonitrile (b) as a function of dose for VDF based polymers containing 7 wt% of TAIC.  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE).

Such threshold undoubtedly evidences the absence of significant gain of crosslinking density by further exposure to radiation. This was also observed with irradiation of pristine samples (see values in Table 1) even if some further network densification can be pointed out by means of the solvent uptake analysis (see Figure 2).

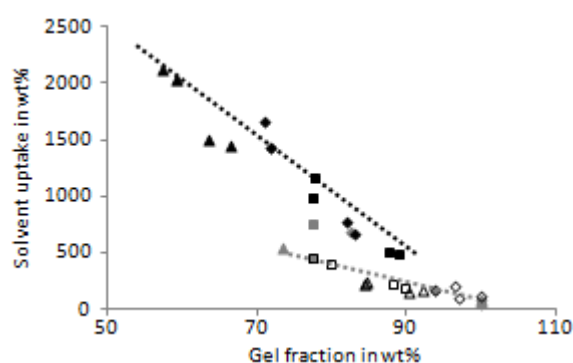
Moreover, the structure of the polymer is still important since the crosslink density is higher with PVDF than with p(VDF-co-HFP) whatever the radiation dose is. The CTFE copolymer is here intermediate as the TAIC content is slightly higher than the one of HFP copolymer.





**Figure 7.** Evolution of the storage modulus taken at 180 °C as a function of dose for  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE) containing 7, 6.4 and 7.4 wt% of TAIC respectively.

The dependence of solvent uptake as a function of gel fraction may be observed in Figure 8 for samples swollen in DMF, which is a good solvent for the three fluorinated polymers. Values are in the same order of magnitude than the ones tabulated in previous studies<sup>9</sup> and may be aligned on a master line indicating that the structure of the networks is similar whatever the polymer is. With the addition of a crosslinking such as TAIC, the solvent uptake becomes lower than for pristine matrices at a same gel fraction, such as a new master line merges. This is explained by a modification of the network structure with a higher density, and which results from the reaction of the double bond of the crosslinking agent with the matrix. Again, a unique line is obtained whatever the polymer or the irradiation dose is, which proves that the structure of the network is comparable and mainly due to the crosslinker.



**Figure 8.** Solvent uptake (with DMF) as a function of gel content. Black symbols stand for polymers irradiated without TAIC at several doses, grey symbols stand for polymers irradiated at 150 kGy containing several rate of TAIC; and white symbols stand for samples irradiated at different doses containing 7wt% of TAIC.  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE). (Lines are guides for the eye)



## CONCLUSION

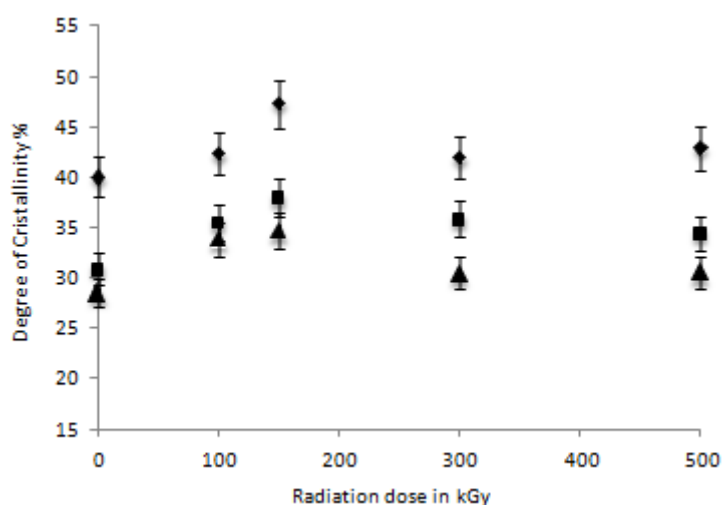
Three fluorinated polymer and copolymers: PVDF, p(VDF-co-HFP) and p(VDF-co-HFP), containing or not triallylisocyanurate (TAIC) as crosslinker were irradiated at different doses under a non oxidative environment. As expected, it appears that the irradiation gives rise to the crosslinking of polymers leading to an increase of the mechanical properties and a decrease of the solvent uptake. Without the addition of a crosslinker, the homopolymer retains the best mechanical and swelling properties whatever the radiation dose is, while the overall improvement is greater in case of copolymer containing HFP unit. When TAIC is incorporated, properties of irradiated polymers are essentially a function of its concentration and a noticeable but relatively low improvement of mechanical properties was observed. However the density of the network being higher than the one without TAIC, the solvent uptake is much reduced to almost no swelling both in a good solvent such as DMF or in acetonitrile, a solvent able to dissolve electrolyte salts. Therefore combining irradiation of blends of fluorinated polymers with TAIC paves the way to the design of new materials suitable for batteries or supercapacitor applications.

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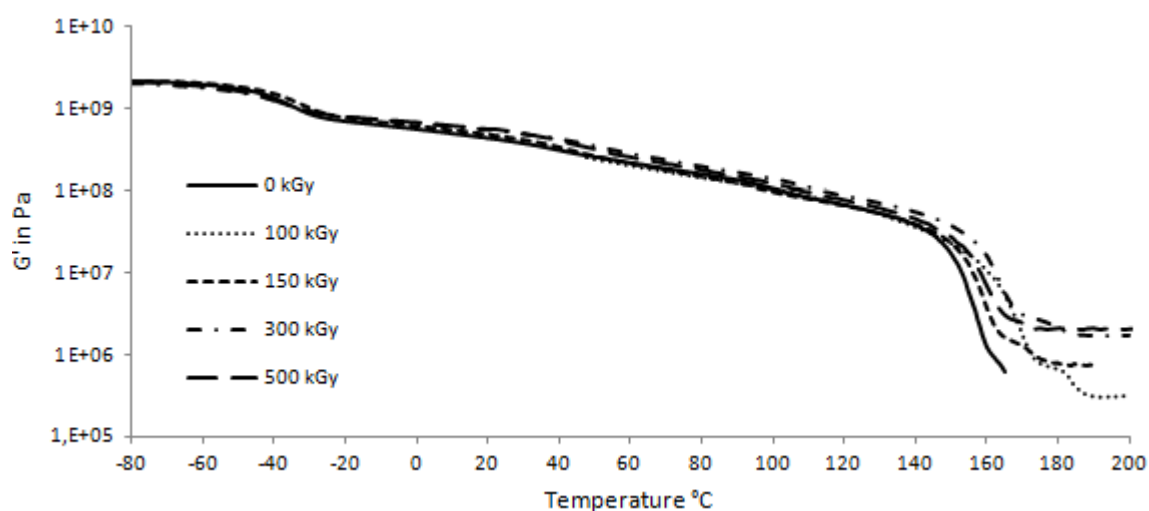
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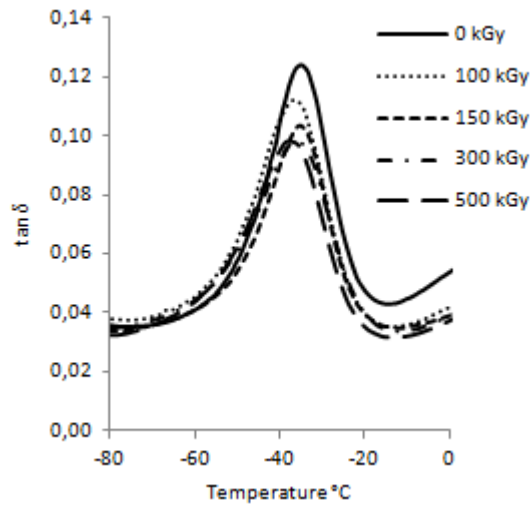
## SUPPORTING INFORMATION AVAILABLE.



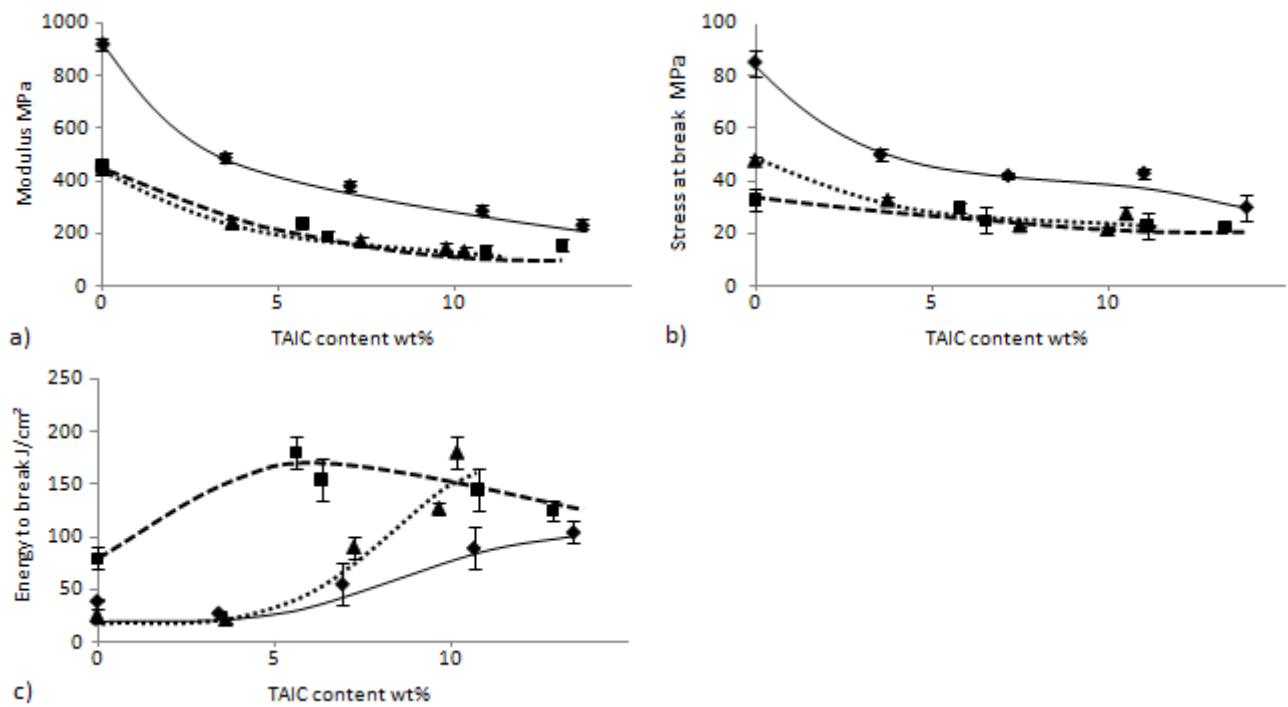
**Figure S1.** Evolution of crystallinity degree of polymers without addition of TAIC as a function of radiation dose. Irradiation under argon.  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE)



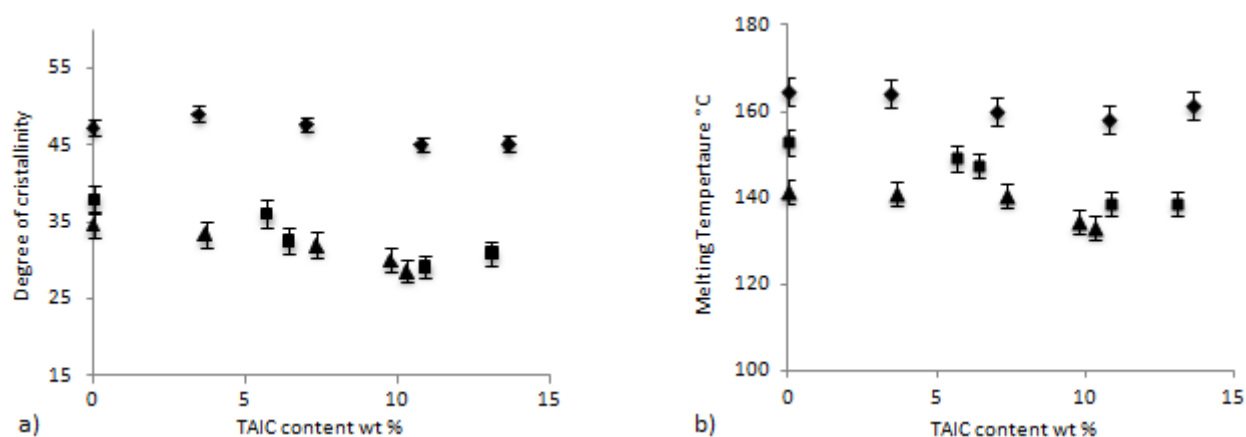
**Figure S2.** Evolution of  $G'$  modulus as a function of temperature for PVDF  $\gamma$ -irradiated under argon at different dose.



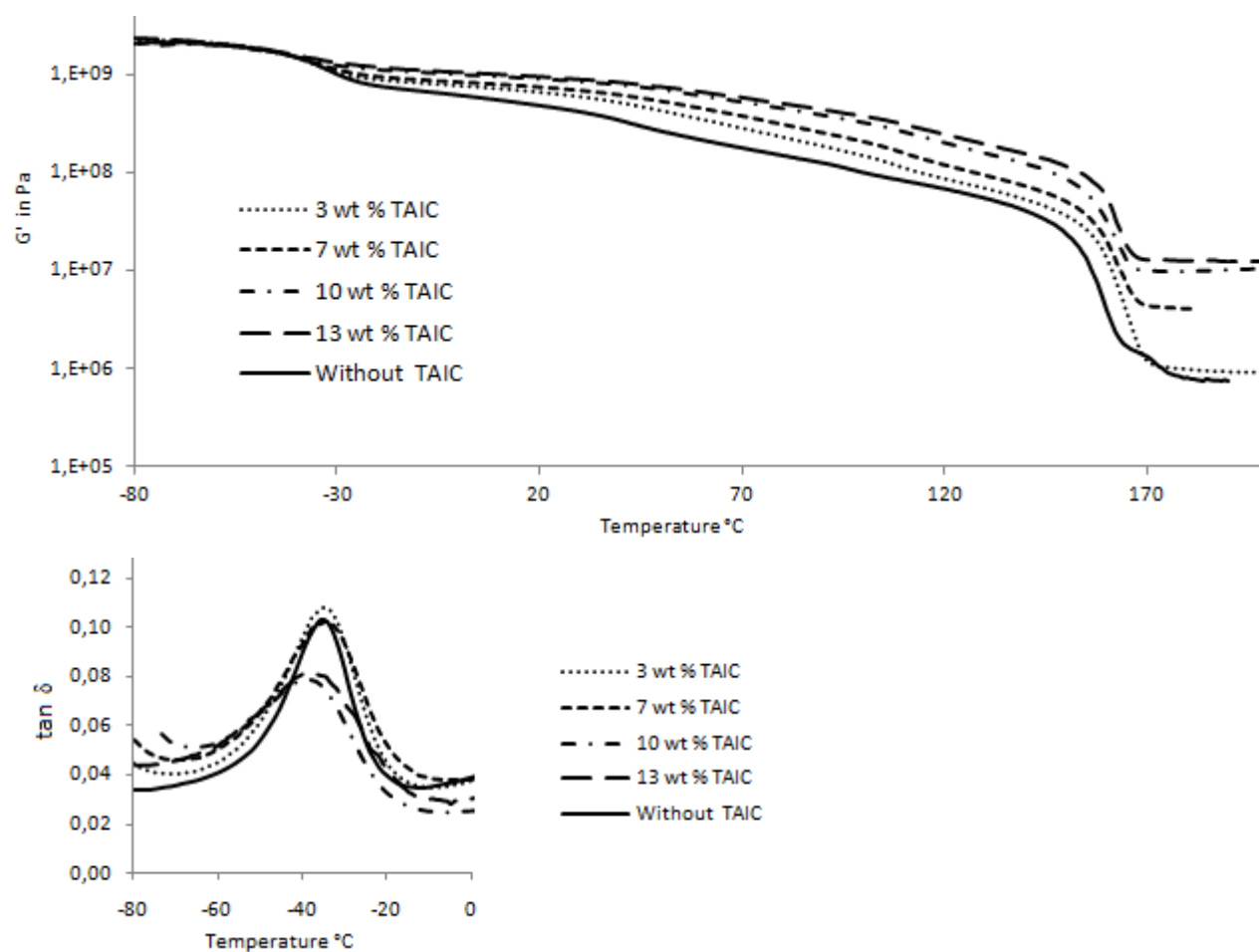
**Figure S3.** Evolution of the loss factor in the range of temperature close to the  $T_g$  for PVDF  $\gamma$ -irradiated under argon at different doses.



**Figure S4.** Evolution of a) modulus b) stress at break and c) energy to break of non-irradiated samples of  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE) as a function of TAIC content.

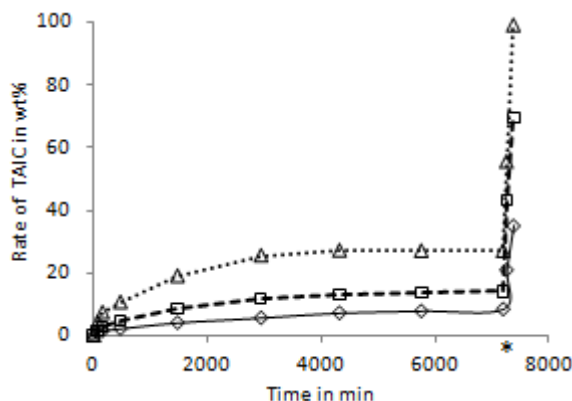


**Figure S5.** Evolution of a) degree of crystallinity b) Melting temperature of irradiated polymers at 150 kGy as a function of TAIC content. ◇ PVDF, □ p(VDF-co-HFP), △ p(VDF-co-CTFE). (from DSC, see exp. Section)



**Figure S6.** Evolution of  $G'$  modulus (a) and loss factor (b) as a function of temperature for PVDF samples with different TAIC content  $\gamma$ -irradiated at 150 kGy under argon. The results obtained for p(VDF-co-HFP) and p(VDF-co-CTFE) look similar.

The peak temperature corresponding to the glass transition is not greatly affected by the rate of TAIC but the peak intensity is lowered when TAIC concentration increases as the crosslinks prevent the relaxation of some chain segments.



**Figure S7.** Absorption of TAIC as a function of time at 120 °C and a 150 °C for the 3 polymers. The star \* indicates the time at which the temperature was changed.  $\diamond$  PVDF,  $\square$  p(VDF-co-HFP),  $\triangle$  p(VDF-co-CTFE).

This Figure illustrates the high capacity of fluoropolymers to absorb TAIC at high temperature and also the dependence of solubility with this parameter.

## II. WETTABILITY ADJUSTMENT OF PVDF SURFACES BY COMBINING $\gamma$ -RAY INDUCED GRAFTING OF 2,3,4,5,6-PENTAFLUOROSTYRENE AND SUBSEQUENT CHEMIOSELECTIVE SUBSTITUTION REACTION

A novel strategy combining 2,3,4,5,6-pentafluorostyrene (PFS) grafting and subsequently post-functionalizing by thiol/*para*-fluorine "click" type substitution is presented to impart specific surface properties to bulky PVDF samples. First, PFS was  $\gamma$ -ray grafted on the surface of PVDF, and both pre-irradiation and simultaneous irradiation techniques were attempted. The extent of modification was higher with the latter strategy, as determined by semi-quantitative ATR-FTIR analyses. Subsequent substitution was then undergone using 3-mercapto-1,2-propanediol (MPD). The chemioselective functionalization was qualitatively and semi-quantitatively evidenced by ATR-FTIR, and lead to p(VDF-g-PFS) decorated with hydroxyl groups. The resulting surface properties were investigated by wettability measurements, and both hysteresis with water and contact angle with acetonitrile evidenced the successful and appropriate modification. This strategy opens the scope of a new means to modify both swelling and surface properties of PVDF samples, as required for specific applications such as separator in electrochemical devices (supercapacitors).

### INTRODUCTION

Poly(vinylidene fluoride) PVDF is a semi-crystalline fluoropolymer combining excellent chemical and thermal resistance, essentially brought by the strong C-F bond, with high mechanical properties and a better processability than perfluoropolymers.<sup>1</sup> Thanks to its remarkable properties, PVDF has been lately used as a component of systems for electrochemical energy storage and conversion, including batteries, fuels cells and electrochemical capacitors (or supercapacitors). Although the energy storage and conversion mechanisms are different, there are similarities between these three systems, one being the use of a porous membrane referred as separator placed between the electrodes of opposite polarity.<sup>2</sup> The separator plays a key role, as its main functions are to keep the electrodes apart to prevent any electrical short circuits, and at the same time allow rapid transport of ionic charge carriers to complete the circuit. Thus, many requirements are to be fulfilled when selecting a separator, such as electronic insulation, sufficient physical strength, mechanical and



dimensional stability, uniformity in thickness and readily wettability by electrolyte.<sup>2</sup> From a chemical point of view, there are still some challenges in developing PVDF-based microporous membrane for such applications, as one need to combine antagonist properties such as a limited swelling and good wettability by a given liquid medium.<sup>4</sup>

Regarding the adjustment of surface properties, some reports nicely presented a direct initiation from the secondary fluorinated site of PVDF using atom transfer radical polymerization (ATRP) of different monomers, either on PVDF used to subsequently elaborate membranes,<sup>5,6</sup> or directly from already prepared PVDF membranes.<sup>7,8</sup> However, all these materials were dedicated to aqueous-based applications, and such strategy could hardly be undertaken if the given application uses a good solvent of PVDF such as acetonitrile. We have been interested in developing novel chemical strategies to prepare microporous membrane as separators for supercapacitors which liquid medium is acetonitrile. To promote surface modification and ensure dimensional stability at the same time, an interesting alternative resides in the use of high energy radiation.

The radiolysis mechanism of PVDF is well known: it involves the formation of radical species as a result of bond scission, which follows different paths such as crosslinking, internal rearrangements and so on. PVDF principally leads to a network when submitted to  $\gamma$ -irradiation,<sup>9-12</sup> but transients such as radicals still exist on the polymer substrate, from which the grafting of a monomer can be initiated. This process is favored by the high radiolytic yield of PVDF and have drawn much attention to produce membranes for various purposes.<sup>9,13-15</sup> This strategy allows tailoring surface properties through the appropriate choice of monomer.<sup>13</sup>

Moreover, the grafting of a monomer that would allow subsequent postpolymerization functionalization to target a specific function is a viable option to extend the usefulness of  $\gamma$ -ray induced grafting. In this context, the grafting of 2,3,4,5,6-pentafluorostyrene (PFS) onto PVDF appears as very promising: modified by another fluoropolymer, the oxidative resistance and the inherent chemical properties of the resulting grafted polymer would remain almost unchanged while a versatile modification of the grafted segments by a softer chemistry is rendered possible. Indeed, it is well known that the *para*-fluorine of the pentafluorophenyl group may undergo regioselective substitution by a panel of nucleophiles such as amines, thiols and alcohols in relatively soft conditions.<sup>16</sup> This reaction was commonly used in biochemistry to synthesize (pentafluorophenyl)porphyrin derivatives<sup>17-22</sup> or in polymer material field to design or crosslink hyperbranched fluoropolymers,<sup>23-25</sup> or to produce hybrid copolymers for self assembling systems.<sup>26</sup> More recently, the reaction found a renewed interest to functionalize poly(pentafluorostyrene) derivatives with amino-PEG or 5-aminopentanol,<sup>27</sup> thiophenol,<sup>28</sup> acetylated thioglycoside<sup>29,30</sup> and was referred as a "click chemistry" type reaction. We recently reported the synthesis of functional

PPFS derivatives by using various mercapto-alcohols; by a careful selection of the experimental conditions, the chemioselective substitution by the thiol group was demonstrated, resulting in OH-modified PPFS polymers which strongly interact with H-bond donor polymers.<sup>31</sup>

In order to prepare a PVDF-based material which present at the same time limited swelling and good wettability in acetonitrile, herein is presented a two-steps strategy combining  $\gamma$ -ray induced grafting of PFS onto PVDF bulk material and subsequent chemioselective thiol/*para*-fluorine substitution with mercapto-alcohols. Two classical  $\gamma$ -ray induced grafting strategies are compared in terms of grafting efficiency of PFS. Moreover, simple and robust characterization tools based on ATR-FTIR were developed to qualitatively and semi-quantitatively evidence both surfaces modifications on a crosslinked PVDF bulk material. Finally, wettability measurements performed on hydroxylated modified PVDF samples, in particular using acetonitrile as a probe, confirmed the benefits of such strategies in obtaining samples which swelling and surface properties are tailored.

## II.1. EXPERIMENTAL METHODS

### II.1.1. MATERIALS

2,3,4,5,6-pentafluorostyrene (PFS) (Aldrich 99%) was purified by passing over a activated aluminum oxide column prior to polymerization. K740 PVDF samples with  $M_n = 110\,000\text{ g}\cdot\text{mol}^{-1}$  were provided by Arkema (CRRA, France). 3-mercapto-1,2-propanediol (MPD) (Aldrich 95%), triethylamine ( $\text{NEt}_3$ ) (Aldrich 99.5%), fluorobenzene (Aldrich 99%) and all other chemicals were used as received. PPFS samples (with  $M_{n(\text{SEC})} = 9300\text{ g/mol}$ ,  $\text{PDI} = 1.35$ ,  $M_n (^1\text{H NMR in CD}_2\text{Cl}_2) = 8900\text{ g/mol}$ ) were synthesized according to published method.<sup>32</sup>

### II.1.2. PREPARATION AND RADIATION GRAFTING OF PVDF

PVDF rectangular specimens with a surface area of  $2\text{ cm}^2$  and a thickness of  $2\text{ mm}$  were obtained by extrusion-injection process using a twin screw DSM microcompounder with a  $100\text{ rpm}$  speed at  $200\text{ }^\circ\text{C}$ .

#### II.1.2.1. PRE-IRRADIATIVE METHOD

PVDF samples were introduced in Schlenk tubes mounted with a septum. The flask was purged and kept under argon before they were introduced in a glass bell purged with argon to avoid any contamination of the flasks by oxygen. The samples were irradiated at  $150\text{ kGy}$ , using an industrial  $^{60}\text{Co}$  gamma source (IONISOS SA, Dagneux, France) at room temperature ( $25^\circ\text{C}$ ) with dose rate of  $0.7\text{ kGy}\cdot\text{h}^{-1}$ . Then monomer (either pure or diluted solutions in fluorobenzene) was

introduced in the irradiated flask without breaking the inert atmosphere, and the mixture was allowed to react for 1 week at 50 °C.

#### II.1.2.2. SIMULTANEOUS METHOD

PVDF specimens were placed into Schlenk tubes and immersed in a grafting solution of PFS in fluorobenzene ( $0.60 \pm 0.01$ ) mol.L<sup>-1</sup>, with [VDF units]:[PFS] molar ratio maintained at  $10.0 \pm 0.1$ . Schlenk tubes were then immersed in liquid nitrogen to be vacuumed and purged with argon several times and finally kept under argon. The tubes were then placed in the glass bell under argon, and submitted to a total dose of 150 kGy at room temperature (25°C) with dose rate of 0.7 kGy.h<sup>-1</sup>. Grafted PVDF samples obtained from both methods were then exposed to THF at 60°C for 24h to extract any free PPFS polymers, and then dried under vacuum for 12h at 100°C.

#### II.1.3. SUBSEQUENT MODIFICATION OF PPFS GRAFTED INTO PVDF.

The nucleophilic aromatic substitution was performed at 50°C for 48h in 3.7 mL of THF using a [MPD]:[NEt<sub>3</sub>] molar ratio of 1:3. The concentration of MPD in THF was fixed at 2 mol.L<sup>-1</sup>, which corresponds to a large excess of MPD with respect to PFS units. Samples were then abundantly washed with a large amount of THF at 60°C for 24 h and dried under vacuum at 100 °C for 12 h.

#### II.1.4. MODIFICATION OF THE REFERENCE PPFS

In a typical synthesis, PPFS homopolymers (100 mg,  $0.52 \cdot 10^{-3}$  mol) were dissolved in 3.7 mL of THF and introduced in a flask mounted with a condenser. Triethylamine (1.581 g,  $15.46 \cdot 10^{-3}$  mol) and MPD (586 mg,  $5.15 \cdot 10^{-3}$  mol) were added, and the temperature was set at 50°C. The reaction time was defined according to the kinetic study as depicted in Figure S1. The solution was then precipitated into a cold methanol/water mixture (1/1 v/v), the solid polymer was recovered and dried under vacuum at 120°C for 12 h.

#### II.1.5. INSTRUMENTATION

FTIR spectra were recorded at room temperature on a Nicolet iS10 Thermo Scientific spectrometer in Attenuated Total Reflectance mode (ATR) with a carbon diamond crystal. Spectra were recorded from 650 to 4000 cm<sup>-1</sup> with a wavenumber resolution of 4 cm<sup>-1</sup>. 32 scans were collected for each sample. The degree of substitution of the reference PPFS used to build the

calibration curve was determined by  $^{19}\text{F}$  NMR analysis on a 400 MHz Bruker apparatus using  $d_8$ -THF as solvent.

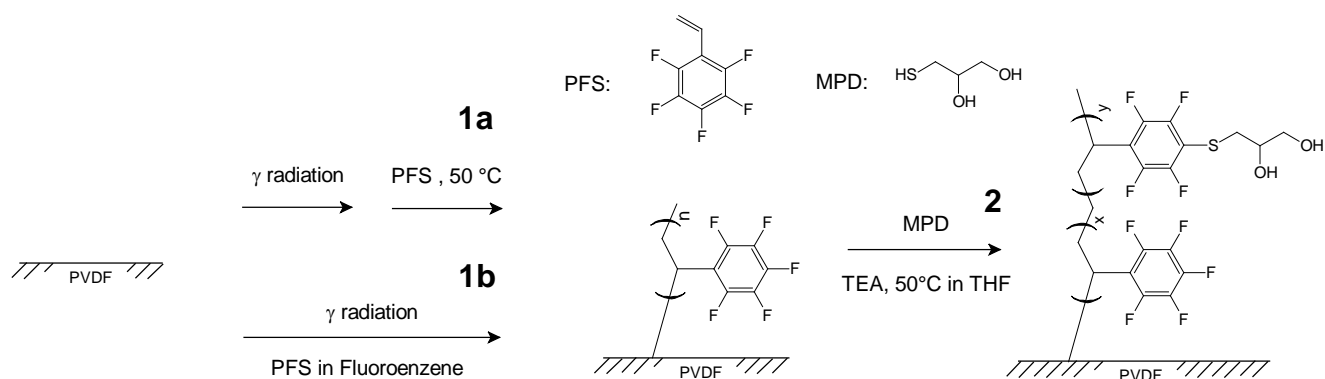
Wettability measurements were performed on a GBX device. Both advancing ( $\theta_a^w$ ) and receding ( $\theta_r^w$ ) water contact angles were measured, as well as contact angles with diiodomethane and acetonitrile.

Swelling measurements were performed with Acetonitrile. Samples of a weight about 1 g were introduced in a closeable flask. Sample weight was determined accurately ( $w_i$ ) and a large excess of solvent (60 mL) was introduced. Samples were heated at 60 °C during 48 h to allow the complete extraction of the soluble component. Swollen gels were carefully wiped with a tissue then weighted ( $w_g$ ). The solvent was then evaporated under vacuum for 24 h at 100 °C to determine the weight of dried gel ( $w_{dg}$ ). The gel content (% gel) and the solvent uptake (% sol) were calculated using the following equations:

$$\% \text{ gel} = \frac{w_{dg}}{w_i} \times 100 \quad \text{and} \quad \% \text{ sol} = \frac{w_g - w_{dg}}{w_{dg}} \times 100$$

## II.2. RESULTS AND DISCUSSION

The synthetic approach to obtain hydroxyl-modified PVDF in a two steps strategy is presented in Scheme 1. The first step consists in radiografting PFS onto the surface of PVDF bulk samples, while the second step consists in a regio- and chemioselective modification of the PPFS grafts on the *para*-position of the benzene ring by a mercapto-alcohol, namely 3-mercaptopropanediol (MPD).



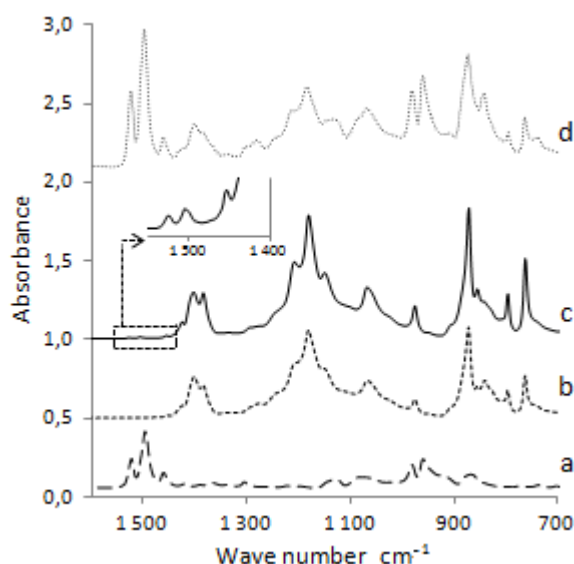
**Scheme 1.** Two-step functionalization of PVDF. Grafting of PFS onto PVDF according to pre-irradiative method (1a) and to the simultaneous method (1b). 2, subsequent modification of the grafted PPFS.

## II.2.1. GRAFTING OF PFS ONTO PVDF

### II.2.1.1 COMPARISON OF GRAFTING STRATEGY

When dealing with radiation grafting process, three main strategies can be envisioned: pre-irradiation, peroxidation or simultaneous irradiation.<sup>33</sup> Pre-irradiation is a two step strategies: the polymer is first irradiated in specific conditions (vacuum, inert gas) to generate radicals, then in a further step the irradiated polymer is treated with the monomer. Peroxidation closely resembles the first one, but irradiation is performed in aerobic conditions in order to form hydroperoxides or peroxides, which are activated in a second step, generally by heating at high temperature, to initiate the polymerization of the added monomer. Simultaneous irradiation is a one step-process, as the polymer and the monomer are irradiated simultaneously. While it might lead to high levels of homopolymer as a byproduct, this strategy not only is faster than the previous ones but also leads to higher grafting rates, by taking advantage of the continuous formation of radicals all along the irradiation process. In order to compare the efficiency of PFS grafting onto PVDF, the pre-irradiation and simultaneous strategies were investigated.

The peroxidation strategy was not considered in this work. Indeed, as the overall modification strategy is dedicated to modify microporous membrane, high thermal treatment required to generate radicals from peroxides might dramatically affect the porosity. In the past, significant research has been dedicated to the radiation grafting of vinyl monomers onto fluoropolymers substrates,<sup>15,34-39</sup> and most of these works dealt with the optimization of the grafting conditions (dose rate, dose, solvent, concentration of monomer...) to achieve high degrees of grafting. As the latter is generally determined by TGA on the modified substrate, this implicitly requires that the part of grafted polymer is important compared to the surface. In our case, as our initial motivation was to tailor surface properties, we voluntarily focused on very low grafting rates which, as a consequence, cannot be evaluated by macroscopic analyses such as TGA. Thus, more local analyses techniques such as ATR-FTIR and wettability measurements were developed. ATR-FTIR is a well-suited technique to evidence the surface modification of polymers by grafting. Figure 1 gathers the FTIR spectra for both PVDF and PPFS homopolymers. As can be seen, some absorption peaks are distinct and well-separated, and we particularly focused on the ones at  $1497\text{ cm}^{-1}$  for PPFS (ascribed to the fluorinated aromatic ring vibrations)<sup>40</sup> and at  $1180\text{ cm}^{-1}$  (ascribed to the stretching and bending modes of the  $\text{CF}_2$  groups of PVDF)<sup>41</sup> to qualitatively qualify the efficiency of PFS grafting. ATR-FTIR spectra obtained for PVDF modified according to pre-irradiation (Figure 1c) and simultaneous irradiation (Figure 1d) are also provided.



**Figure 1.** ATR-FTIR spectra of PPFS (a) and PVDF (b) homopolymers, p(VDF-g-PFS) obtained from pre-irradiation (c) and simultaneous radiation method (d).

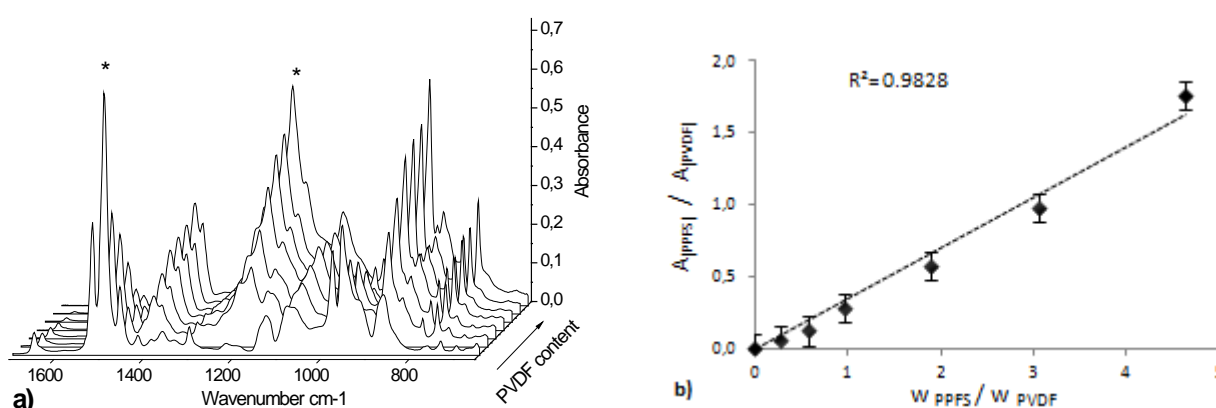
Regarding pre-irradiation strategy, PVDF was priority  $\gamma$ -irradiated at 150 kGy; the lowest dose for which the concentration of radicals was maximal in our irradiation conditions.<sup>42</sup> By the way, PVDF is partially crosslinked when exposed at this dose, the gel content and the solvent uptake obtained in DMF being 72 wt% and 1400 wt%, respectively.<sup>43</sup> The value of solvent uptake obtained in acetonitrile, a common solvent used in electrolyte, is only of 18 wt% while the apparent gel fraction is 100 wt%. Once irradiated, PVDF was exposed to different solutions of PFS; almost no grafting was evidenced by ATR-FTIR even after a very long time. A small contribution of PFS was visible only when pure PFS was considered (Figure 1c), attesting that the grafting is poorly effective in this condition. This can be explained by the relatively low concentration of radicals that are accessible on the surface, and by the low swelling of irradiated PVDF by PFS. Considering Chapiro's *Grafting Front Mechanism*, which turned out to apply to most studies on the grafting of vinyl monomers into fluoropolymers<sup>34,44-48</sup> grafting initially takes place at the substrate surface when the polymer matrix scarcely swells in the given liquid medium, which is the case when pure PFS is used (the swelling of irradiated PVDF in PFS is around 0.3 wt.%). In a previous report, we determined by ESR spectroscopy that the concentration of radicals remaining in PVDF irradiated at 150 kGy is  $5.21 \cdot 10^{18} \text{ spin.g}^{-1}$  (*i.e.* 1 radical per 1800 repetition units).<sup>49</sup> As  $\gamma$ -ray is a highly penetrating radiation, these radicals are produced in the overall bulk PVDF sample and thus only a few part of these radicals are located on the surface.

This low modification rate is circumvented when the simultaneous irradiation strategy is applied. PVDF was irradiated at 150 kGy, with a dose rate of  $0.7 \text{ kGy.h}^{-1}$  in the presence of PFS monomer diluted in fluorobenzene (10 wt%). These experimental conditions are anticipated to favor grafting, as it is generally well-accepted that low dose rate slows down the decay of radicals by

recombination, then increasing the ability of radicals for grafting reactions.<sup>39</sup> Moreover, grafted polymer chains are also subjected to slower termination and/or degradation at low dose rate.<sup>38, 50</sup> Fluorobenzene was selected for many reasons: (i) it is a very good solvent for PPFS,<sup>32</sup> a criterion which turns out to be critical in favoring grafting;<sup>34, 38, 51</sup> (ii) the chain transfer constant of PFS toward fluorobenzene is very low ( $0.117 \times 10^{-4}$ ),<sup>52</sup> which also promotes grafting.<sup>44</sup> As can be seen on Figure 1d, very intense absorption peaks related to PPFS are visible on the ATR-FTIR spectrum, attesting for an efficient and large grafting on the upper thickness of the PVDF substrate.

## II.2.1.2 CHARACTERIZATION OF THE GRAFTING EFFICIENCY

In order to provide semi-quantitative data upon PFS grafting, a calibration line was built-up, using blends of PVDF and PPFS homopolymers varying in their composition. Their ATR-FTIR spectra were recorded, and as expected, the richer the mixture in PPFS, the higher the peaks at  $1497 \text{ cm}^{-1}$  compared to the ones of PVDF (Figure 2a). The corresponding calibration line (Figure 2b) representing the ratio of ATR-FTIR intensity peaks  $I_{(1496\text{cm}^{-1}, \text{PFS})} / I_{(1180\text{cm}^{-1}, \text{PVDF})}$  vs composition is perfectly linear on a composition range up to 83 wt.% in PPFS, which evidences that the composition can be determined on the probed thickness, around  $\sim 2 \mu\text{m}$ . This plot was applied to determine the composition of p(VDF-g-PFS) samples prepared by  $\gamma$ -ray grafting. In the case of the pre-irradiation strategy, a composition of 4.7 wt.% (corresponding to 1.6 mol.%) in PPFS was revealed, while a composition of 83 wt% of PPFS (around 60 mol.%) was found in the case of simultaneous strategy. As anticipated, the grafting is all the more facilitated that radicals are continuously generated along the irradiation process. The acetonitrile uptake through swelling measurements was also determined for the latter sample, and was found to be around 15 wt% while the gel content reached 97 wt%. This value, which is in the same range as the one determined for pre-irradiation strategy, confirms that  $\gamma$ -ray irradiation can promote both cross-linking and grafting whatever the undertaken strategy is.



**Figure 2.** a) ATR-FTIR spectra of different mixtures of PVDF and PPFS. b)  $I_{(1496\text{cm}^{-1}, \text{PFS})} / I_{(1180\text{cm}^{-1}, \text{PVDF})}$  peak intensities ratio vs weight composition.



Another well-adapted technique to evidence surface grafting is wettability measurements, which probe the roughness, chemical heterogeneity or swelling properties of the upper nanometers of a given flat surface. Table 1 gathers the contact angle values obtained with water (advancing and receding values) and diiodomethane for PPFS, PVDF, irradiated PVDF after washing and p(VDF-g-PFS). As expected for fluoropolymers, PVDF and PPFS present water contact angles higher than  $90^\circ$ , attesting for their hydrophobic character. The values obtained for a PVDF bulk sample submitted to THF are also presented. This sample is taken as a reference for comparison with the p(VDF-g-PFS) sample, as extraction with THF was applied to thoroughly extract the non-grafted PPFS chains which might be embedded in the grafted layer. By the way, such a treatment can also induce some rearrangements of the surface and thus affect the contact-angle values. The water contact angle value is slightly higher ( $\theta_{\text{water}} = 100 \pm 3^\circ$ ) when compared to untreated PVDF, attesting that the roughness has slightly increased due to the exposure to solvent. This is confirmed by the increased water contact angle hysteresis. When p(VDF-g-PFS) prepared by simultaneous irradiation was probed, a slight increase in water contact angle is observed, associated with a slightly higher water contact angle hysteresis. All these differences are ascribed to an overall increase of roughness due to the presence of PPFS grafts on the probed thickness. As a conclusion, this technique also confirms the presence of PPFS on the upper nanometric layer of the modified PVDF sample.

**Table 1.** Surface properties of PVDF substrates after each modification.

	$\theta_{\text{advancing}}^{\text{water}}$	$\theta_{\text{receding}}^{\text{water}}$	$\Delta\theta^{\text{water}}$	$\theta_{\text{advancing}}^{\text{diiodomethane}}$
PPFS <sup>a</sup>	$101 \pm 5$	$96 \pm 6$	$5 \pm 11$	$65 \pm 7$
PVDF <sup>b</sup>	$90 \pm 5$	$64 \pm 5$	$26 \pm 10$	$64 \pm 5$
PVDF <sup>b</sup> (washed)	$100 \pm 3$	$43 \pm 10$	$57 \pm 13$	$51 \pm 7$
p(VDF-g-PFS)	$116 \pm 3$	$60 \pm 8$	$54 \pm 11$	$60 \pm 3$
p(VDF-g-PFS-g-MPD)	$100 \pm 7$	$73 \pm 10$	$27 \pm 17$	$55 \pm 3$

<sup>a</sup> Pellets

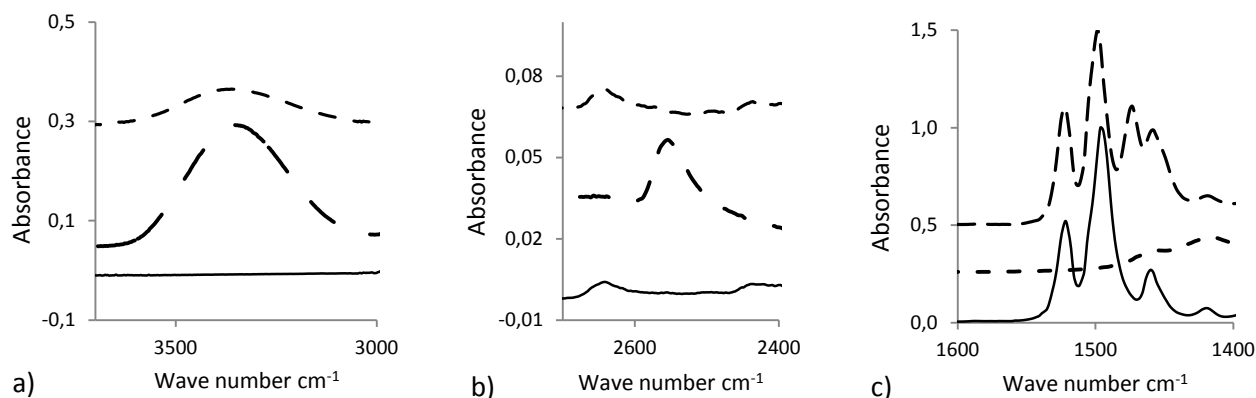
<sup>b</sup> PVDF sample obtained by an extrusion-injection process.



## II.2.2. SUBSEQUENT MODIFICATION OF THE p(VDF-G-PFS)

### II.2.2.1. THIOL PARA-F SUBSTITUTION REACTION

As the PVDF sample modified by simultaneous irradiation strategy present a higher relative content in PPFS than the pre-irradiated one, only the former was dedicated to subsequent modification by mercapto-alcohol MPD. We previously reported the successful modification of PPFS homopolymers with various mercapto-alcohols; by using a mild base such as triethylamine, the selective deprotonation of thiol group was verified, allowing a chemoselective modification on the *para*-position of the PPFS aromatic ring and thus leading to hydroxy-modified PPFS.<sup>31</sup> A similar strategy was applied here to the modification of p(VDF-g-PFS) samples. The reaction was performed in THF at 50 °C during 48 h, using a [MPD] : [NEt<sub>3</sub>] molar ratio of 1 : 3. While the use of DMF has been reported in the literature for such type of thiol-PPFS reaction,<sup>17, 29</sup> this solvent is not appropriate in modifying PPFS-modified PVDF samples as it is a very good solvent of PVDF and then would lead to a partial dissolution and/or swelling of our irradiated sample. Moreover, at this temperature, no modification of PVDF such as partial dissolution in THF or extra cross-linking promoted by triethylamine was observed, as much higher temperature is needed to promote crosslinking of PVDF with tertiary amines.<sup>53</sup> The concentration of MPD in THF was fixed to 2 mol.L<sup>-1</sup>, corresponding to a large excess of thiol with respect to PFS units. Such an excess is all the more favorable as it improves both the kinetics and the extent of the substitution reaction (Figure S1). After the reaction, the substrate was thoroughly washed with THF (see experimental section) to remove excess of reactants, and finally dried under vacuum at 100 °C during 12 h. The close-ups of the ATR-FTIR spectrum in relevant wavenumber domains are presented in Figure 3, altogether with the ones corresponding to MPD and PPFS.



**Figure 3.** FTIR spectra of — PPFS, MPD ..... and p(PFS-g-MPD) (DS = 28.5%) ----- in the area of: a) O-H, b) S-H and c) fluorinated ring vibration.

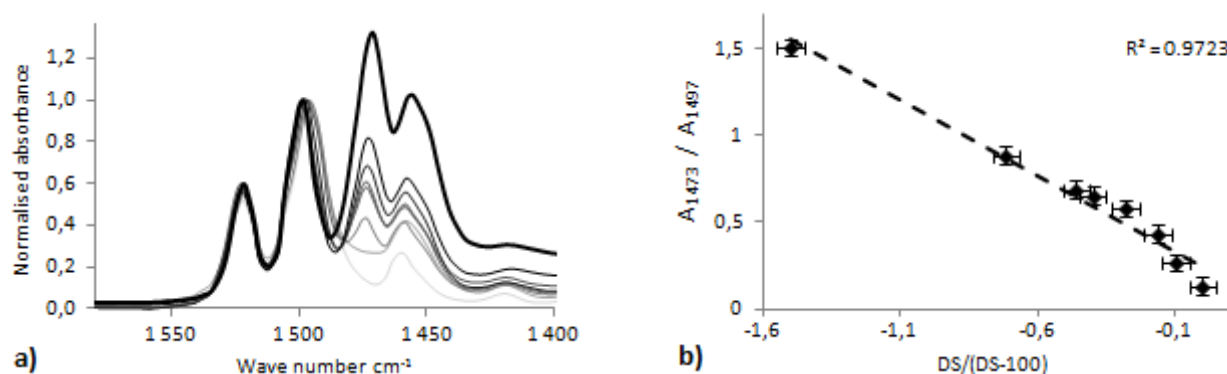
As expected, a large band centered at  $3375\text{ cm}^{-1}$  corresponding to (self-associated) OH groups is visible, and the absence of the characteristic band ascribed to the SH group at  $2556\text{ cm}^{-1}$  is also noticed. This confirms the chemoselective modification of PPFS ring.

#### II.2.2.2. EVALUATION OF DEGREE OF SUBSTITUTION OF THE GRAFTED PFS

When PPFS is modified, a new band appears at  $1473\text{ cm}^{-1}$  in the range of the fluorinated aromatic ring vibrations (Figure. 3 (c)). As this peak is absent from the FTIR spectra of PPFS or any other species, it must be related to the fluorinated aromatic ring vibrations of the MPD modified PFS units. This peak has not been reported so far for *para*-substituted PPFS. To confirm this assumption, different PPFS-g-MPD samples with various degree of substitution (DS) were synthesized, and their ATR-FTIR spectrum was collected. The modification rate was achieved according to our previously reported study,<sup>31</sup> and the DS was calculated by  $^{19}\text{F}$  NMR, thanks to the integral of the *ortho*'-fluorine peak ascribed to modified PPFS (at  $\delta = -133\text{ ppm}$ ) compared to the integral of (*ortho*- + *meta*'-fluorines) (at  $\delta = -143\text{ ppm}$ ), related to the overall (modified + unmodified) PFS units (see Figure S2). Then, p(PFS-g-MPD) samples with DS of 9, 14, 21.9, 28.6, 31.5, 41.7 and 60 % were obtained. Figure (4a) presents the ATR-FTIR spectra of these samples, which have been normalized to the vibration band at  $1497\text{ cm}^{-1}$ . As can be seen, a relative increase of the vibration band at  $1473\text{ cm}^{-1}$  is noticed while the DS increases, which tends to confirm our initial assumption. Moreover, taking into account Beer-Lambert law, the ratio between the peak intensity of modified PFS units and the one of non-modified PFS units can be related to DS according to:

$$\frac{A_{sub}}{A_{not\ sub}} = k \cdot \frac{DS}{DS - 100}$$

(The assumptions leading to this relationship are presented in SI). The corresponding evolution is presented in Figure 4b. A fairly linear variation with an acceptable regression factor is revealed, proving that the DS of PPFS units can be estimated by FTIR by comparing the appropriate bands intensity.



**Figure 4.** a) FT-IR spectra of reference PPFS modified with MPD (Intensity normalized by the intensity of the band at  $1497\text{ cm}^{-1}$ ). From light grey to black: unmodified PPFS, p(PFS-g-MPD) with DS of 9, 14, 21.9, 28.6, 31.5, 41.7, and 60 %. b) peaks intensity ratio of peaks at  $1473$  (modified PFS) to  $1497\text{ cm}^{-1}$  (unmodified PFS) vs  $\text{DS}/(\text{DS} - 100)$ .

This calibration line allows determining the extent of MPD grafting onto p(VDF-g-PFS), as the bands at  $1473$  and  $1497\text{ cm}^{-1}$  are sufficiently well separated from any signal related to PVDF. In the case discussed above (Figure 2d), the estimated DS is around  $(31 \pm 5)\%$  in the layer probed by ATR FTIR. Another evidence of the effective modification is seen through wettability measurements (Table 1). The water contact angle has slightly decreased ( $100 \pm 7^\circ$ ) while the corresponding hysteresis has increased compared to the reference p(VDF-g-PFS) sample; the extreme surface of substrate globally remains hydrophobic, but the introduction of hydroxyl groups has significantly affected the receding water contact angle, which is influenced by adhesion between hydroxyl groups on the surface and water. Moreover, the most relevant result is obtained with acetonitrile as the probe liquid.



**Figure 5.** Pictures of acetonitrile droplet deposited on PVDF washed with THF (a); p(VDF-g-PFS) (b), and p(VDF-g-PFS) subsequently modified by MPD (c).

As can be seen in Figure 5, when acetonitrile is deposited onto the reference PVDF and p(VDF-g-PFS), distinguishable drops with low contact angle are obtained, as a result of good solvent/substrate chemical affinity. It is important to remind that acetonitrile is a solvent of PVDF; a first advantage in  $\gamma$ -ray irradiating PVDF resides in the cross-linking of PVDF whatever the grafting strategy, thus avoiding the complete dissolution on the one hand, and leading to a limited swelling

on the other hand. Moreover, when the subsequent modification with MPD is achieved, the drop completely spreads out on the surface, such as no angle can be measured anymore. This phenomenon is particularly suitable for membrane applications.<sup>4, 54</sup> In our opinion, the enhanced wettability of the MPD modified substrate with the target liquid medium is essentially due to hydrogen bond interactions formed between hydroxyl groups of MPD as H-bond donor and the lone pair of electrons of nitrogen in acetonitrile as H-bond acceptor.<sup>31</sup>

## CONCLUSION

A novel 2-steps strategy based on  $\gamma$ -radiation of (2,3,4,5,6-pentafluorostyrene) onto PVDF with a subsequent chemioselective functionalization using mercapto-alcohol was presented. Pre-irradiation and simultaneous irradiation strategies were evaluated, and the latter turned out to be much more effective as determined by semi-quantitative ATR-FTIR analyses. The *para*-substitution reaction was also confirmed by ATR-FTIR, and the introduction of hydroxyl groups largely improved the wettability with acetonitrile, as the liquid totally spreads out on the surface. As the subsequent modification of PFS units with nucleophiles such as thio- or amino-derivatives is possible, the modification of polymeric substrate by PFS appears as very promising means to build-up a platform of novel materials with adjustable properties through the careful selection of nucleophile.

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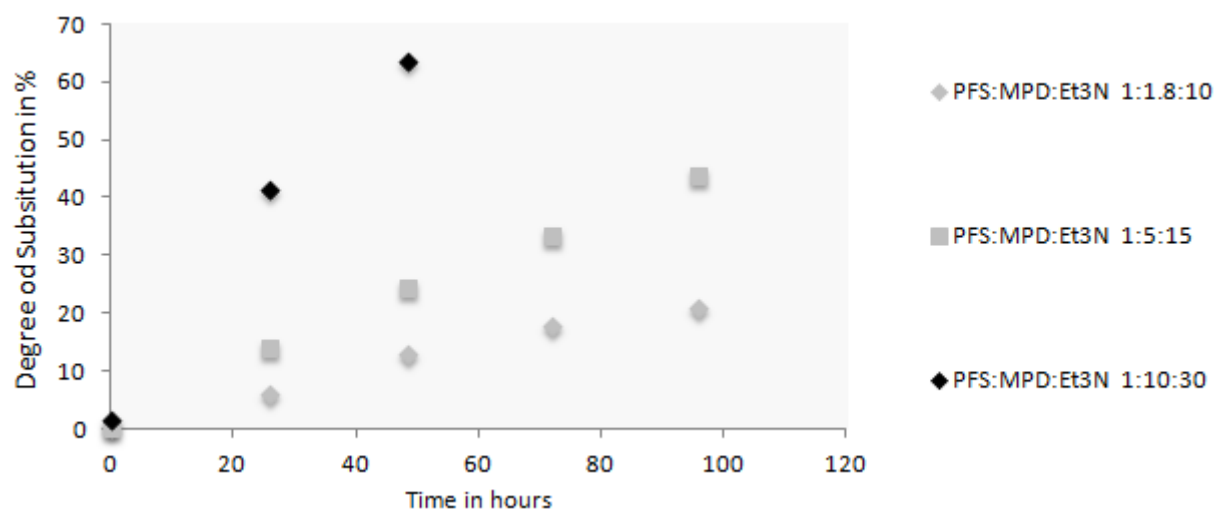


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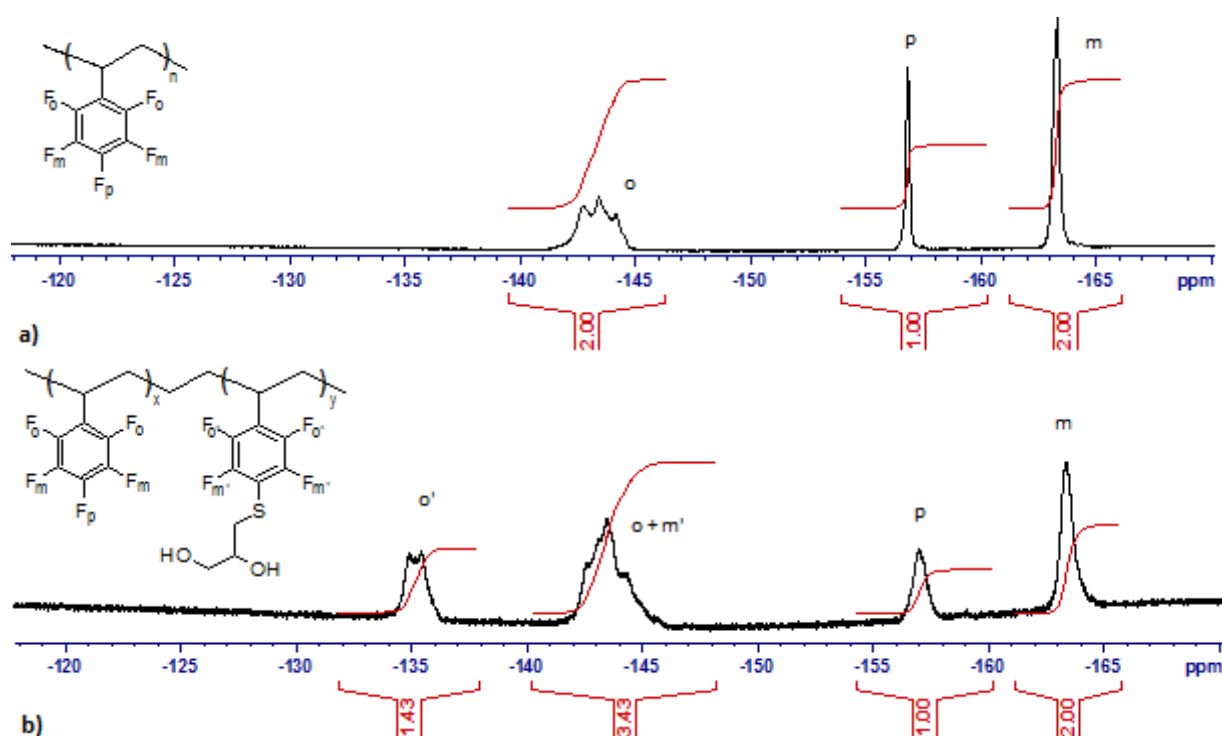
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## SUPPORTING INFORMATION



**Figure S1.** Degree of substitution of reference PPFS as a function of reaction time for different reagent ratios. Solvent: THF; temperature: 50 °C, [PPFS]: 20 mg.mL<sup>-1</sup> of mixture. DS determined by <sup>19</sup>F NMR.



**Figure S2.** <sup>19</sup>F NMR spectra of PPFS and p(PFS-g-MPD) with a DS of 41.7 %.

**Assumptions made to establish the calibration curve of DS.**

*Beer Lambert Law :* 
$$A_v = \varepsilon_v \cdot C \cdot l \quad (1)$$

so 
$$C = \frac{A_v}{\varepsilon_v \cdot l} \quad (2)$$

With  $A_v$  the absorbance at the wavenumber  $v$ ,  $\varepsilon_v$  the molar absorptivity,  $C$  the concentration and  $l$  the thickness probed.

Expression of the Degree of Substitution: 
$$DS = \frac{n_{sub}}{n_{sub} + n_{not\ sub}} = \frac{C_{sub}}{C_{sub} + C_{not\ sub}} \quad (3)$$

By combining (2) and (3): 
$$DS = \frac{A_{sub}/\varepsilon_{sub} \cdot l}{A_{sub}/\varepsilon_{sub} \cdot l + A_{not\ sub}/\varepsilon_{not\ sub} \cdot l} \quad (4)$$

By reorganizing (4): 
$$DS = \frac{A_{sub}}{A_{sub} + A_{not\ sub} \cdot \frac{\varepsilon_{sub}}{\varepsilon_{not\ sub}}} \quad (5)$$

By factorizing and reorganizing (5): 
$$\frac{A_{sub}}{A_{not\ sub}} = \frac{-\varepsilon_{sub} \cdot DS}{\varepsilon_{not\ sub} \cdot (DS - 1)} = k \cdot \frac{DS}{DS - 1} \quad (6)$$

If DS is expressed in %: 
$$\frac{A_{sub}}{A_{not\ sub}} = k \cdot \frac{DS}{DS - 100} \quad (7)$$

With the peak at  $1473\text{ cm}^{-1}$  and  $1497\text{ cm}^{-1}$  corresponding to the substituted and non substituted fluorinated ring respectively, the relation becomes:

$$\frac{A_{1473}}{A_{1497}} = k \cdot \frac{DS}{DS - 100} \quad (8)$$

## CONCLUSION DU CHAPITRE

La première section avait pour objectif principal de quantifier l'impact de la radiolyse de trois matrices polymères sur leurs propriétés macroscopiques. La particularité de cette étude résidait dans la comparaison de trois grades polymères PVDF, p(VDF-co-HFP) et p(VDF-co-CTFE) dans les mêmes conditions d'irradiation et dans la caractérisation du réseau formé selon deux méthodes complémentaires.

L'irradiation des trois matrices sans le concours d'agent de réticulation conduit à leur réticulation partielle. Les propriétés mécaniques ne sont pas dégradées sur le domaine de dose étudié. Une amélioration de la résistance et de la rigidité, plus marquée dans le cas des copolymères p(VDF-co-HFP) et p(VDF-co-CTFE) est d'ailleurs observée et est principalement due à la formation du réseau. La densité de réticulation dépend quant à elle de la nature du comonomère et de la dose. Ainsi, le comonomère HFP favorise la réticulation de la matrice tandis que le comonomère CTFE, plus sensible au rayonnement limite la formation du réseau. Bien que la densité de réticulation des trois polymères soit augmentée lorsque la dose augmente, le réseau formé reste trop lâche pour l'application envisagée. En effet, le gonflement excessif et la réticulation partielle limite l'utilisation de ces trois grades en tant que tels comme polymère de base pour réaliser des membranes séparatrices dans les supercapacités.

Lorsque le TAIC est ajouté, les propriétés des trois grades polymères sont essentiellement fonction de la concentration en agent réticulant. Avant irradiation, l'incorporation du co-agent de réticulation a un effet plastifiant qui améliore sensiblement la processabilité des trois polymères. Pour une dose d'irradiation de 150 kGy, les propriétés mécaniques des copolymères, initialement nettement en dessous de celles de l'homopolymère, sont relevées au niveau de celles du PVDF lorsque le pourcentage de co-agent atteint 10 %. Pour le même taux de TAIC et quelque soit la nature de la matrice polymère, le matériau devient insoluble et le gonflement est limité à quelques pourcents. Les effets combinés du TAIC et du rayonnement deviennent optimaux pour une concentration en agent de réticulation de 10 % massiques et une dose de 150 kGy.

Par ailleurs, l'utilisation du TAIC présente un intérêt singulier. Il permet en effet d'augmenter la quantité de radicaux résiduels issus de l'irradiation. (Annexe 3). Le réseau de chaînes macromoléculaires étant particulièrement dense, la mobilité des chaînes est fortement réduite et permet de limiter la recombinaison des radicaux. Le nombre d'espèces réactives susceptibles d'amorcer des réactions de greffage suivant une chimie radicalaire est de ce fait augmenté.

Enfin, la possibilité de s'affranchir des conditions contraignantes d'irradiation sous atmosphère inerte a été évaluée (Annexe 4). Si nous pouvions penser que la présence d'oxygène lors du processus d'irradiation favoriserait les phénomènes de dégradation en raison des processus radicalaires impliqués, l'influence de l'atmosphère sur les propriétés macroscopiques est en fait peu marquée et rend possible l'irradiation sous air.

La seconde section se consacrait à la modulation des propriétés de surface du PVDF par un procédé de radiogreffage. L'étude se focalisait seulement sur la matrice PVDF. L'originalité de la stratégie mise en œuvre réside dans le choix du monomère à greffer, le 2,3,4,5,6-pentafluorostyrène (PFS), qui n'altère pas la résistance chimique du PVDF tout en permettant sa modification ultérieure par une chimie relativement douce et chimiosélective. La difficulté principale était de pouvoir quantifier le taux de PFS greffé, le PFS et le PVDF étant tout deux fluorés et le PVDF devenant de plus insoluble lors de l'irradiation.

La première partie visait à déterminer les possibilités de radiogreffer le PFS sur le PVDF, selon les stratégies dite par "pré-irradiation" ou par "irradiation simultanée" sous atmosphère inerte, et de mettre en place une méthode de caractérisation pour évaluer et quantifier l'efficacité du greffage. La méthode par pré-irradiation ne permettant pas d'avoir une quantité suffisante de radicaux accessibles en surface du PVDF pour conduire à un taux de greffage élevé, la stratégie de greffage par irradiation simultanée est la plus adaptée dans les conditions évaluées. La quantification du rendement de greffage a été rendue possible par l'utilisation de la spectrométrie infrarouge en mode ATR qui est une méthode robuste, rapide et simple à mettre en œuvre. Ainsi, un taux de greffage de 60 % molaire a pu être déterminé dans la couche de polymère sondée, ce qui représente une base solide pour la mise en évidence de l'étape de post-modification.

La seconde partie a été l'occasion de démontrer la possibilité de post-modifier les greffons de PPFS par une chimie plus conventionnelle consistant en la substitution nucléophile du fluor en position *para* du cycle aromatique pentafluoré par un thiol  $\omega$ -fonctionnalisé : le mercaptopropanediol (MPD). Les conditions expérimentales optimales, déterminées à partir d'un PPFS modèle, ont été transposées avec succès à la modification des greffons portés par le substrat PVDF radioréticulé. La détermination de l'efficacité de la réaction de modification, difficile compte tenue de la quantité que représentent les greffons de PPFS sur le substrat massique de PVDF, a pu être réalisée avec le concours de la spectrométrie infra rouge en mode ATR. Le degré de substitution des greffons de PPFS a ainsi pu être estimé avec une précision très acceptable à  $(31 \pm 5) \%$ . Malgré cette valeur qui peut paraître faible, d'excellentes interactions avec l'acétonitrile, solvant utilisé dans l'application supercapacité, sont obtenues. La mouillabilité a pu être ainsi améliorée tout en limitant le gonflement du substrat PVDF.

