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Account

Suitable radicals and monomers to obtain innovative fluorinated polymers based on vinylidene fluoride and their applications

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Abstract. Thanks to their exceptionally useful properties, fluoropolymers are irreplaceable materials involved in many High-Tech applications, such as aerospace, automotive, internet of things, optics and electronic industries. They are usually synthesized by radical (co)polymerization of fluoroalkenes under high pressure. While many radical initiators have been used, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) releases a trifluoromethyl radical, as well as sodium trifluoromethyl sulfinate, initiating the homopolymerization of vinylidene fluoride (VDF) or the copolymerization of VDF with a wide range of fluoroolefins. Among the latter, functional 2-trifluoromethacrylates (MAF-funcs) have shown characteristics leading to various materials such as anticorrosion coatings, gel polymer electrolytes for Lithium-ion batteries, and polymer exchange membranes for fuel cell. Finally, facing per- and polyfluoroalkyl substances (PFAS) issues, mineralizations of polyvinylidene fluoride (PVDF) and other VDF-containing copolymers were recently studied in subcritical water to generate fluoride anions, as an original source of CaF₂, thus closing the loop of the fluorine chemistry.

Keywords. 2-trifluoromethacrylic acid, Batteries, Fluoropolymers, Radical polymerization, Trifluoromethyl radical, Vinylidene fluoride.

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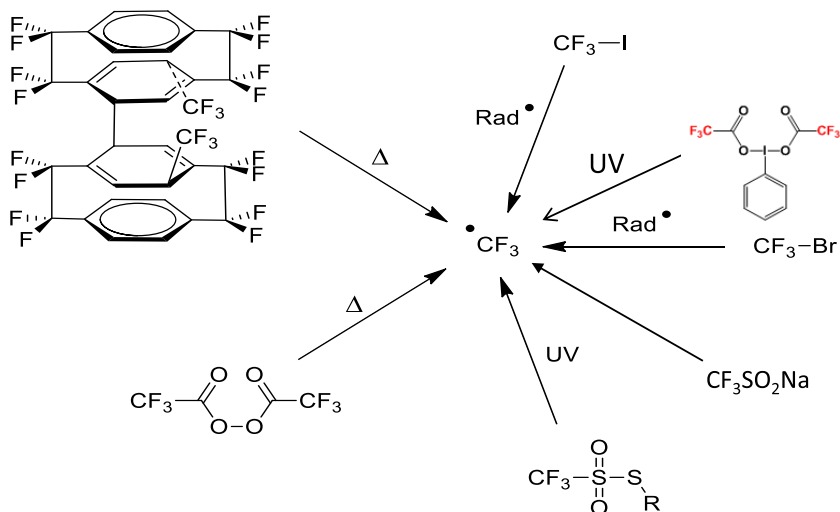
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1. Introduction

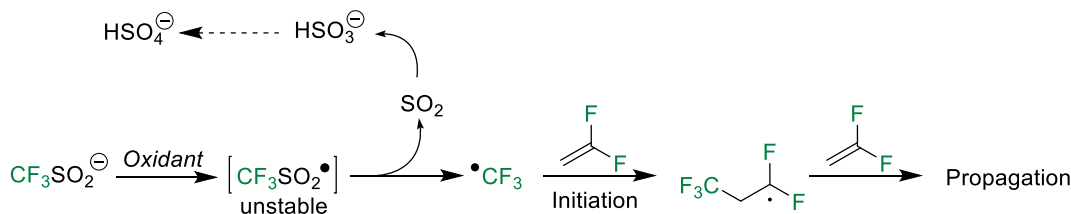
Fluoropolymers are niche macromolecules regarded as irreplaceable materials, endowed with exceptional chemical, thermal, electrical, optical, and UV resistance properties. Hence, they have found many applications in high-tech domains, such as aerospace, automotive, internet of things, optics and electronic industries [1–6]. Many specific items such as high performance elastomers, stable cables in photonics (core and cladding in optical fibers), chemically

resistant membranes for desalination or in ion exchange for fuel cells, gaskets, binders for batteries in lithium (or sodium) ion batteries, lubricants for wind mills, for O-rings and diaphragms, protective paints, coatings and backsheets for photovoltaic panels [1–6]. The aims of this mini-review are: (i) elucidating efficient radicals can be used to initiate (co)polymerization of one of the most manufactured monomer, vinylidene fluoride (VDF), (ii) proposing a comonomer as an efficient VDF partner and (iii) presenting applications expected from the resulting copolymers.

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Scheme 1. Non-exhaustive strategies to generate a trifluoromethyl radical.



Scheme 2. Mechanism of oxidation of trifluoromethyl sulfinite, leading to the generation of $\bullet\text{CF}_3$ radicals [7].

2. Use of fluorinated radicals to initiate the polymerization of fluoroolefins

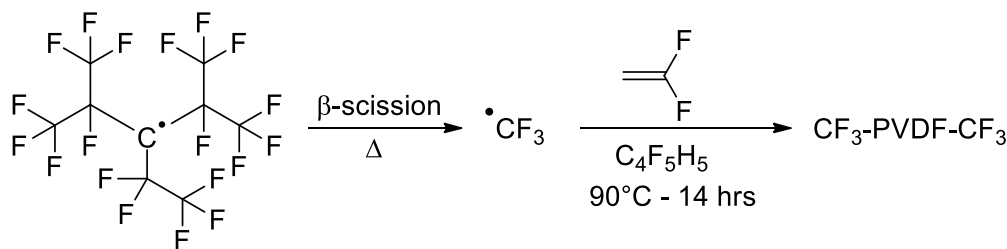
Fluoropolymers are classically prepared by radical (co)polymerization of fluoroalkenes under high pressure [1–6]. While many radical initiators have been utilized [8], fluorinated ones have already demonstrated their high efficiency to initiate such a reaction. A distinct example is the trifluoromethyl radical which can be released from various reactants (Scheme 1). This halogenated radical and its addition to fluoroalkenes was comprehensively studied by Tedder and Walton [9].

Among reactants, trifluoromethyl sulfinite ($\text{CF}_3\text{SO}_2\text{Na}$) enables generation of $\bullet\text{CF}_3$ radical in the presence of an oxidant (Scheme 2) but has scarcely been used to initiate the radical polymerization of fluoroolefins [7]. Typically, in aqueous polymerization processes, persulfates are suitably used as ox-

dants to favor the (co)polymerization(s) of VDF with hexafluoropropylene (HFP) and/or perfluoromethyl vinyl ether (PMVE).

One of the main insights gleaned from this strategy is that the resulting fluoropolymers (e.g., PVDF [7]) displays a higher thermal stability than those synthesized from conventional persulfates (Figure 1) since CF_3 end group slows down the “unzipping” depolymerization of such fluoropolymers.

As displayed in Scheme 1, various fluorinated reactants can release trifluoromethyl radical, which can also be generated at $T > 80^\circ\text{C}$ from perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) at stable room temperature (Scheme 3) [10,11], or from by using CF_3I as a chain transfer agent involved either in telomerization [12] or in iodine transfer (co)polymerization of fluoroolefins [13]. This strategy was also extended to



Scheme 3. Perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical (PPFR) generates a trifluoromethyl radical capable of initiating radical polymerization of VDF [10,11].

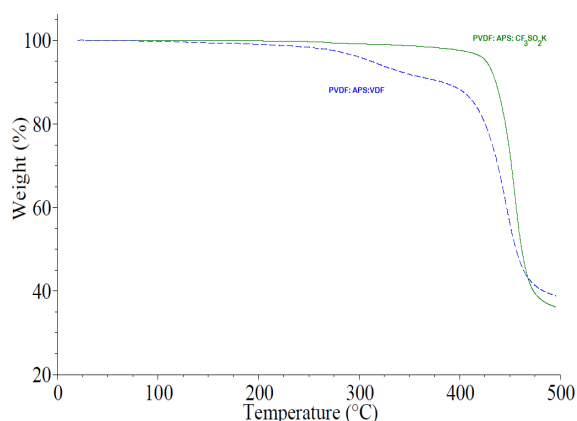


Figure 1. TGA thermograms of PVDF achieved in various initiations: ammonium persulfate (APS only, dotted line) and potassium trifluorosulfate with $\text{CF}_3\text{SO}_2\text{K}$: APS (0.9: 1.0), full line) under nitrogen (reproduced with permission from *Amer. Chem. Soc.* [7]).

copolymerization of VDF with a wide range of fluoroolefins (Scheme 4) [14].

Following these findings, the simultaneous use of PPRF and iodinated chain transfer agents (CTAs) can enable the obtaining of ω -iodo and telechelic diiodo vinylidene fluoride (VDF)-based (co)polymers [15–17] (Scheme 5). Different CTAs, such as trifluoroiodomethane and 1,4-diiodoperfluorobutane, were used with/without *tert*-butyl 2-trifluoromethacrylate (MAF-TBE). All of the obtained (co)polymers were characterized by ^1H and ^{19}F NMR spectroscopies and their thermal properties were assessed.

A mechanistic investigation of these reactions evidenced the competitive presence of CF_3 end group

in CF_3 -PVDF-I originating from the CTA and showed a negligible amount of CF_3 -PVDF oligomer dead chains produced by the direct initiation from $\cdot\text{CF}_3$ radical (released by PPRF) onto VDF. Very low chain defects of chaining (i.e., reversed $-\text{CH}_2\text{CF}_2-\text{CF}_2\text{CH}_2-$ and $-\text{CF}_2\text{CH}_2-\text{CH}_2\text{CF}_2-$ in VDF-VDF dyads, even the absence of latter types) led to high melting points (161–173 °C) of the resulting polymers [13].

3. Radical copolymerization of vinylidene fluoride (VDF) with 2-trifluoromethacrylates

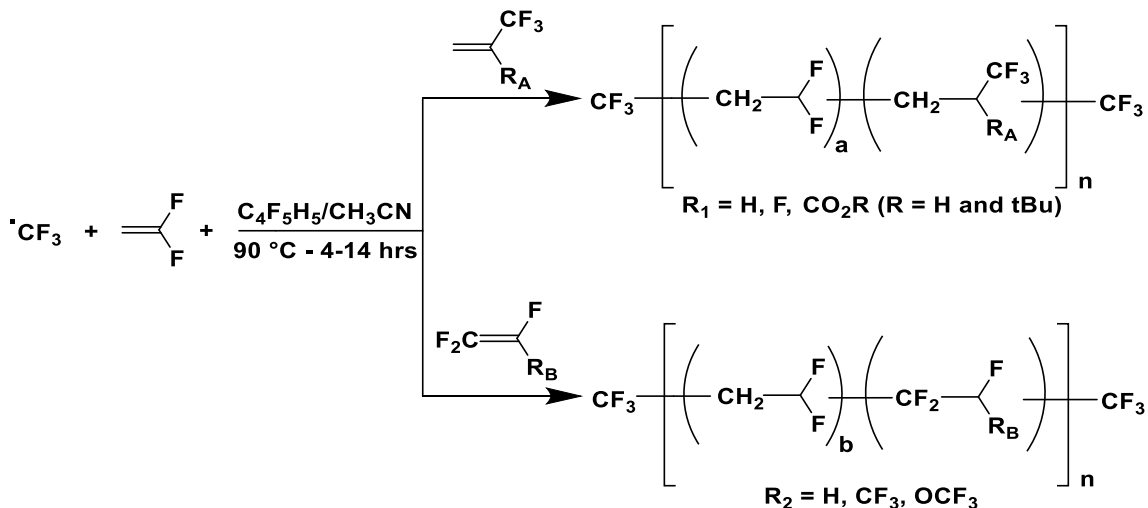
3.1. Introduction

VDF has been copolymerized with a wide range of fluorinated or non-halogenated monomers [18] (Scheme 6), Q-e Alfrey and Price parameters [19,20] to fine-tune the efficiency of the reaction.

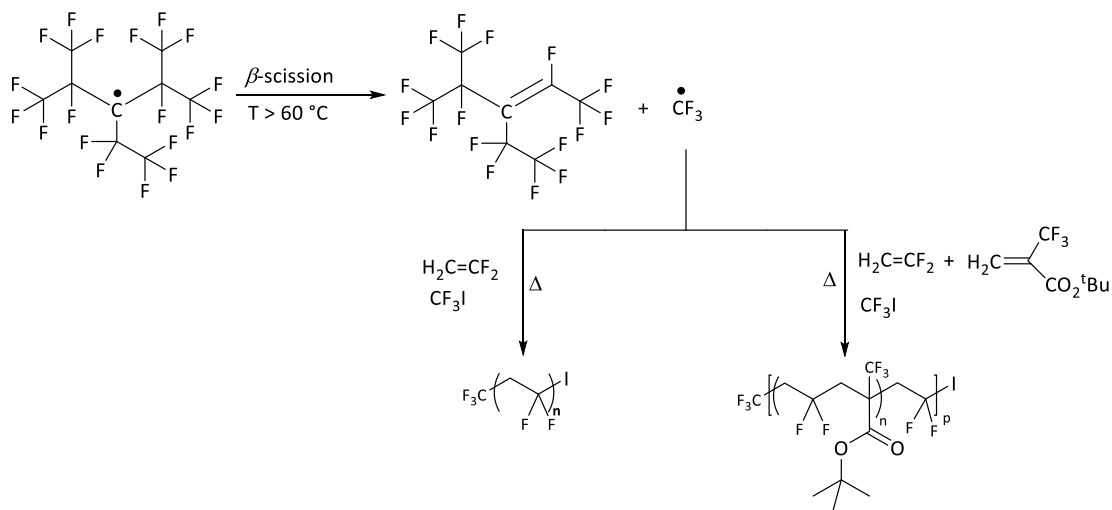
3.2. Copolymerization of VDF with 2-trifluoromethacrylic acid

Among functional comonomers, 2-trifluoromethacrylic acid (MAF), discovered by Ojima et al. in the early 80s (Scheme 7) [21] and later manufactured by the Tosoh Finechem Corp. (ex-Tosoh F-Tech), has shown an efficiency leading to a wide range of materials [22,23] including polymer electrolytes for Lithium-ion batteries [24] and polymer exchange membranes for fuel cells [25,26].

Among the first series, functional 2-trifluoromethacrylates (MAF-funcs) have been shown to be suitable partners to VDF [22–27]. Interestingly, though this monomer cannot homopropagate under radical polymerization, *tert*-butyl 2-trifluoromethacrylate (MAF-TBE) is quite efficient



Scheme 4. Radical copolymerization of VDF with various comonomers initiated by PPFR [14].

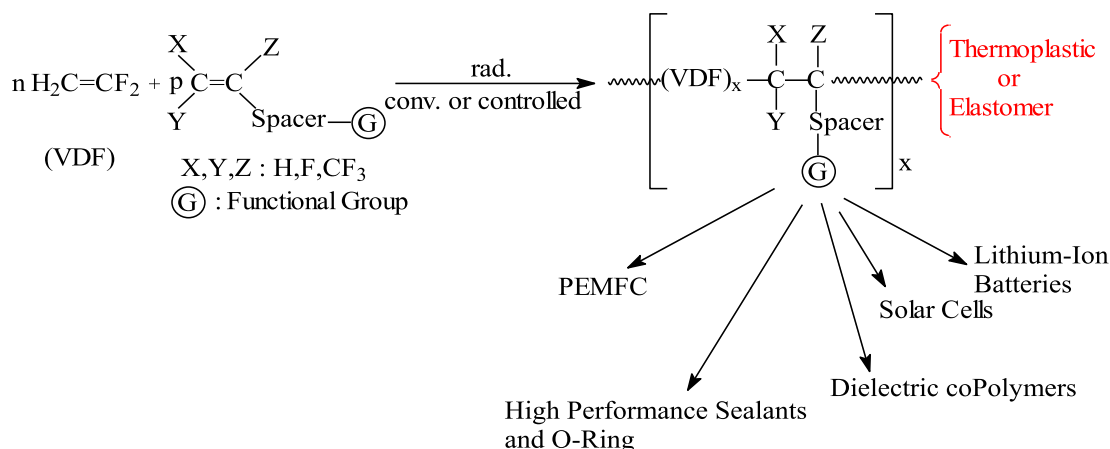


Scheme 5. Strategic routes to obtain PVDF-I and poly(VDF-co-MAF-TBE)-I from PPFR, a persistent radical at RT, which releases a $\bullet\text{CF}_3$ radical from 60 °C. (PVDF, PPFR and MAF-TBE stand for polyvinylidene fluoride, perfluoro-3-ethyl-2,4-dimethyl-3-pentyl persistent radical and *tert*-butyl 2-trifluoromethacrylate, respectively) [13].

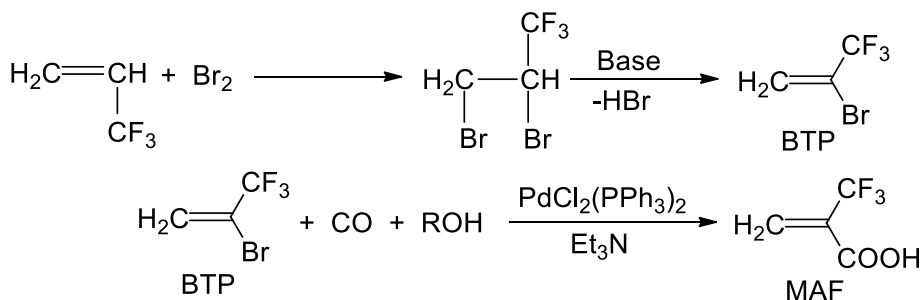
in copolymerization with VDF leading to quasi-alternating copolymers, as displayed in Scheme 8 that mainly highlights crosspropagation steps. Their reactivity ratios were calculated to be: $r_{\text{VDF}} = 0.040$ and $r_{\text{MAF-TBE}} = 0.036$ at 57 °C [27].

A wide variety of MAF-func monomers were synthesized from the condensation of MAF acid chloride onto functional alcohol (Figure 2) [22,24,28–32].

As an example, dimethyl phosphonate 2-trifluoromethyl acrylate (MAF-DMP) was prepared in two steps. First, paraformaldehyde was reacted with dimethyl phosphite to afford 2-hydroxydimethyl phosphonate [30]. Then, the latter was condensed onto MAF acryloyl chloride to yield such a MAF-DMP (Scheme 9), the kinetics of copolymerization of which led to the reactivity ratios ($r_{\text{VDF}} = 0.76 \pm 0.34$



Scheme 6. Conventional or controlled (RDRP) radical copolymerization of VDF with functional comonomers and use of the resulting copolymers for diverse applications [18].



Scheme 7. Synthesis of 2-trifluoromethacrylic acid (MAF) from bromination of 3,3,3-trifluoropropene and further steps [21].

and $r_{\text{MAF-DMP}} = 0$ at 74 °C [30], determined using Mayo-Lewis law from the data listed in the diagram of composition (Figure 3).

The application of such original poly(VDF-*co*-MAF-DMP) copolymers deals with anticorrosion coatings of steel (Figure 2) [30]. The presence of phosphonic acid (after hydrolysis of dimethyl phosphonate function in the copolymers) enables a strong adhesion onto steel surface, the PVDF chain, making the protection.

Using the same strategy, an original fluorinated monomer bearing a cyclocarbonate function, (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB), was synthesized in 70% overall yield from glycerol 1,2-carbonate (Scheme 10) [31].

Thus, a functional monomer was successfully copolymerized with VDF under radical initiation (Scheme 11).

Then, the resulting copolymers were chemically modified by 3-aminopropyl triethoxysilane from the nucleophilic substitution of amino function that opens the cyclocarbonate yielding a PVDF bearing triethoxysilane side groups reinforced by a urethane link (Scheme 12) [31]. Then, hydrolysis of these trifunctional groups under acidic conditions (to avoid any dehydrofluorination of VDF units) followed by condensation led to a crosslinked network.

In addition, these poly(VDF-*co*-MAF-cyCB) copolymers were used as relevant polymer gel electrolytes dissolving Lithium perchlorate for Lithium ion batteries [24] (Figure 4), the electrochemical properties (conductivities and stability in cyclic voltammetry (Figure 5) of which were determined.

A similar strategy was also applied to PVDF bearing oligoPEG side groups [29] (Scheme 13), whose ionic conductivities are illustrated in Figure 6.

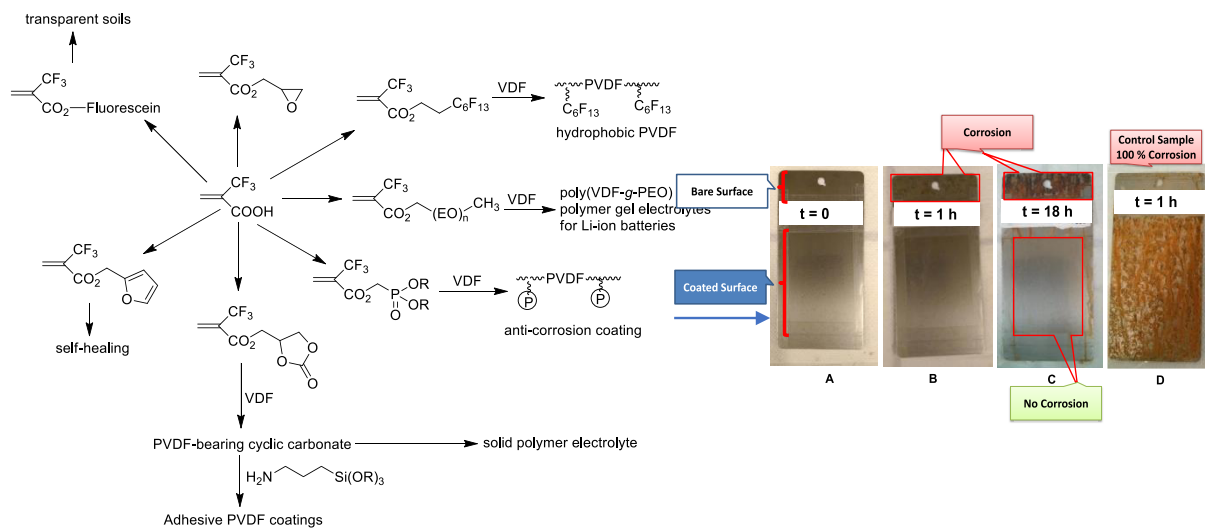
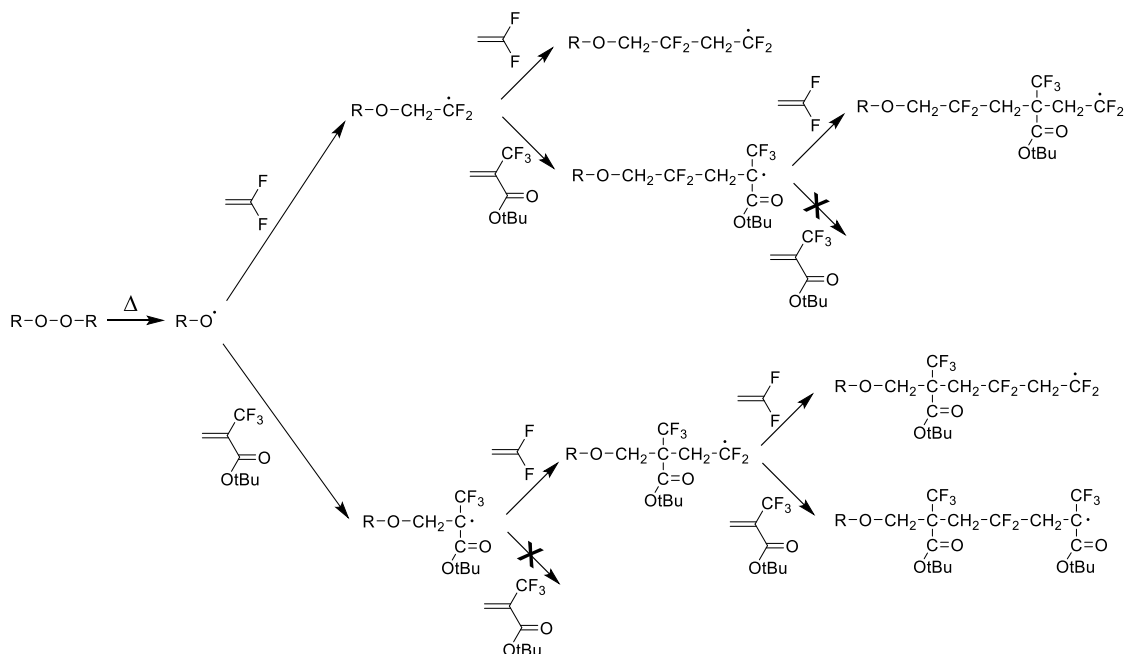
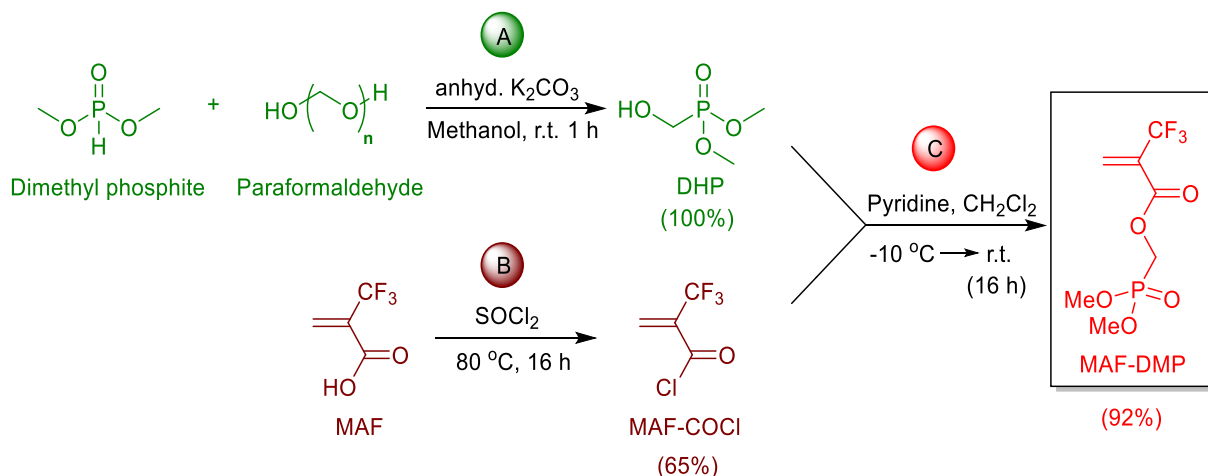
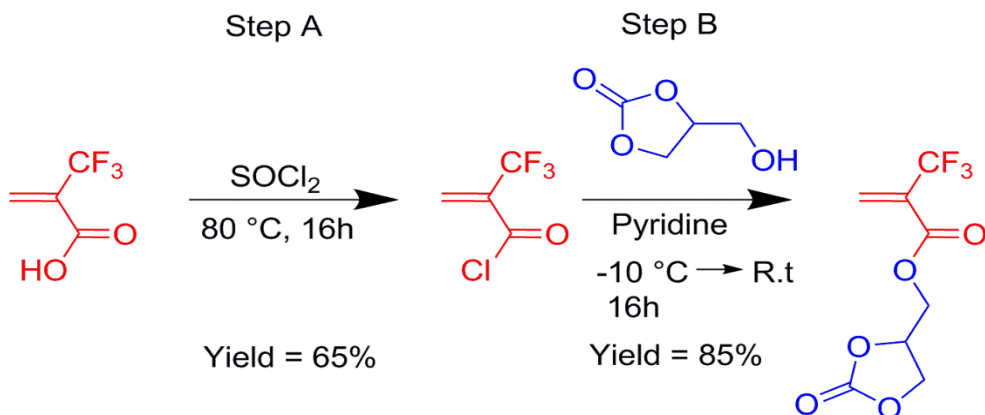


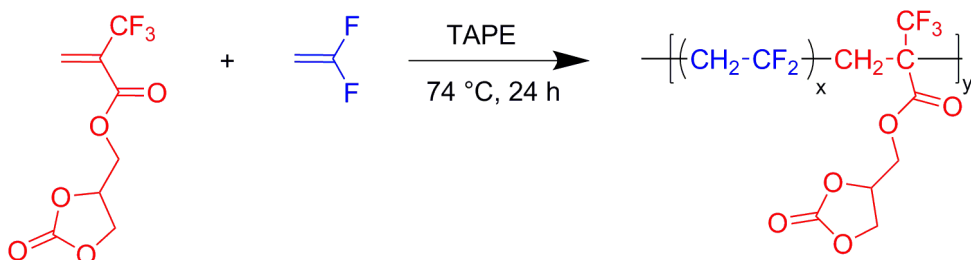
Figure 2. Overall strategies to synthesize novel functional 2-trifluoromethyl monomers from MAF and their radical copolymerization with VDF (left). Steel plates coated with poly(VDF-co-MAF Phosphonate) copolymer at the beginning of the experiment (A), after 1 h (B), and after 18 h (C). (D) Uncoated steel plate as reference sample after 1 h (right).



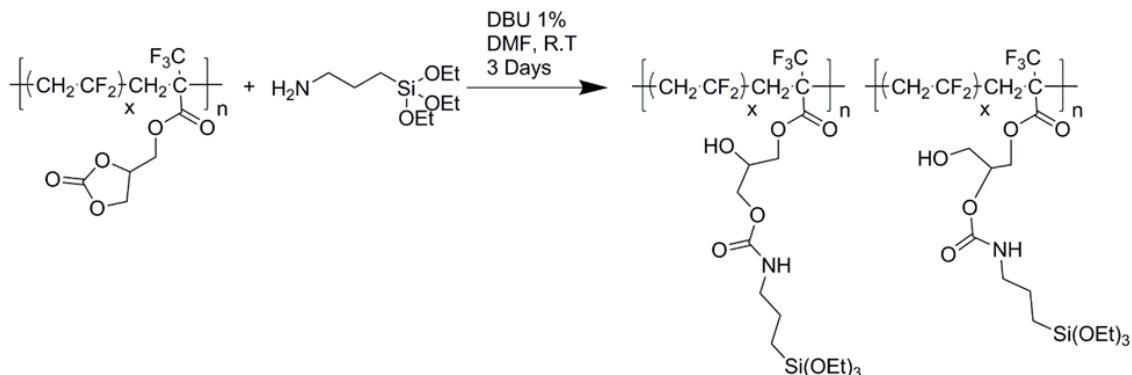
Scheme 9. Synthesis of dimethyl phosphonate 2-trifluoromethyl acrylate (MAF-DMP) by condensation of MAF acryloyl chloride onto 2-hydroxy dimethyl phosphonate [30].



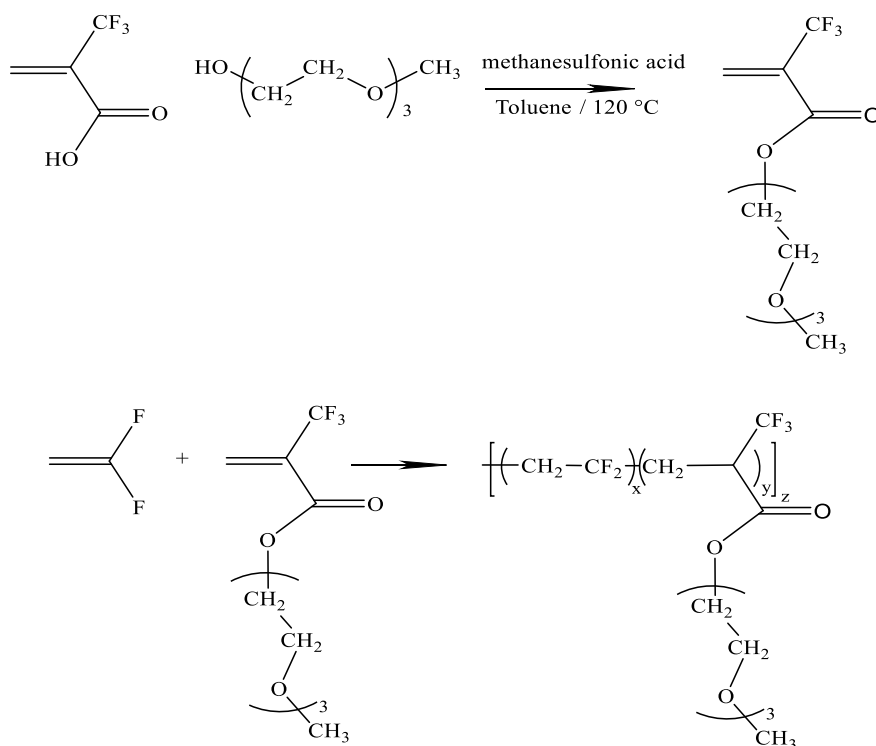
Scheme 10. Synthesis of (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB) from the condensation of glycerol 1,2-carbonate with MAF-acryloyl chloride [31].



Scheme 11. Radical copolymerization of VDF with (2-oxo-1,3-dioxolan-4-yl)methyl 2-(trifluoromethyl)acrylate (MAF-cyCB) initiated by *tert*-amyl peroxy-2-ethylhexanoate (TAPE) [24,31].



Scheme 12. Chemical modification of poly(VDF-*co*-MAF-CyCB) copolymers by ring opening of cyclo-carbonate with an aminopropyl triethoxysilane [31].



Scheme 13. Synthesis of oligo(ethylene oxide) 2-trifluoromethyl acrylate and its radical copolymerization with VDF [29].

In addition, another MAF-func could be prepared by changing oligo(ethylene oxide) moiety with a polyfluoroether in an original comonomer able to copolymerize with VDF as novel solid polymer electrolyte (Scheme 14) [32].

Besides conventional radical copolymerization of VDF with MAF-func derivatives, the reversible deactivation radical copolymerization (RDRP) of MAF with VDF has also been studied, either via iodine transfer copolymerization in presence of

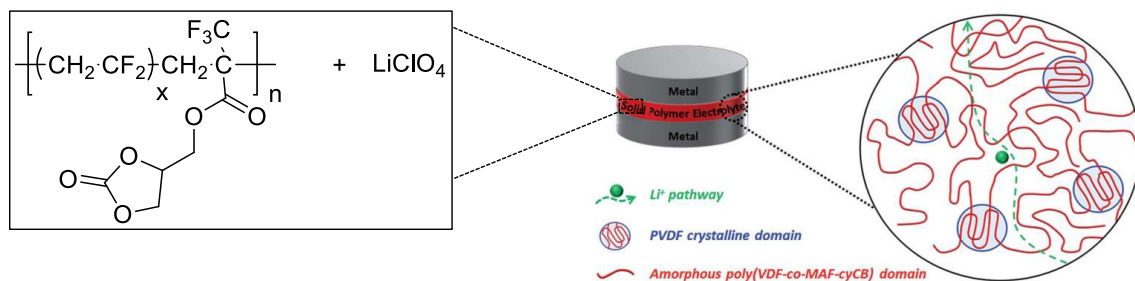


Figure 4. Single polymer electrolyte based on poly(VDF-co-MAF-cyCB) copolymers and LiClO₄ salt for which the Li⁺ cation transport may occur via the amorphous state (reproduced with permission from RSC [24]).

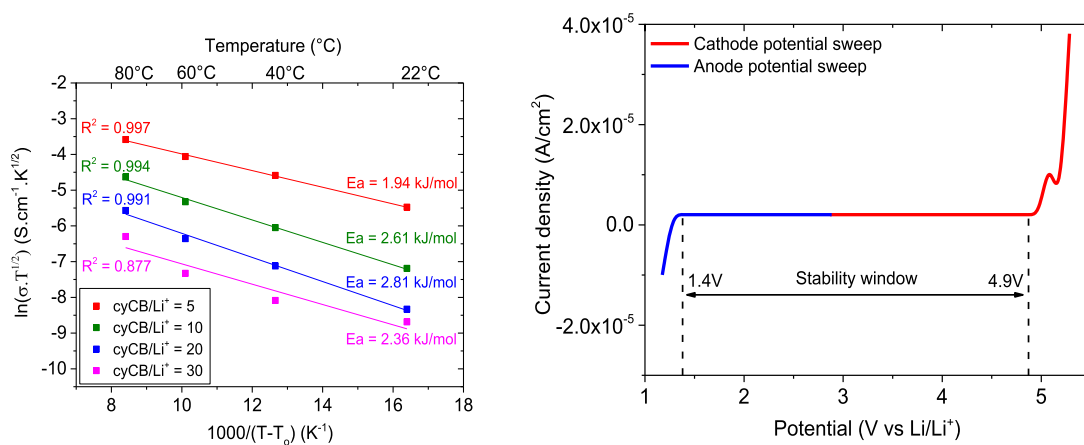


Figure 5. Temperature dependence of the ionic conductivity (left) and linear sweep voltammetry curves of polymer electrolyte with cyCB/Li⁺ = 5. The scan rate is 0.5 mV/s (right) for the investigated SPEs using VTF model (reproduced with permission from RSC [24]).

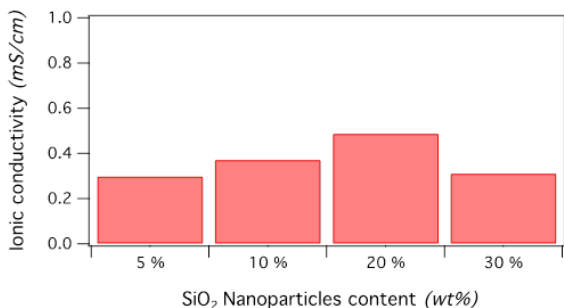
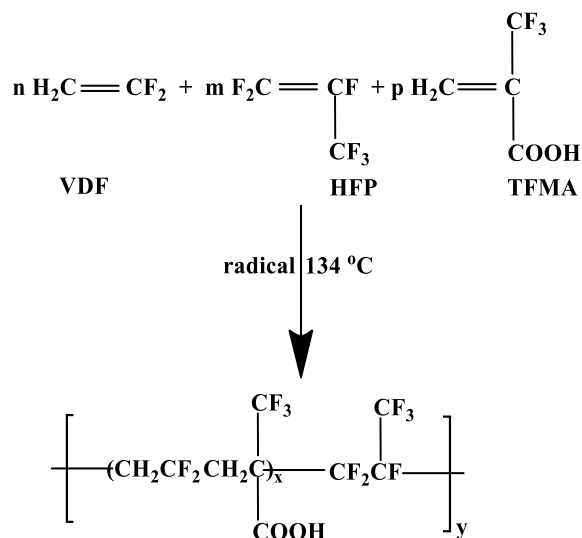


Figure 6. Ionic conductivities of PVDF-g-oligo(ethylene oxide) copolymers filled with Li salt and nanosilica (reproduced with permission from RSC [29]).

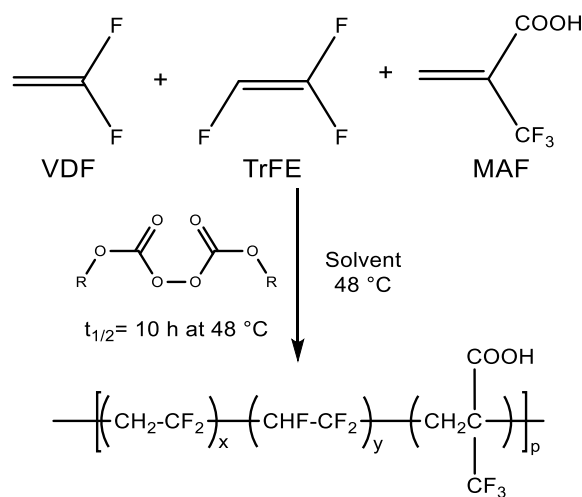
thermogram of the resulting film exhibits Curie (T_C) and melting (T_m) temperatures (Figure 7), T_C being the temperature at which its spontaneous polarization undergoes an induced polarization and vice versa (i.e., the transition temperature at which a ferroelectric product becomes paraelectric material and vice-versa).

3.3.3. 2H-pentafluoropropylene (PFP) as a termonomer

On another note, the terpolymerization of MAF-TBE with VDF and 2H-pentafluoropropylene (PFP) (Scheme 17) was reported with various monomer ratios, enabling PFP (that does not homopolymerize) to be reactive leading to poly(VDF-co-PFP)



Scheme 15. Radical terpolymerization of VDF with MAF and HFP [40].



Scheme 16. Conventional radical terpolymerization of VDF, trifluoroethylene (TrFE) and 2-trifluoromethacrylic acid (MAF) to obtain electroactive devices. In the peroxydicarbonate initiator, R stands for *tert*-butyl(cyclohexyl) [43].

copolymers in low yields [44]. It was initiated by a mixture of two initiators (Trigonox[®] 101/*di**tert*-butyl peroxide) in 1,1,1,3,3-pentafluoropropane as the solvent. The incorporation of PFP in the terpolymerization was favored by termonomer-induced copolymerization [45,46].

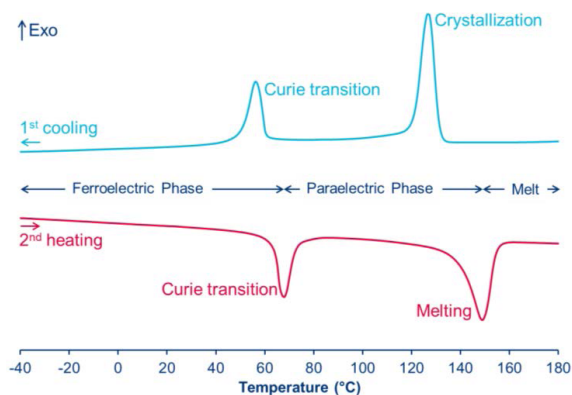


Figure 7. DSC thermograms of poly(VDF₆₄-*ter*-TrFE₃₅-*ter*-MAF₁) terpolymer (reproduced with permission from RSC [41]).

A mechanistic sketch of radical terpolymerization, based on the homopropagation of VDF and cross-propagation of PFP and HFP, is proposed (Scheme 18) that also takes into account the recombination step of macroradical (Scheme 19) [44].

It is worth noting that the radical (co)polymerization of fluorinated monomers is usually terminated by recombination (and not disproportionation) [47]. Thus, the recombination of two growing macroradicals bearing PFP and VDF end-groups can be observed in Scheme 19.

3.4. Chemical modification of poly(VDF-*co*-MAF) copolymers

Thanks to the carboxylic acid side function, poly(VDF-*co*-MAF) copolymers may undergo some grafting or chemical modification. Actually, thermal stability of such copolymers is not as good as expected and the higher the MAF content [25,26], the poorer the stability of these copolymers because of strong decarboxylation (Figure 9).

Thus, the reduction of such acid groups was reported, the resulting hydroxyl group undergoing a Mitsunobu reaction with para phenol sulfonic acid (route 2, Scheme 20), hence inserting strong acid as a possible example of fuel cell membranes [25,26]. As expected, this etherification enhanced the thermal stability of the copolymer and could be straightforward compared to an esterification in medium yields (way 1, Scheme 20) and for which the ester link is poorly stable in acid media [25,26].

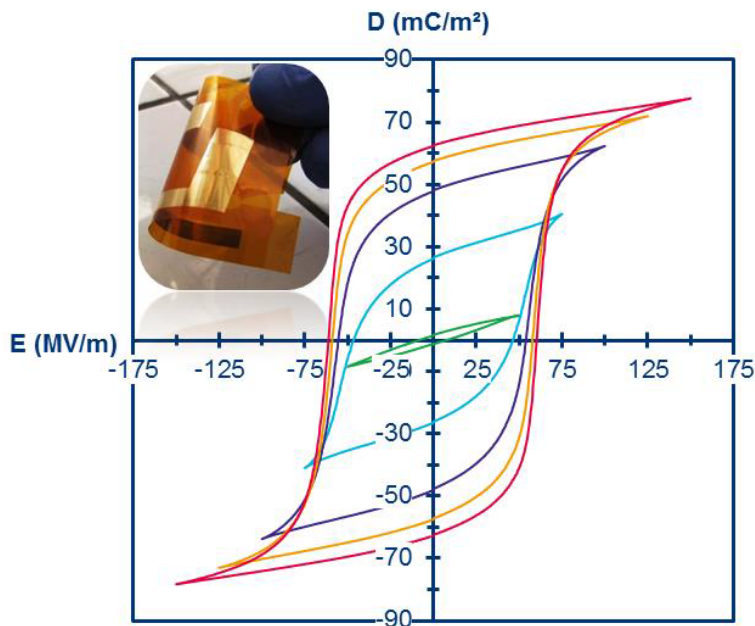
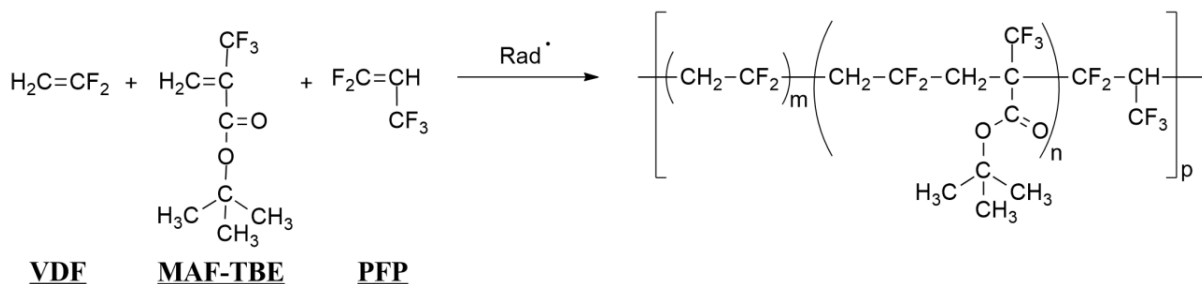


Figure 8. Continuous D–E loops of a poly(VDF₆₉-*ter*-TrFE₃₁-*ter*-MAF₁) terpolymer (inset is a photograph of the flexible gold electrode coated with a 20 µm thick film) (reproduced with permission from RSC [43]).



Scheme 17. Radical terpolymerization of 2H-pentafluoropropylene (PFP) with VDF and *tert*-butyl 2-trifluoromethyl acrylate (MAF-TBE) [44].

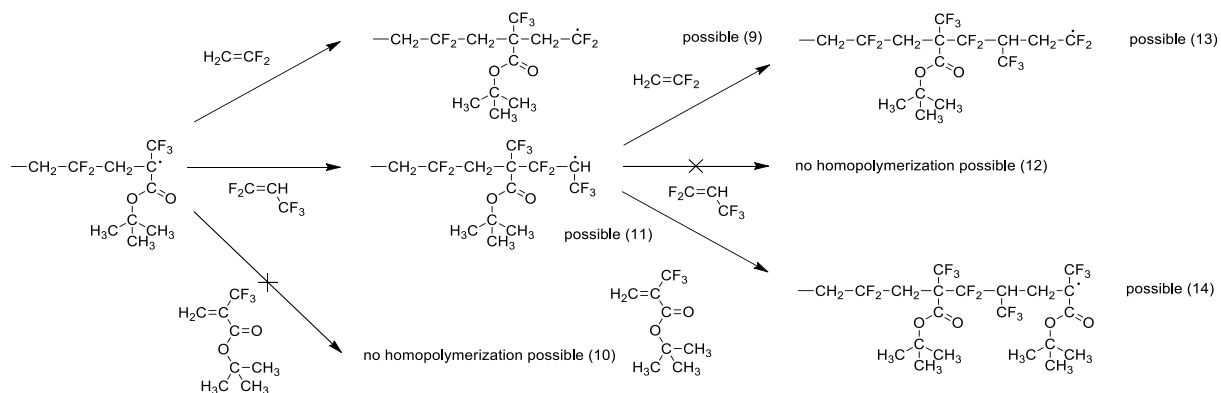
4. Issues on PFAS

In recent years, per- or polyfluoroalkyl substances (PFAS) have attracted significant attention [48,49]. However, one must distinguish different categories linked to molar masses of PFAS (Figure 10) [48]. The lower ones are water soluble and are found in creeks, rivers and oceans, which are exposed to their toxicity, bioaccumulation and persistency [49].

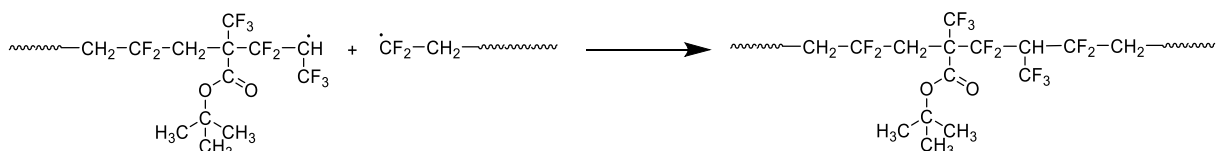
Except persistency (that can be also an advantage in resistance to aggressive media), these issues are not assigned to fluoropolymers (FPs) which

are biocompatible and can be tolerated by human body [50–52]. In addition, FPs fulfill the 13 criteria of polymer of low concern (PLC), in terms of residual monomers, molar masses, dispersities, charges, etc. [53,54] and really behave and contrast to low molar mass-compounds (Figure 11). However, 5 member states have pushed ECHA and the regulatory agencies to restrict them [55], though more than 5600 answers to the consultation were submitted [55].

Searching alternatives to fluorosurfactants has been well-reported in the last few years [49,56] and



Scheme 18. Mechanism of the radical terpolymerization of PFP with VDF and MAF-TBE [44].



Scheme 19. Recombination of growing macroradicals based on PFP and VDF end-units [44].

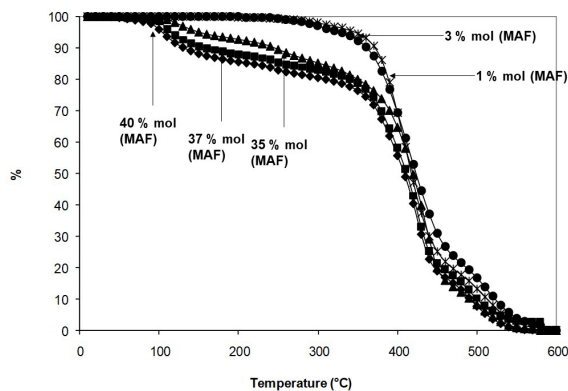


Figure 9. TGA thermograms of poly(VDF-*co*-MAF) at various MAF molar contents [25,26].

one strategy lies on the simple addition of water onto MAF (Scheme 21) [57]. This original and simple surfactant was successfully involved in emulsion homopolymerization of VDF [58] and copolymerization of VDF with PMVE [59].

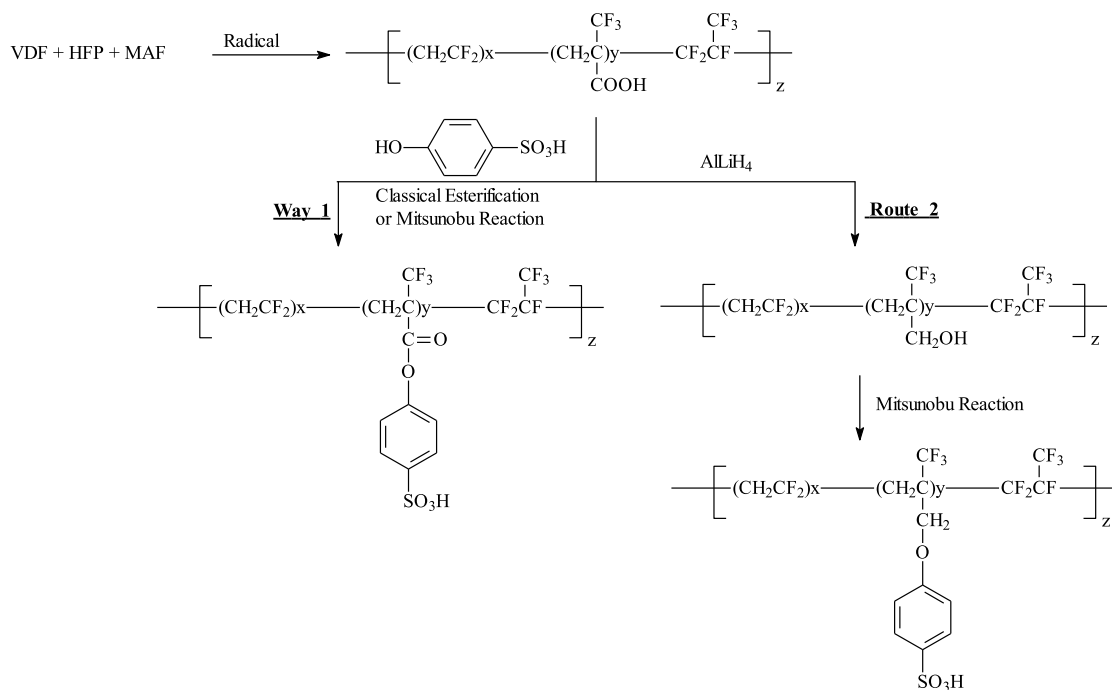
Though many strategies attempted recycling FPs [60], thermal unzipping [61–65], even achieved

at the pilot scale at 3M/Dyneon Company on PTFE, FEP and PFA [66,67], seems an appropriate option to recover TFE. The question lies on minimizing the released low molar mass compounds that led to hazardous issues.

Finally, mineralizations of PVDF [68] and poly(VDF-*co*-MAF) copolymers [69] were recently studied in subcritical water (Figure 12) to generate fluoride anions, which in the presence of $\text{Ca}(\text{OH})_2$, leads to an original source of CaF_2 , thus closing the loop of the fluorine chemistry.

5. Conclusion

Fluoropolymers (FPs) are niche macromolecules with outstanding properties, designed by radical (co)polymerization. Their synthesis depends on the choice of the initiators, processes (not mentioned in this review), compared reactivity of the comonomers by the assessment of their reactivity ratios and the functional group that induces specific features for the searched applications of the targeted fluorinated copolymers. Polyvinylidene fluoride (PVDF) can



Scheme 20. Insertion of sulfonic acid function into poly(VDF-*co*-MAF) copolymers for possible fuel cell membranes (reproduced with permission from *Amer. Chem. Soc.* [25,26]).

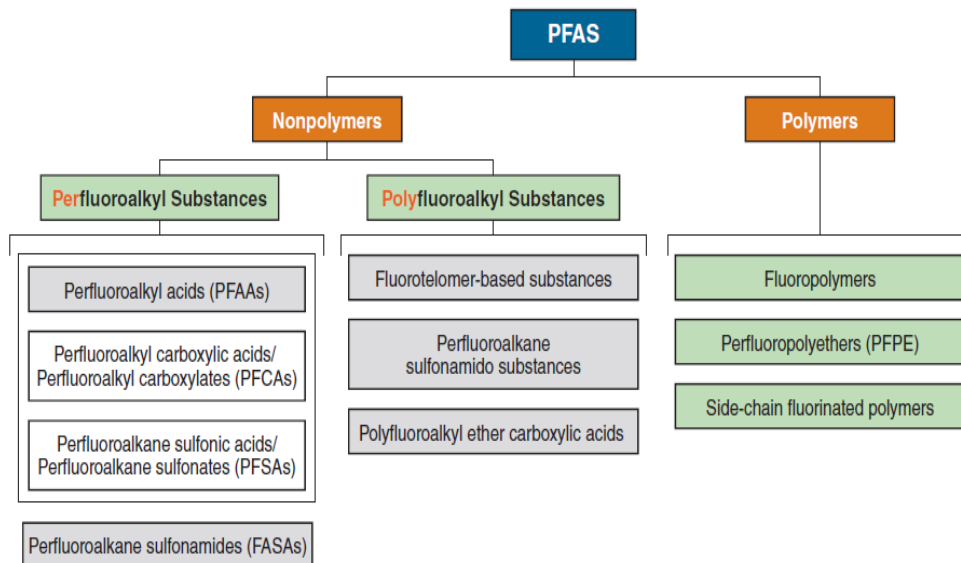


Figure 10. Distinguishing families of per- or poly-fluoroalkyl substances (PFAS) into two domains (reproduced with permission from MDPI [48]).

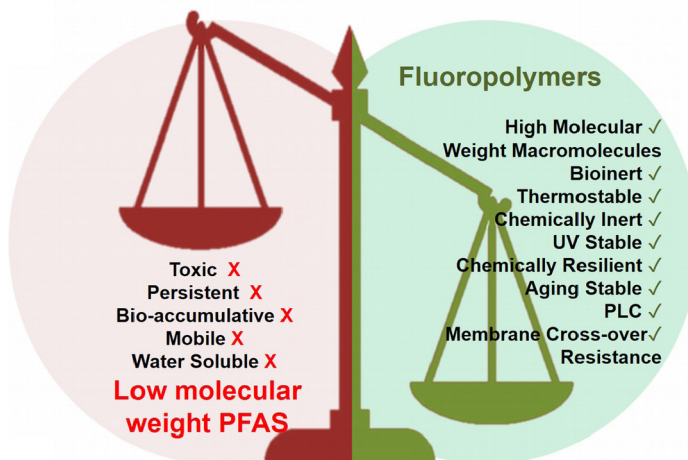
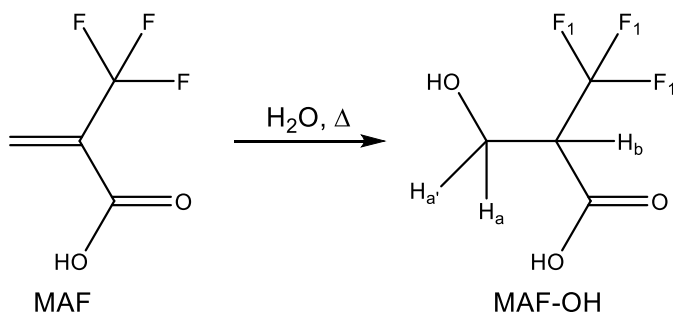


Figure 11. The categorization of PFAS by their molar masses displays totally different advantages and issues (reproduced with permission from MDPI [48]).



Scheme 21. Addition of water into MAF to yield a fluorinated short chain surfactant [57] in emulsion (co)polymerizations of VDF [58] and VDF and perfluoromethyl vinyl ether (PMVE) [59].

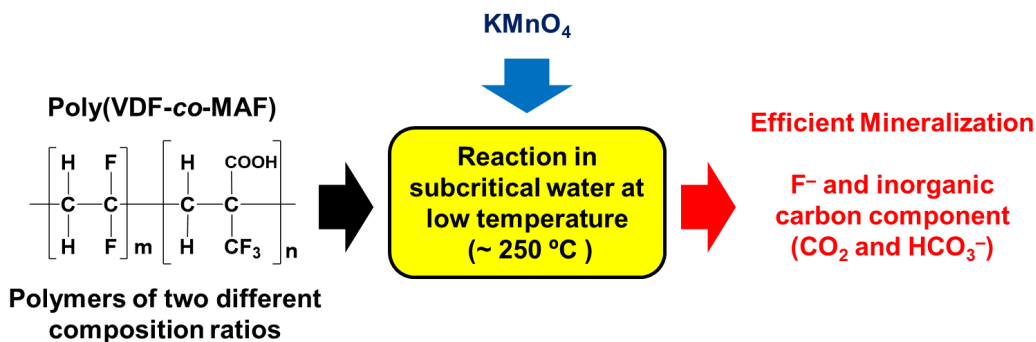


Figure 12. Mineralization of poly(VDF-co-MAF) copolymers in subcritical water (and oxidant in certain cases) (reproduced with permission from *Amer. Chem. Soc.* [68,69]).

be used in many areas as protective coatings, specific membranes for water purification, binders for cathodes in batteries, and electroactive (ferro- or piezoelectric) devices for haptics, actuators, organic transistors or sonars. Structures and reactivities of comonomers must also be considered in order to bring a specific property to the resulting materials. Among comonomers, MAF is a suitable partner for VDF and also opens up to a wide range of various reactive functional comonomers offering original VDF-containing copolymers for various applications (anticorrosion coatings, gel polymer electrolytes and possible binders for batteries, fuel cell membranes to name a few). The controlled radical (co)polymerization (or RDRP) of MAF with VDF has also been studied (ITP or RAFT polymerizations) leading to new architectures such as block, graft, gradient, alternated copolymers as original materials. Finally, related to recent severe pressure and regulations linked to PFAS issues, these fluorinated copolymers do not show any toxicity, bioaccumulation and crossing the cellular human membrane in addition to fulfilling the 13 PLC criteria. Hence, it can be anticipated that these macromolecules will exit from the PFAS family following scrutiny. Regarding recycling of VDF-containing copolymers, though several routes exist, one relevant strategy lies in their mineralization in subcritical water leading to fluoride anions as precursors of CaF₂ as a starting point of fluorine chemistry as a circular economy process.

Declaration of interests

The authors do not work for, advise, own shares in, or receive funds from any organization that could benefit from this article, and have declared no affiliations other than their research organizations.

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