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Bruno Ameduri. Fluoropolymers as unique and irreplaceable materials: Challenges and Future Trends of these specific perfluoroalkyl substances. *Molecules*, 2023, 28, pp.7564. 10.3390/molecules28227564 . hal-04283750

HAL Id: hal-04283750

<https://hal.science/hal-04283750>

Submitted on 14 Nov 2023

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Fluoropolymers as unique and irreplaceable materials: Challenges and Future Trends of these specific perfluoroalkyl substances

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Abstract: In contrast to some low molar-mass per- and polyfluoroalkyl substances (PFASs), well-established to be toxic, persistent, bioaccumulative and mobile, fluoropolymers (FPs) are water insoluble, safe, bio-inert, durable. These niche high performance polymers fulfil the 13 polymer of low concern (PLC) criteria in their recommended conditions of use. In addition, more recent innovations (e.g., the use of non-fluorinated surfactants in aqueous radical (co)polymerization of fluoroalkenes) from industrial manufacturers of FPs are highlighted. This review also aims at showing how these specialty polymers endowed with outstanding properties are essential (even irreplaceable since hydrocarbon polymer alternatives used in similar conditions fail) for our daily life (electronics, energy, optics, internet of things, transportation, etc.) and constitute a special family *a part* from other “conventional” C₁-C₁₀ PFASs found everywhere on the Earth and Oceans. Furthermore, some information reports the recycling (e.g., the unzipping depolymerization of polytetrafluoroethylene, PTFE, into TFE), end of life of FPs, their risk assessment, circular economy and regulations. Various researches are devoted to environment involving FPs, though they represent a niche volume (with a yearly production of 330,300 tonnes) compared to all plastics (with 460 million tonnes). Complementary to other reviews on PFASs, which lack of such above data, this review presents both fundamental and applied strategies as evidenced by major FP producers.

Keywords: end of life; fluoropolymers; per- and polyfluoroalkyl substances (PFAS); polymerization aids; recycling; regulators; surfactants.

1. Introduction

According to the Organization for Economic Co-operation and Development (OECD)¹⁻², perfluoroalkyl (and polyfluoroalkyl) substances (PFASs) are artificial/anthropogenic products which contain multiple C–F bonds.³⁻⁹ Because of their unique hydrophobic/lipophobic physicochemical properties, this specific group of chemicals displays quite different physical, chemical, and biological properties⁵⁻⁹ than other hydrocarbon compounds and have been involved in many applications in different areas⁵⁻¹⁰. The OECD¹ has reported more than 4700 PFAS molecules and, according to the US environment Protection Agency,^{3,11} this number reaches more than 12,000 compounds.¹² However, PFAS molecules, especially those of low molar mass have been found in many soils, water, seas and oceans as reported by plethora of articles and reviews.⁴⁻¹⁰ Thanks to the high electronegativity and small radii of the fluorine atom that confers a short and quite stable C-F bond, fluorinated products have remarkable chemical inertness and thermal stability (the dissociation energy of this C-F bond worth ca. 120 kcal . mol⁻¹ ^{7,9}). However, such characteristics further induce some limitations since PFASs are known to be water soluble, mobile, toxic, persistent and bioaccumulable.^{9,12-14} Since 2000, many regulations have been proposed, modified and multiplied.^{5-8,10,12-17} Various fluorinated compounds have been banned for several years and a continuous procedure from competent authorities still maintain their pressure to impose drastic legislations/regulations.¹⁶

Thomas et al.¹⁷ comprehensively reported the global situation on the regulation of PFASs in both the scientific and legislative communities, and analyzed the different regulatory actions launched both in Europe and in the USA (including federal and state-level initiatives). These authors supplied an exhaustive list of different dossiers of legislation and carefully reported how regulators have approached the concerns of PFASs from different perspectives. Last March 2023, China added PFOA and PFOS to its list of New Pollutants for Priority Management to modify their production, use, import, and export.¹⁸ Presently, 152 countries have ratified the Stockholm Convention, that puts in place elimination and restriction of listed PFASs with exemptions for specific uses such as hard metal plating and firefighting foams (AFFFs). As of April, 5th 2023, Israel, Haiti, USA, Malaysia, and Brunei Darussalam have not

ratified the convention. Although ratified, there is no indication that a number of the member nations have made efforts to regulate PFASs *via* other independent mechanisms.¹⁷

This review aims first at making a distinction between various classes of PFASs, showing major issues from low molar mass-ones in contrast to the high molar mass fluoropolymers, which display specific advantages (safety, bio-inertness, non-toxicity and fulfilling the 13 polymer of low concern (PLC) criteria in their conditions of use).



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Figure 1: Historical scheme of the fluorochemicals from the discovery of polytetrafluoroethylene (PTFE) to REACH regulations (reproduced with permission from RSC, ref 9) (APFO, ECF, EPA, FT, PFBS, PFCA, PFNA, PFOA, PFOS, POP and REACH stand for ammonium perfluorooctanoate, electrochemical fluorination, environment protection agency, fluorotelomer, perfluorobutanesulfonate, perfluorocarboxylic acid, perfluorononanoic acid, perfluorooctanoic acid, perfluorooctanesulfonic acid, persistent organic pollutants, and Registration, Evaluation, Authorisation and Restriction of Chemicals, respectively).

In addition, advanced technologies from industrial manufacturers of FPs have led to recent innovations such as the use of non-fluorinated surfactants in aqueous radical (co)polymerization of fluoroalkenes to yields FPs with similar performances. This above innovations have unprecedented been reported before. This review also aims at showing how these specialty polymers endowed with outstanding properties are essential (even irreplaceable) for our daily life (electronics, energy, optics, internet of things, transportation, etc.) and constitute a special family *a part* from other “conventional” C_1 - C_{14} PFASs found everywhere on the Earth and Oceans. Furthermore, some information report the recycling (e.g., the unzipping depolymerization of polytetrafluoroethylene, PTFE, into TFE), end of life of FPs, their risk assessment and circular economy. Various researches are devoted to environment involving FPs, though they represent a niche volume. Complementary to articles on PFASs, which lack of this information above, this review gathers both fundamental and applied strategies as evidenced by major FP producers. Various features are still attracting a huge interest from both academic and industrial players.

2. History of PFASs

Fluorinated plymers have been known for eighty-five years¹⁴ and a brief historic sketch showing their extraordinary evolution is depicted in Figure 1, that includes fluorinated gases (discovered in the 20-ies), intermediates, monomers, oligomers and polymers, as well key methods to supply them either by electrochemical fluorination⁹ or telomerization.²⁰ Among them, surface-active products (surfactants) are specific amphiphilic PFASs which display much lower surface tension and surface energy than those of hydrocarbon surfactants.^{9,19}

They are currently used in more than 200 applications: such as aqueous firefighting/film forming foams,¹⁹⁻²² food packaging, cosmetics, photoacid generators,^{9-10,19} paints, semiconductors, electroplatings²² and as polymerization aids in the emulsion radical polymerization of fluorinated alkenes.^{9;22} There are many examples related to PFAS including their production sites,¹² or storage areas such as military bases equipped with extinguishers²³⁻²⁴ and airports²⁵⁻²⁶ where many PFASs have been found. Ruyle et al.²⁴ analyzed groundwater samples from a fire training area between September 2007 and July 2021 (six time points; Figure 2). All groundwater measurements were from samples collected from the same well to control the hydrological variability. The samples represent concentrations in the upper 2–3 m of groundwater. These authors directly compared PFAS concentrations from those of samples collected in 2007. Their analyses were achieved in order to supply quantitative and qualitative information from complementary techniques such as liquid chromatography-tandem mass spectrometry (LC-MS/MS), combustion ion chromatography, high-resolution mass spectrometry, and a comparison of measured and library MS/MS spectra.

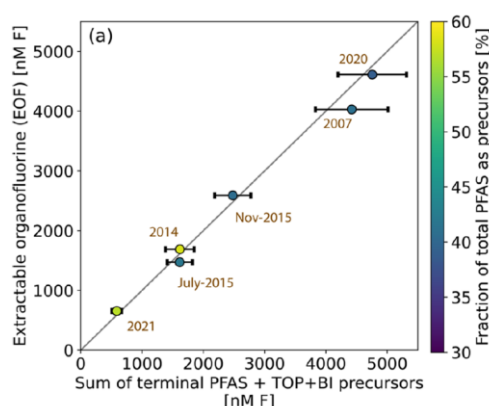


Figure 2: Mass budget for PFAS in groundwater below the fire training area at Joint Base Cape Cod, USA. (a) Comparison of detected extractable organofluorine (EOF) and PFAS concentrations. The x -axis represents the sum of terminal PFAS and oxidizable precursors inferred from the total oxidizable precursor (TOP) assay using Bayesian Inference. The sum of differences from duplicate extracts for targeted PFAS (9%; $n = 1$) and the standard deviation of inferred precursor concentrations are shown by x -axis error bars. Circles are shaded in purple by the fraction of EOF explained by oxidizable precursors. The one-to-one line (gray) is used to compare the sum of terminal PFAS and precursors measured using targeted analysis and the TOP inference with EOF.²⁴ (Reproduced with permission from Amer. Chem. Soc.).

3. Issues on Mobility, Persistency, Toxicity and Bioaccumulation of PFASs

As a matter of fact, major concerns arise from their high-water solubility²⁷ and thus mobility, as well as their chemical stability, toxicity, persistence^{26,28-30} and bioaccumulation in

the environment in the food chain and in humans.^{5-6,10,12,23,28-31} A growing attention has been paid to PFAS as a specific chemical class^{4,7,31} because of their adverse health effects, modes of action, and physical and biochemical properties,⁴ mainly linked to their too stable small perfluorinated chain that cannot degrade or be metabolized.

Actually, modern powerful analytical apparatus and machines are able to detect very low chemical concentration (as low as several tenth of ppb³² (or even hundreds of ppt); knowing that one ppb is a drop of water in an Olympic-size swimming pool!).

Globally, environmental officials from five-member states¹⁶ launched actions to push regulatory agencies (as Registration, Evaluation, Authorisation and Restriction of Chemicals, REACH) and consequently EU to restrict PFASs (including FPs) with some plans to ban all PFASs by 2030.³³ In addition, more than a dozen of states in the USA have been also influencing authorities to ban PFASs in the coming years (Maine and Minnesota have already started). Consequently, synthesizing alternatives to face perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) issues (since 2006, PFOA and PFOS, their salts and similar compounds have been banned in many countries) led to much research that has been well-summarized in various review²¹ or book chapters,^{22,34} (though China is still currently using PFOA as polymerization aid as well as other PFASs containing shorter chain lengths). On the other hand, Chemours and Dyneon industrially produced hexafluoropropylene oxide dimer ammonium carboxylate (Gen®X or HFPO-DA) and 4,8-dioxa-3H-perfluorononanoate (Adona®), respectively, enabling to yield FPs, the quality and performances of which were similar to those of FPs obtained in presence of PFOA or PFOS. However, several years later, these surfactants had also been detected in soils and rivers probably because of their persistency and mobility issues.^{9,34,35}

4. Different Categories of PFASs

PFASs have been categorized into two distinct families of fluorinated compounds,^{4,7,27,36} the major differences being their molar masses (Figure 3) and dispersities for their separated uses.

4.1. Non-Polymeric PFASs

4.1.1. *Introduction.*

Low molar mass-PFASs ($< 1,000 \text{ g} \cdot \text{mol}^{-1}$) including PFOA, PFOS and fluorinated telomers (Scheme 1)^{9,20} have contaminated many places on Earth and oceans or decompose in the stratosphere leading to trifluoroacetic acid (that is extremely difficult to separate from

water) and trifluoroacetate,³⁷ polluting waters and soils and thus bringing negative impact. These compounds also cross the cellular membranes of animals and human beings.^{1,32,38}

4.1.2. Strategies to eliminate low molar- mass PFASs.

Beside the thermal (low³⁹ or high⁴⁰⁻⁴¹), biological,⁴² microbial⁴³ degradation and that under subcritical water⁴⁴, well summarized by Mueller and Yingling⁴⁵ a variety of porous sorbents such as carbon-based materials, ion exchange resins or polycationic gels have been investigated to remove PFASs.⁴⁶⁻⁴⁹ The adsorption behaviors of PFASs are dramatically affected by pH values of environmental conditions, as well as substances of several orders of magnitude higher concentrations than PFASs in natural water sources.⁴⁶⁻⁴⁸ Therefore, selective PFASs separation under environmental friendly conditions reveals highly challenging.^{49,50} Actually, endowed with its fluorophilicity feature, fluoropolymer nanoparticles (FPNPs) (e.g., star polymers with fluorinated nanogel cores and hydrophilic poly(ethylene oxide) arms able to remove PFOA from 10 ppm to ppb level⁵¹⁻⁵²) are interesting candidates for PFASs adsorption, because they display strong and selective affinity to PFASs, FPNPs being highly resistant to non-fluorinated ions spread in the environment.

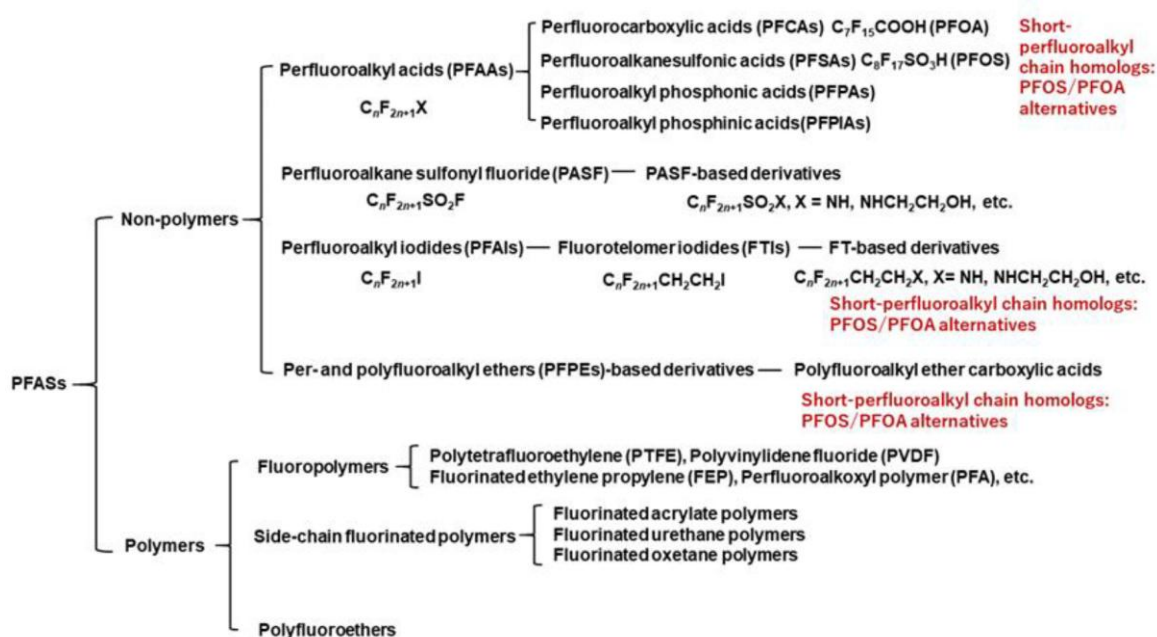


Figure 3: General classification of PFASs according to the Organization for Economic Co-operation and Development (OECD)¹.

In addition, Song et al.⁵³ recently succeeded in eliminating PFOA by chlorine radical triggered electrochemical oxidation, while Chen et al.⁵⁴ synthesized original FPNP-embedded

hydrogel for PFAS adsorption. These FPNPs were produced from tandem photo-mediated RDRP (Figure 4). The FPNPs showed significant adsorption performance to a many cationic, anionic, neutral and zwitterionic PFASs. The strong and selective affinity toward fluorinated compounds enabled clearance of PFASs at high environmentally relevant concentrations in water without being dramatically disturbed by acidic/basic conditions. Furthermore, such an FPNP-embedded hydrogel displayed good mechanical properties inclined to facilitate separation, regeneration and recycling of hydrogel.

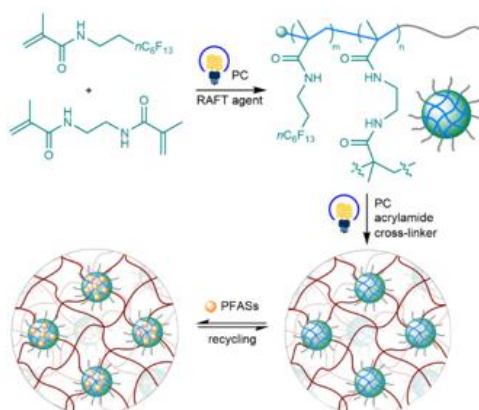


Figure 4: synthesis of fluoropolymer nanoparticles (FPNP)-embedded hydrogel and study on PFASs adsorption. Reproduced with permission from ref.⁵⁴ (copyright 2020 Amer. Chem. Soc.)

Beyond FPNPs, other fluorinated sorbents have been reported as relevant host molecules for PFAS guests. One example deals with cross-linked fluoropolymer gels,^{46, 49} while β -cyclodextrin-based polymers,⁵⁵ granular activated carbon⁴¹ are evidenced to capture neutral and/or anionic PFAS efficiently. The outstanding performance of these FPs further highlights that the fluorophilicity effect could be used as a basic feature to promote PFASs adsorption toward a sustainable society.

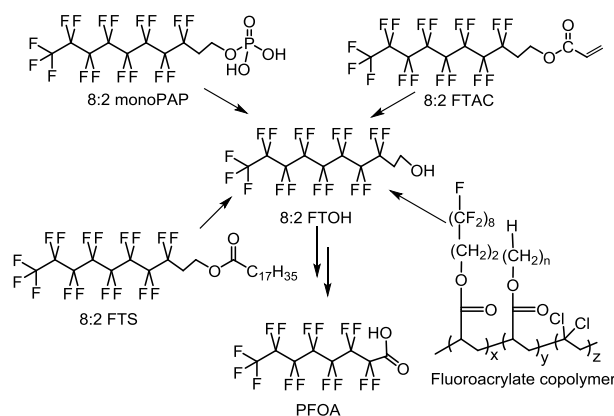
4.2. Fluorinated Polymers

4.2.1. FPs containing fluorinated side chain or oxygen atoms

A wide variety of fluorinated polymers has been reported in some monographs⁵⁶⁻⁵⁹ and reviews.⁶⁰⁻⁶⁴ While fitting the PFAS definition because of their chemical composition, structure, and presence of fluorine atoms,^{4,7,64} FPs represent a specific family and are significantly different from other substances of PFAS category (Figure 3). Indeed, they can be composed of: i) polymers bearing fluorinated dangling chains such as poly[fluoro(meth)acrylate]s,⁶⁵⁻⁶⁶ or fluorinated polyurethanes or poly[fluoro(oxetane)]s, ii) perfluoropolyethers, PFPEs, prepared by ring opening polymerization of either

hexafluoropropylene oxide (HFPO) or oxetanes, or achieved from the photochemical polymerization of TFE and hexafluoropropylene (HFP) in the presence of oxygen⁶⁷ and finally iii) polymers containing carbon and fluorine atoms in their backbones. As an example, from durable water repellent (DWR) clothing, the poly[fluoro(meth)acrylate]s⁶⁶ undergo some leaching out of the fluorinated side groups by weathering yielding PFAS (mainly fluorinated hydroxy telomers).

Actually, polymers bearing (per)fluorinated side group have undergone major issue as evidenced by Liu and Avendaño⁴³ on their microbial degradation. It can be assumed that, because of their high chemical and ageing stability, to the best of our knowledge, no similar study has already been reported on FPs bearing fluorine atoms in the backbone. These poly(fluoroacrylate)s possessing ω -perfluorinated dangling moieties have led to 8:2 fluorotelomer derivatives (Scheme 1) while several studies have described the decomposition and releasing of the fluorinated side chain under various conditions.⁶⁶



Scheme 1: Illustration of microbial degradation of poly(fluoroacrylate)s that generate 8:2 fluorotelomer derivatives.⁴³ (reproduced with permission from Elsevier).

4.2.2. FLUOROPOLYMERS (i.e., backbone containing C-F bonds)

4.2.2.1. Valuable Fluoropolymers with exceptional properties. This sub-section is devoted to polymers bearing C-F bonds within the backbone, and it is divided into four parts. These unique specialty polymers are niche products (production: 330,000 tonnes/year⁶⁴ compared to >400 million tonnes/year of all polymers), known to be safe, bio-inert, persistent and not degradable under environmental conditions. These durable materials display outstanding properties,⁵⁶⁻⁶⁴ prolong lifetimes, increase fire safety, reduce maintenance needs and keep good performances (even in extreme conditions or aggressive/corrosive media) where other materials fail. One example is the Challenger dramatic explosion in 1986, 73 seconds after liftoff, related to poly(thioether) seals which had too high Tg values. Since then,

all shuttle packings and gaskets have been made of fluoroelastomers.⁶⁸ Advantageously, they are the unique candidates displaying the best heat and oil resistance (e.g., aircraft fluids as Skydrol®)⁶⁹ (Figure 5) and excellent flexibility. Essential for our daily life⁶³ and involved in many high-tech areas, FPs are endowed with exceptional features,⁵⁶⁻⁶⁴ their molar masses being able to reach several million g.mol⁻¹ (as PTFE). Because of the growing need for higher requirements and engineering materials that combine specific properties for high-tech applications, FPs are currently undergoing an increasing development.⁷⁰

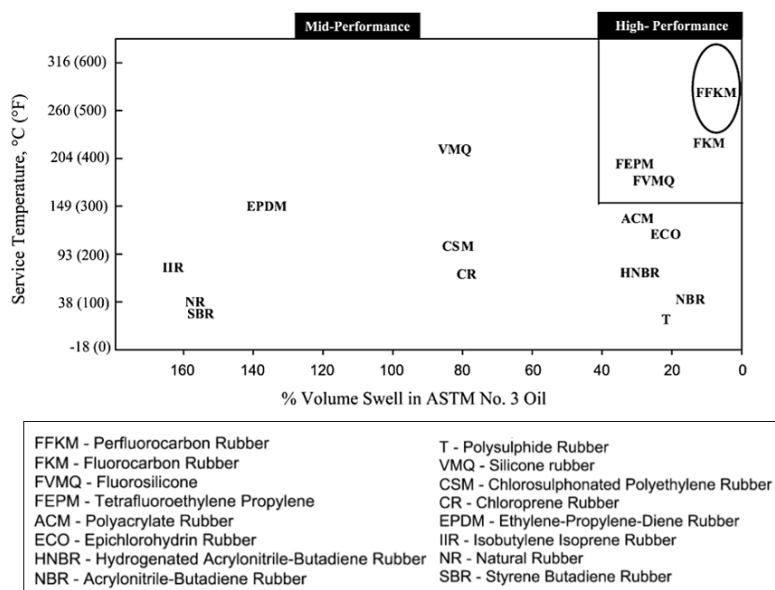


Figure 5: Compared relative heat and oil resistances of elastomers (ASTM D2000). Reproduced with permission from Elsevier⁶⁸.

One example is poly(vinylidene fluoride), PVDF, which satisfies stringent leachable limits and other national health regulations, ensuring that it is safe for use in water treatment. In addition, this FP is durable, withstanding high pressures while maintaining structural integrity.

Actually, these specialty polymers are also involved in specific UV and aging resistant coatings and have been involved in many other applications: i) wires and cables in wide domains such as aerospace (because of high limiting oxygen index value, PTFE coatings ensure fire retardancy to several hundred km-cables and connections in planes, insulation (insulation resistance $\geq 1500 \text{ M}\Omega\cdot\text{km}$), electrical and high frequency (5000 V) performance, coaxial cables for avionics and high temperature resistant cables for aero engine services.⁷¹ The resilience and inertness of crosslinked elastomers provide in exceptional performance to gaskets in shuttles⁷²); ii) materials for energy storage and conversion (as key-candidates for the energetic transition: cathode binders in lithium ion batteries, proton exchange fuel cell

membranes, backsheets of photovoltaic panels, electroactive (piezoelectric and electrothermal) devices,⁷³ haptics, printed electronics, dielectrics, for virtual reality, actuators for artificial muscles, and are indispensable drivers of the European Green Deal], iii) chemical process industry (e.g., injection molded PVDF tower packing is used over and over in sulfuric acid and chlorine scrubber systems and does not lose its properties like other polymers when exposed to harsh chemistries and high temperature.), iv) transport (transmission fluids and specific seals and gaskets)^{57,74}, telecommunications (optical fibers among more than 4 million km of undersea cables are carrying information *via* a huge network),⁷⁵ food and water treatment, electronics,⁷⁶ pharmaceutical and medical devices.⁷⁷⁻⁸²

FPS should only be involved in uses required for health, safety, or are critical for the functioning of society and no alternatives are available.^{9,63,64,83-84} In addition, searching alternative materials would reduce the time required for toxicological analyses.

The most prevalent materials are PTFE,⁶¹ PVDF,^{73,85} poly(chlorotrifluoroethylene), PCTFE,⁸⁶ and the copolymers based on tetrafluoroethylene, TFE,⁸⁷ and vinylidene fluoride, VDF,⁸⁸ which can be either thermoplastics or elastomers.⁷² Usually, in their conditions of uses, FPS are safe, stable (thermally, chemically to UV and aging, and biologically), durable, non-toxic, non-bioaccumulative, insoluble in water and thus non-mobile, are hydrolytically stable, and are not subject to hydrolysis catalyzed or metabolized degradation. For these features, they are not considered as substances of very high concern (SVHC) and fulfil the 13 criteria (see section 4.2.2.3.).^{35,89-90} Furthermore, their relevant combinations of properties are not matched by any of the alternative hydrocarbon polymers,^{9,63,83-84} hence making them so unique and valuable.

The regulatory agencies, such as Registration, Evaluation, Authorization and Restriction of Chemicals (REACH),³² Toxic Substances Control Act (TSCA) and Japanese Existing New Chemical Substances Inventory (ENCSEI) support initiatives aimed at regulating the substances of greatest concern. They will endeavor to contribute to the broad and complex scientific, technical but also economic forthcoming debate on those substances. Actually, FPS seem to be impacted by the upcoming restriction on PFASs under the EU REACH Regulation, published on February 2023.³²

4.2.2.2. Improvement of FP production in more environmentally friendly processes. Because they are concerned about the negative aspects of fluorinated polymerization aids (FPAs or surfactants) currently used to replace PFOA, FP manufacturers have been overcoming the great challenge to produce FPS free from FPAs. They are currently searching

solutions in both replacing such PFAs by non-FPAs (NFPAs) and processing by reducing fluorinated effluents and gas emissions. Indeed, a few years ago, the Chemours and Dyneon companies developed and used Gen®ex and Adona®, respectively, though these FPA have been found as traces in rivers and soils.³⁴ However, the regulatory agencies are currently pushed from various authorities in helping the industry to swiftly move towards sustainable technologies and many efforts from these FPs producers have been recently taken in two main strategies: i) absence of FPA, as well as matching the PLC criteria are more appropriate to specific syntheses (as FKM). Much progress has been observed in the last decade after several FP manufacturers modified their production using NFPAs (or surfactants) leading to major innovations by the whole industry (such as 3M,⁹¹ AGC,⁹² Arkema,⁹³ Chemours,⁹⁴⁻⁹⁵ Daikin,⁹⁶ Gujarat Fluorochemicals⁹⁷⁻⁹⁹, Solvay¹⁰⁰ and others in filing multiple patents claiming such a “NFPA Technology” for various products (Table 1).¹⁰¹

Table 1: Industrial developments of non-fluorinated polymerization aids (NFPA) technology in the manufacturing of fluoropolymers.

Type of Fluoropolymer	Reference
PTFE Aqueous dispersions	89,93
PTFE Fine powders	90,94
PVDF	88,93,95
FKM	89,92,95
PFA	94

FKM stands for poly(VDF-*co*-HFP) or poly(VDF-*ter*-HFP-*ter*-TFE) copolymers while PFA means poly(TFE-*co*-perfluoroalkyl vinyl ether) copolymer, respectively.

However, the use of NFPAs in a specific recipe (for example, in aqueous radical polymerization of M1 fluoromonomer, e.g., TFE), does not necessary lead to the same success for that of another M2 monomer; e.g., VDF or a mixture of various fluorinated comonomers). The legislation process should be focused on the use of FPA and the emissions of fluorinated derivatives. In this regard, a regulatory decision tree was suggested¹⁰¹ (Figure 6), linked to the manufacturing FPs in presence or absence of such surfactants

(with process abatement to get a PFAS concentration lower than 25 ppb³⁸), essential use criteria in terms of safety, performance, health, improvement of the process and alternatives.

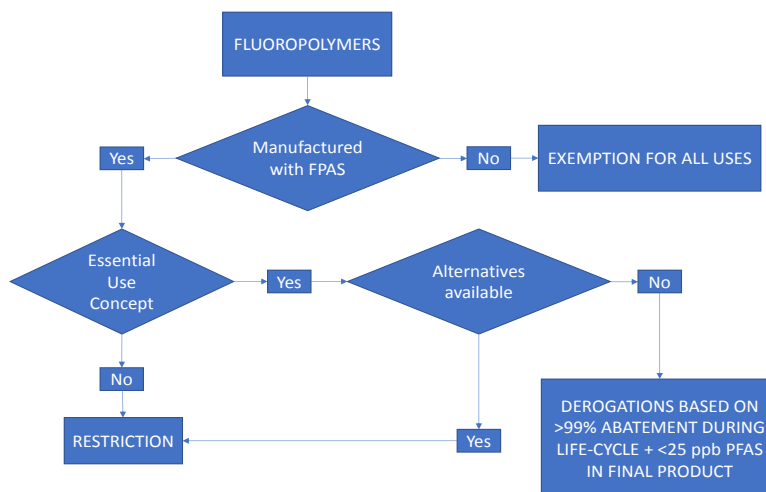


Figure 6: Regulatory decision tree for fluoropolymers (reproduced with permission from Lexxion¹⁰¹).

Hence, FPs produced without any FPAs should be exempted for all uses across all industries including consumer applications as they raise no risk to environment, to mammal and to the human health, in addition to the fact that FPs also match the PLC criteria.

ii) Manufacturing modification. The second action taken by many FP manufacturers aimed at changing their process to eliminate fluorinated side-products such as residual reactants, oligomers, low molar mass-derivatives and intermediates, aqueous residues and volatiles. Actually, improving the abatement processes and PFAS recovery in the manufacture of FPs have enabled the reduction of 99% of fluorosurfactant emissions since the 1990s¹⁰² while recent studies have brought it as high as 99.99%.¹⁰³ For example, though severe analyses were published in the last decade¹⁰⁴, the Arkema Company strongly reacted and announced that, since February 2023, this innovative solution made it possible to reduce C₆F₁₃-telomer sulfonates (6:2 FTS) emissions by more than 90% and that emissions of such a telomer now represents less than 1 kg per day¹⁰⁵ in the FP manufacture in Pierre-Bénite (France) without the use of any fluorosurfactants. Actually, by the end of 2024, a similar process will equip all its other production sites around the world.¹⁰⁵

Other companies have also been modifying their process to significantly reduced their emissions, many of them having announced such strategies.¹⁰⁵⁻¹¹¹ An abundant literature is available in relation to the control and treatment of emitted PFASs from industrial processes⁴³⁻⁴⁵ while many studies are still ongoing.^{39,113}

4.2.2.3. Polymer of Low Concern criteria. More recently, the American Chemical Council led the Fluoropolymer industry Group (*Fluoropolymergroup*) to investigate a similar study on 14 additional fluorinated (co)polymers.⁹⁰ FPs and the Stockholm Convention persistent organic pollutants (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria.

According to OECD definition,^{1,36,114} the criteria of polymers of low concern (PLC) that result from the combined experience and knowledge of global regulatory authorities on predictive parameters of health and environmental hazards induced by polymers have been extensively reported in several reviews.¹¹⁴⁻¹¹⁶ Indeed, to be regarded as a PLC, a polymer must not have any known hazard classification while they also should commit to the following criteria:

i) a high average molar mass in number (M_n) and a minimum oligomer amount are the most important requirements for PLC assessment, as claimed by EU:¹¹⁵ *“most potential health concern polymers have a low number average molecular weight, M_n , (< 1000 Da) and an oligomer content $>1\%$.”* The higher the amount of oligomers, the more the polymer ecotoxicological.¹¹⁴ Actually, by comparing the potential health concern of polymers with varying the oligomer percentage, *“the distribution of potential health concern polymers showed an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content”*.¹¹⁴

ii) Reactive functional groups (RFG) requirements;

iii) solubility in solvents and in water lower than $10 \text{ mg} \cdot \text{L}^{-1}$;

iv) other criteria such as a low cationic density, not containing any CF_2 or CF_3 groups; being stable under the conditions in which it is used. The primary concern for such FPs is its degradation in the environment to release persistent, bioaccumulative or toxic products, not being a high molar mass water absorbing polymer ($\geq 10,000 \text{ g} \cdot \text{mol}^{-1}$) and not having any known hazard classification.

Indeed, regarding the RFGs and RFG ratio to M_n ,^{90,115-116} FPs fulfill the PLC criteria. PTFE most typically bears terminal $-\text{CF}_3$ groups³⁶ that is not considered as an RFG. Furthermore, M_n value is an important feature of biological effect because very large molecules (>1000 – $10\,000$ Da) are too big to cross the cellular membrane¹¹⁷⁻¹¹⁹ and thus cannot react with “target organs,” such as the reproductive system. Hence, as the M_n of a polymer increases, a reduced incidence of potential health concern effects might be expected,¹¹⁴ and, as a proof, expended PTFE (e-PTFE) materials are currently used for stents, cardiovascular prostheses, and many other medical items.⁸⁰⁻⁸¹

In contrast and as expected, a polymer is not suitable to the PLC criteria if it decomposes considerably, degrades or depolymerizes during use. In other words, it undergoes a deep modification into simpler, lower molar mass-chemicals as the result of oxidation, hydrolysis, heat, sunlight, attack by solvents or microbial action or any other reaction(s). Indeed, FPs are resistant to such reactions/decompositions.⁵⁹ Based on such relevant features and above PLC criteria, Henry et al.³⁵ supplied key-evidences on four main FPs (PTFE, FEP, PFA and ETFE) matching the 13 PLC criteria.¹²⁰ By gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) analyses, these authors characterized the extractible fractions from these FPs and detected less than 2 ppm leachable from PTFE (Table 2).³⁵ As expected, since the monomers are gases, they were not detected.

Advantageously, as most FPs, PTFE is insoluble in water and, therefore, is not mobile in the environment. Using the descriptive solubility table for the US Pharmacopeia,¹²¹ the water solubility of PTFE would be classified as insoluble (10^{-5} mg . L⁻¹ or 0.01 mg . L⁻¹) to very slightly soluble (10^{-4} mg . L⁻¹ or 0.1 mg . L⁻¹).

Table 2: Results of gas chromatography/mass spectrometry and liquid chromatography/mass spectrometry analyses of extractible fraction from PTFE to match the PLC criteria (readapted with permission from Wiley)³⁶

Final PTFE Results		
Properties of interest	Concentration	PLC Criteria
*% oligomer	Not detected	< 2% wt/wt (20,000 ppm)
**residual monomers	Not detected	No Limit Established by OECD, 2009
low molar mass leachables & extractables	#2 ppm	No Limit Established by OECD, 2009

*Polymers with potential health concern have an increased incidence of higher oligomer content that began at 5% for <1000 Da and 2% for <500 Da oligomeric content (OECD, 2009). The table lists the lower limit, 2%.

**The data set used by OECD¹¹⁴ to establish the PLC criteria was insufficient to establish a universal limit for all residual monomers, though residual monomer content was established as a PLC criteria.¹⁰⁸ According to U.S. EPA's Safer Choice criteria (SCP, 2015), TFE is a residual of concern, which is not allowed to be present in Safer Choice recognized products at 0.01% or higher. There is no specific limit on residual monomer in the PLC criteria.¹¹⁴

#Isopar K, an unavoidable ambient air contaminant adsorbed to the PTFE fine powder, was detected at ≤ 2 ppm.

The polymer policies of 10 countries, including the EU REACH handling of polymers, were examined¹¹⁴ and concluded that “Polymers with <1% of M_n <1000 Da and low water

extractivity are not able to cause systemic effects which are toxicologically or ecotoxicologically relevant.” In the case of high molar mass-FPs, such characteristics are not observed (Table 2).

Among all FPs, PTFE is not a substance currently registered under REACH regulations supplying the definition of a polymer substance: “*a molecule that contains a sequence of at least 3 monomer units, which are covalently bound to at least one other monomer unit or other reactant*”.¹²² But, because PTFE, as all FPs, is an identifiable organic substance, the suggested Universal Basic Asset (UBA) framework for assessment using the proposed PMT criteria (persistent, mobile and toxic) would be applicable. Moreover, PTFE is highly stable in the environment and is resistant to thermal degradation. Being stable for years at temperatures up to 260 °C;^{36,123,124} it is stable to hydrolysis, oxidation, and light, as well as to anaerobic and aerobic degradations.¹²⁵ Therefore, PTFE would fulfill the UBA’s proposed persistence criterion.

As stated by USEPA, regarding PFAS and PFCA, the regulatory agency suggests a clarification about the nature of the linkage, stating “*How these materials are incorporated into the polymer is immaterial (they may be counter ions, terminal/end capping agents, or part of the polymer backbone)*.”¹²⁶ Surprisingly, the key characteristic is the presence of a –CF₃ group that is attached to, or forms part of, the polymer backbone and “*this link (between the polymer backbone and the –CF₃ group) is susceptible to degradation and cleavage*.”¹²⁶ Thus, in a USEPA’s report, the presence of –CF₃ group is relevant since it is a structural alert to consider potential degradation products.¹²⁷ This statement is quite surprising since a CF₃ end-group prevents from depolymerization by unzipping.⁵⁹

As listed in Table 2, these FPs are not subject to degradation.

Another advantage of PTFE deals with its non-toxicity. Thanks for a too high (several million) average M_n of PTFE mentioned above, it cannot cross the cellular membrane, indicating it is not toxic or bioavailable. Indeed, this polymer has been extensively tested in the European Union and USA to allow commercial applications for global medical device regulations, food contact, and surgery.⁷⁷⁻⁸¹ Furthermore, FPs contain none or tiny monomer(s) (which are gaseous), oligomer(s), and leachable amounts and no reactive functional groups with high toxicity (Table 2).³⁶ These comparisons of PLC and various regulatory assessment criteria demonstrate that, in contrast to conventional PFASs, high molar mass-FPs display quite different characteristics. Therefore, they should fall in a separate class of materials that must be determined on their own features.

More recently, the American Chemical Council led the Fluoropolymer industry Group (*Fluoropolymergroup*) to investigate a similar study on 14 additional fluorinated (co)polymers.⁹⁰ FPs and the Stockholm Convention persistent organic pollutants (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria. Actually, their physico-chemical properties prevent bioavailability, bioaccumulation, toxicity, and degradation. Presently, 96 % of FPs fulfill these 13 PLC criteria.

4.2.2.4. Recycling, End of Life and Reuse of FPs. Recycling is the re-introduction of utilized compounds (or polymers) into the cycle of products (i.e., polymers in the context). They are collected, sorted and refined to be re-used as materials or energy source. Recycling should help to preserve resources and to avoid waste.¹²⁸⁻¹³⁰ Indeed, the recycling of plastics is a real challenge¹³¹⁻¹³³ since only ca. 9% of polymers is recycled, less than three time more that of FPs.¹³⁴ The global plastics production was 460 million tonnes (Mt) in 2021,¹³¹ predicted to reach 1120 Mt annually by 2050¹³² and should increase up to 1231 Mt by 2060. In the 2000-2019 period, the growth of plastics has outpaced that of economic growth by almost 40%. MacLeod et al.¹³³ highlighted the global threat induced by the plastic pollution, based on the high environmental persistence of plastics. In contrast to commodity polymers, the consumption of FPs represents a quite small volume (estimated to 330,300 metric tonnes in 2021⁶⁴, hence representing less than 0.1% among all polymers). In 2015, its global consumption was 270 kt evidencing a 22.2 % increase since then. Actually, the global situation on the fate of FP waste is as follows: 83.5% of incineration, 13.1% landfill and 3.4% of recycling,¹³⁴⁻¹³⁵ briefly summarized hereafter.

i). *Different techniques of recycling.* FP waste from commercially available and industrial waste manufacturers are either pre-sorted or arise from dismantling processing or can also be incinerated for energy recovery. Fractions of pre-sorted FP waste are devoted to recycling, either to be exported for recycling in various countries¹³⁴⁻¹³⁶ or to domestic recyclers. Other recycling includes sintering, re-grinding or chemical recycling of FP materials. Four main ways of recycling are possible:¹²⁸ i) primary (or mechanical) recycling; ii) secondary recycling; iii) tertiary recycling and iv) quaternary (or energy) recycling.

ii) *Decomposition and recycling of FPs*

Several examples are supplied here after:

PTFE. The thermal degradation and pyrolysis of PTFE was studied by many authors. In 1947, it was pioneered by Lewis and Naylor (under vacuum at 600 °C);¹³⁷ 9 years later, by Wall and Michaelson (at 450-510 °C, under the presence of various gases),¹³⁸ then reported by Simon

and Kaminski¹³⁹ (who pyrolyzed PTFE at 500–600 °C in a fluidized bed reactor, the primary products of decomposition being TFE and $\cdot\text{CF}_2\cdot$ bisradicals) and comprehensively described by Ellis et al.,¹⁴⁰ followed by Schlipf and Schwalm,¹⁴¹ further up dated by Puts and Crouse,¹⁴²⁻¹⁴³ carefully reviewed by Lakshman and Chakraborty in 2015 in a book.¹⁴⁴ Puts and Crouse,¹⁴²⁻¹⁴³ could deeply detect and quantify the released fluorinated compounds (especially fluoroolefins and octafluorocyclobutane, OFCB) in the pyrolysis of PTFE from 35 °C to 800 °C in presence or absence of various metals or salts. These authors highlighted that, in absence of salts, TFE was produced in 98% while the nature of the salt induced other released gases with the influence of inorganic oxides of Al, Cr, Co, Cu, Fe, Ga, In, La, Mn, Ni, V, Zn and Zr (Scheme 2).¹⁴²⁻¹⁴³

Industrially, while various thermal processes (smoldering, pyrolysis, open burning, etc.) were claimed in the patent literature (recently summarized),¹³⁶ reuse of fluoromonomers have scarcely been reported, as scaled up in a pilot plant at Dyneon Company,¹⁴⁵⁻¹⁴⁶ (Figure 7) via a robust process so-called “*FP upcycling technology*” yielding more than 90% TFE/HFP. This technology was scaled-up into a new demonstration plant (capacity is presently >500 tonnes year).

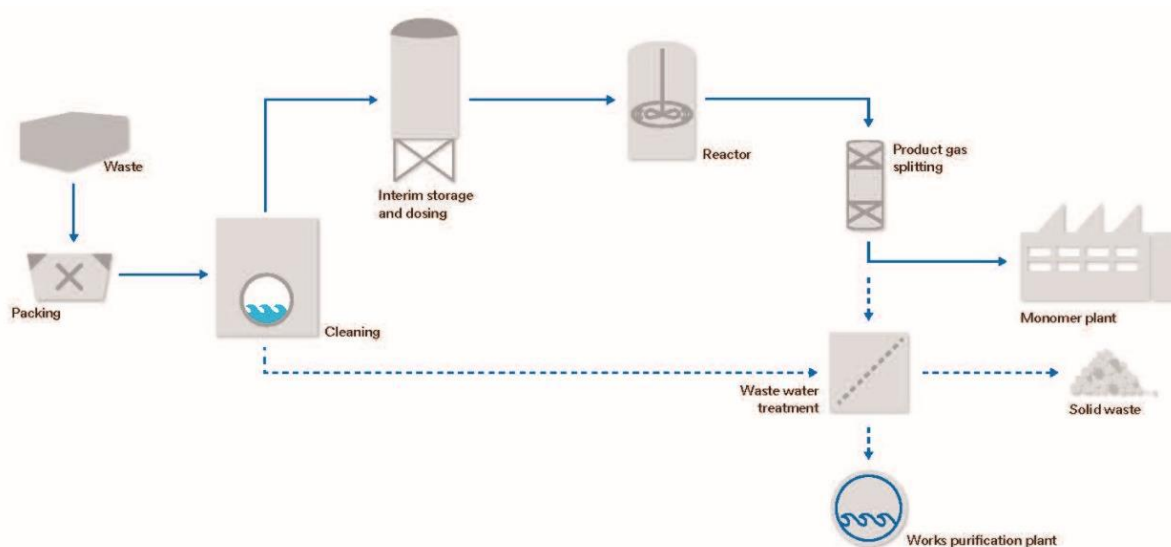


Figure 7: Sketch of the world’s first pilot plant for recycling perfluorinated polymers in Germany¹⁴⁵ (with courtesy from 3M/Dyneon).

Recycling of other thermoplastics. The Arkema Company¹⁴¹⁻¹⁴² claims to use PVDF copolymers as processing and recycling aid (PPRA) for polyethylene and polypropylene films, pipes, cables, and injection molded parts. Such a PPRA increases output and flow,

enhances surface finish, reduces extruder pressure and allows a steady gauge control and a processing at lower temperatures. This company has involved a process which enables 20-30% only of recycled materials before losing some feature and being reprocessed up to 90 or even 100% recycled materials to make such above items.¹⁴⁷ Materials already containing the PPRA recycle behave almost the same as a virgin material in which polymer processing aid (PPA) was added as a master batch at the extruder.¹⁴⁸ PVDF and VDF copolymers are currently assisting the reprocessing of high-volume polyolefins as a PPRA. In addition, Takahara's group¹⁴⁹ reported that PVDF used for fishing lines could not be degraded by UV radiation and biodegradation and thus, may be recycled after use.

Recycling of Fluorinated Elastomers. The recycling of fluorinated elastomers has been reported in a few studies, well-summarized by Schuster et al.¹⁵⁰ These authors reported only two relevant methods to achieve the recycling of poly(VDF-*ter*-HFP-*ter*-TFE) terpolymers (also named FKM) in an industrially acceptable way by i) milling FKM into fine powders to be mixed to virgin FKM and ii) the mechanical devulcanization of FKM, followed by successive compounding with virgin rubber. Both techniques give suitable thermostable products by preserving the mechanical features of original FKM. Indeed, these authors' review cites many patents mainly while the quoted articles just refer to the degradation and not to de-vulcanization. These authors concluded that recycling FKM is possible and leads to products with competitive properties to those obtained in presence of virgin FKM. But, as known, Schuster et al.¹⁵⁰ stated that fluorinated elastomers are usually crosslinked and thus recycling is rather complex in addition to the fact that they also contain fillers and additives.

Degradation and recycling of perfluorosulfonic acid membranes. Another key-functional FP is a copolymer based on TFE and a perfluoroalkyl sulfonyl fluoride vinyl ether further processed into proton exchange membranes for fuel cells, PEMFC, such as Nafion®, Flemion®, Fumion and Aquivion®, called perfluorosulfonic acid (PFSA) membranes (Figure 8).¹⁵¹ These high performance polymers are also involved in chloro-alkali process to produce chlorine and sodium hydroxide from brine, desalination for drinkable waters, and electrolyzers able to produce "clean" hydrogen from water. Though the thermal degradation of Nafion® N117 membrane was reported by Feng et al.¹⁵² or by Zaton et al.¹⁵³, its recycling is really challenging.

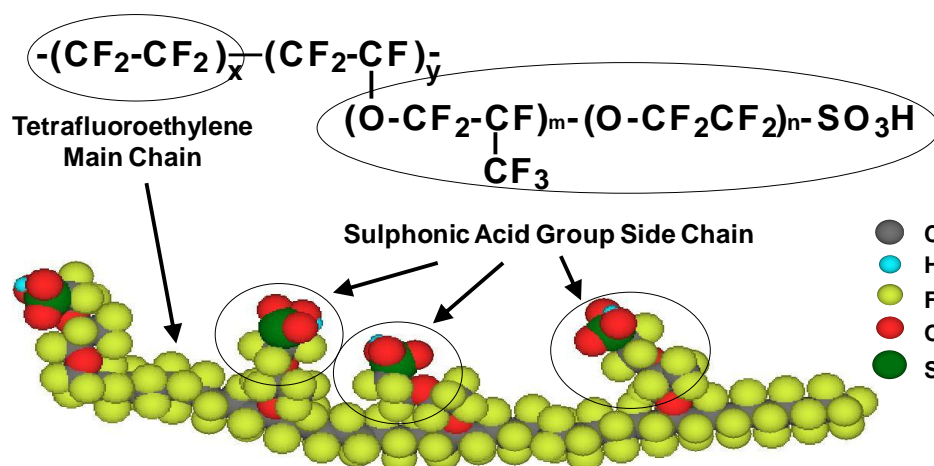
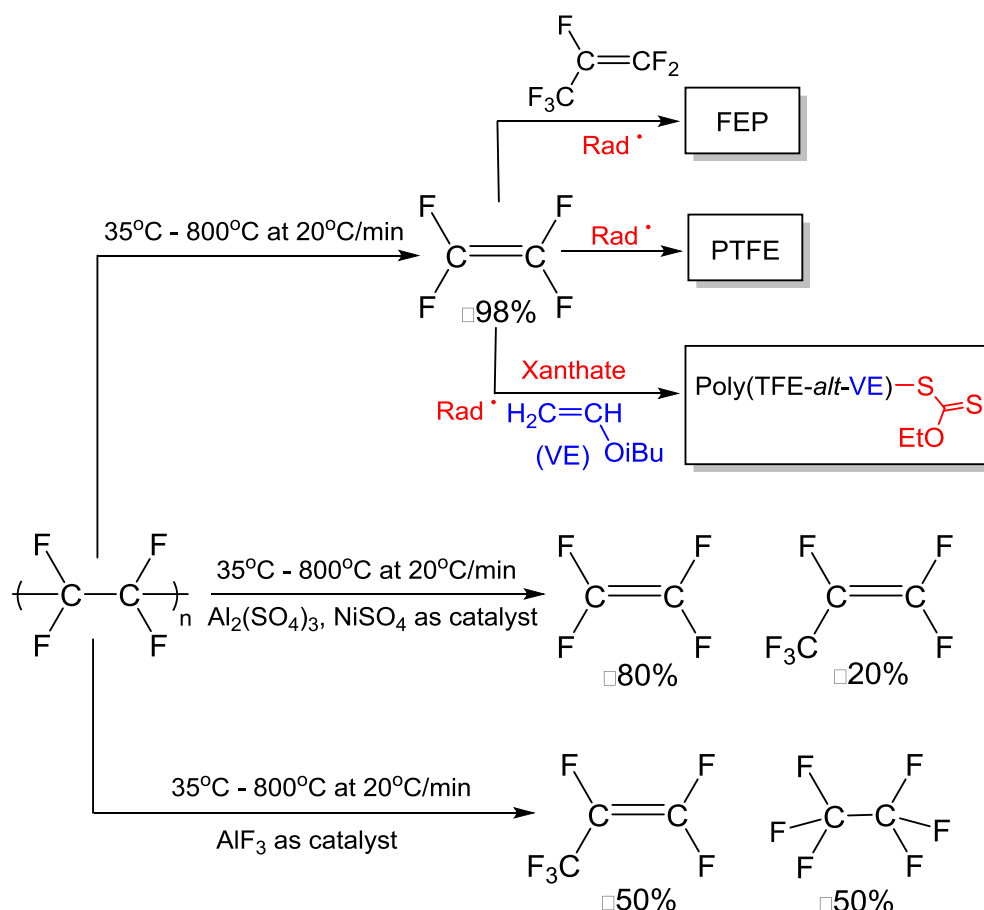


Figure 8: perfluorosulfonic acid (PFSA) for PEMFC membranes used in fuel cells and electrolyzers (reproduced from RSC,2016)

Nowadays, no alternative is foreseen to be able to substitute such highly performance materials,^{9,59,63,83-84} essential to the functioning of the hydrogen value chain and electrolyzers. These are produced and used in a highly controlled industrial environment, where their emissions are negligible and, due to their high initial price, their reusability and recyclability are actively investigated. So far, a patent from Grot¹⁵⁴ (by dissolving the membrane and separating the components), a report from Park¹⁵⁵ and a British Research and Innovation project, called Frankenstack¹⁵⁶ (dealing with the recovery and reuse at the end of the lifecycle membrane) are the only documents describing the recycling of PFSA membrane.

4.2.2.5. Chemical recycling to monomer and reuse of the released fluoromonomers. The chemical recycling of FP to fluoromonomer (CRM) is a real challenge. One example is illustrated by Scheme 2 that represents the depolymerization of PTFE into TFE or other fluorinated compounds according to the conditions. Actually, the generated TFE could be involved in various reactions enabling to close the loop: i) in radical homopolymerization initiated by peroxides or persulfates to lead to PTFE¹⁵⁷; ii) by conventional radical copolymerization of either HFP¹⁵⁸ or isobutyl vinyl ether (iBuVE)¹⁵⁹ to produce either poly(TFE-*co*-HFP) copolymer (or FEP) or alternated poly(TFE-*co*-iBuVE) copolymer (as commercially available Zeffle® homologues¹⁶⁰), and finally iii) under reversible addition–fragmentation chain-transfer (RAFT) copolymerization of TFE and iBuVE, controlled by a xanthate, to yield well-defined poly(TFE-*co*-iBuVE) copolymers.¹⁵⁹



Scheme 2: Thermal decomposition of PTFE in absence or presence of various metals or salts to lead back to TFE (and other fluorinated compounds).¹⁴²⁻¹⁴³ The recovered TFE was homopolymerized,¹⁵⁷ or copolymerized with HFP¹⁵⁸ or isobutyl vinyl ether (iBuVE)¹⁵⁹ to produce either PTFE, poly(TFE-*co*-HFP) copolymer (i.e., FEP) or alternated poly(TFE-*co*-iBuVE) copolymer.¹⁵⁹

Anastasaki et al.¹⁶¹ reported the catalyst-free depolymerization of poly(2,2,2-trifluoroethylmethacrylate), PTFEMA, at 180 °C. This polymer was previously synthesized by reversible addition–fragmentation chain-transfer polymerization (RAFT) of TFEMA controlled by a trithiocarbonate (TTC). The kinetics of depolymerization, monitored by ¹H NMR spectroscopy, evidenced the unzipping reaction and evidenced that at the end of the reaction only TFEMA and the TTC remained in the flask (Figure 9). Though it required heat, that reaction did not need any toxic reactants.

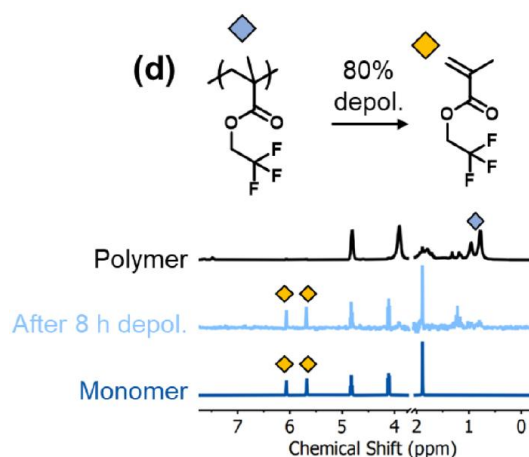


Figure 9: reaction scheme of the thermal depolymerization of poly(2,2,2-trifluoroethylacrylate), PTFEMA, and ¹H NMR spectra of PTFEMA (up), of the total product mixture after 8 hrs (middle spectrum) and of TFEMA after depolymerization (bottom). (copyright reproduced with permission from Amer. Chem. Soc)¹⁶¹.

4.2.2.5. Reuse of degraded FP

Bai's team¹⁶² described that commercially available FKM elastomer [poly(VDF-*co*-HFP) or poly(VDF-*ter*-HFP *ter*-TFE) fluoroelastomers, $M_n > 300,000 \text{ g.mol}^{-1}$], the average molar mass in number and dispersity of which were $M_n=134,000 \text{ g.mol}^{-1}$ and PDI=3.7 (while the VDF:HFP molar ratio was 3:1) could undergo a tertiary recycling yielding to cooligomers. The M_n of these latter was ranging between 3,300 and 10,400 g.mol^{-1} . This reaction occurred in presence of sodium hydroxide, hydrogen peroxide and triethyl ammonium chloride. These transparent dicarboxyl telechelic cooligomers were first chemically changed into diacrylates and then photocrosslinked. The resulting network exhibited suitable mechanical and hydrophobic properties.¹⁶²

A more recent work on the use of FEP waste for transparent soils was achieved by the coating of specific terpolymers onto such waste (thanks to Fluorine-Fluorine interactions). The growing of lettuce roots was monitored by optical system and the roots were able to live in such an environment.¹⁶³

4.2.2.6. Incineration

Incineration is the last method to process end of life of FPs. Recent studies on the disposal of end-of-life PTFE have highlighted the incineration to be an appropriate way to dispose of FP too, with no environmental concern. It is a high-temperature flaming process, happening in open air space, whereas smoldering is a flameless combustion process that occurs on the surface of a condensed fuel. While both methods can be utilized to decompose fluorinated

waste, the main difference is that smoldering is self-sustaining and, hence, is more energy efficient compared to incineration which needs a continuous energy input.

Table 3: FPs and their main decomposition products at various temperatures from in the literature. In parenthesis: PFC-code¹⁶⁵ (reproduced with permission from Norwegian Institute of Air Research).

Polymer	T (°C)	Main products	References
PTFE	450	COF ₂ , HF	124
	400~500	TFE, HFP, PFIB	166
	500	HFP, TFA	140
	530	CF ₄ , C ₂ F ₆ , TFE, HFP, <i>c</i> -C ₄ F ₈ (<i>c</i> -OFCB)	167
	550	CF ₂ O, C ₂ F ₆ , CF ₃ CFO, C ₅ F ₄ , CF ₃ CF ₂ CFO, (CF ₂) ₃ O ₂	168
	600-700	TFE, OFCB	169
	750-800	HFP	169
	850-900	PFIB	169
	800°C	CF ₄	124
	>900 °C	C ₂ F ₆	124
	850	HFP, TFE	170
	750-1050	C ₂ F ₆ , CF ₄	170
ETFE	350	COF ₂ , PFBE, TFE, CO	124
ECTFE	500	TFA, CDFA	124
FEP	400	COF ₂ , HFP, TFE, PFIB	124
PFA	400	COF ₂	124
PEEPE	500	TFA	140
CPTFE/	500	CPFP, CDFA	124
PCTFE			
PTFE/PFA +	800	CH ₄ , CHF ₃ (HFC-23), C ₂ F ₆ (PFC-116)	171
PTFE/FEP			

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PTFE	450	COF ₂ , HF	124
	400~500	TFE, HFP, PFIB	166
	500	HFP, TFA	140
	530	CF ₄ , C ₂ F ₆ , TFE, HFP, <i>c</i> -C ₄ F ₈ (<i>c</i> -OFCB)	167
	550	CF ₂ O, C ₂ F ₆ , CF ₃ CFO, C ₅ F ₄ , CF ₃ CF ₂ CFO, (CF ₂) ₃ O ₂	168
	600-700	TFE, OFCB	169
	750-800	HFP	169
	850-900	PFIB	169
	800°C	CF ₄	124
	>900 °C	C ₂ F ₆	124
	850	HFP, TFE	170
	750-1050	C ₂ F ₆ , CF ₄	170
ETFE	350	COF ₂ , PFBE, TFE, CO	124
ECTFE	500	TFA, CDFA	124
FEP	400	COF ₂ , HFP, TFE, PFIB	124
PFA	400	COF ₂	124
PEEPE	500	TFA	140
CPTFE/	500	CPFP, CDFA	124
PCTFE			
PTFE/PFA + PTFE/FEP	800	CH ₄ , CHF ₃ (HFC-23), C ₂ F ₆ (PFC-116)	171

The incineration or combustion, differs from thermolysis in that a source of fuel is used in order to purposefully favor a complete degradation of FPs (as a source of trifluoroacetic acid or acetate, TFA, and chlorodifluoroacetic acid, CDFA).¹⁴⁰ Furthermore, due to the high temperatures and oxidizing conditions used, it is unlikely to produce environmentally significant levels of TFA or TFA precursors. On the other hand, low-temperature burning of domestic waste, as an important source of furans and polychlorinated dioxins to the atmosphere, may analogously be a huge source of fluorinated acids.

Incineration has been adopted by various countries.^{134-135,164-165} In the case of Norway,¹⁶⁵ though the municipal solid waste incineration (MSWI) conditions are achieved at about 850 °C, emissions of FP degradation products from household waste incineration have not been investigated yet. However, on the laboratory scale, the decomposition of PTFE and other FPs was comprehensive studied in the 700-1050 °C temperature range, yielding various main released products such as CF₄, CHF₃, C₂F₆, TFE, HFP and OFCB (Table 3).^{124, 140,165-171}

Most of these substances are non-toxic, but highly toxic ones like perfluoroisobutylene (PFIB) or fluorophosgene (COF₂) may possibly be released under some severe conditions.

Wang et al.¹⁷² suggested that PFASs may be generated from FP waste via a MSWI process, probably at temperatures lower than 500 °C. Thanks to its high thermal and chemical stabilities, PTFE is inert in the environment and Taylor et al.¹⁷³ found that municipal waste incinerators operating with an average gas temperature of 1000 °C can be used to totally decompose PTFE.

In contrast, in Germany, Aleksandrov et al.¹⁷⁴ reported that the incineration of PTFE, using best available techniques (BAT), did not release any PFAS. By comparing with the possible formation of 31 PFAS compounds as references, these authors noted that PTFE could almost fully decomposed into fluorine (as HF) and concluded that the municipal incineration of PTFE should be considered as an acceptable form of waste treatment. They tested for the presence of 31 different PFASs and 11 of these were detected but deemed to be due to contamination from the environment. A constant mass flow of wood pellets was utilized while these authors added PTFE into the reactor to maintain a consistent thermal profile, as shown in Figure 10.

Furthermore, the Dutch Institute for Public Health and Environment (RIVM)¹⁶⁴ drew slightly fewer concrete conclusions, mentioning that, although it can be assumed that the polymers are destroyed with the gasification process, this does not provide enough information on the kind and degree of by-products formed and on the rate of mineralization.

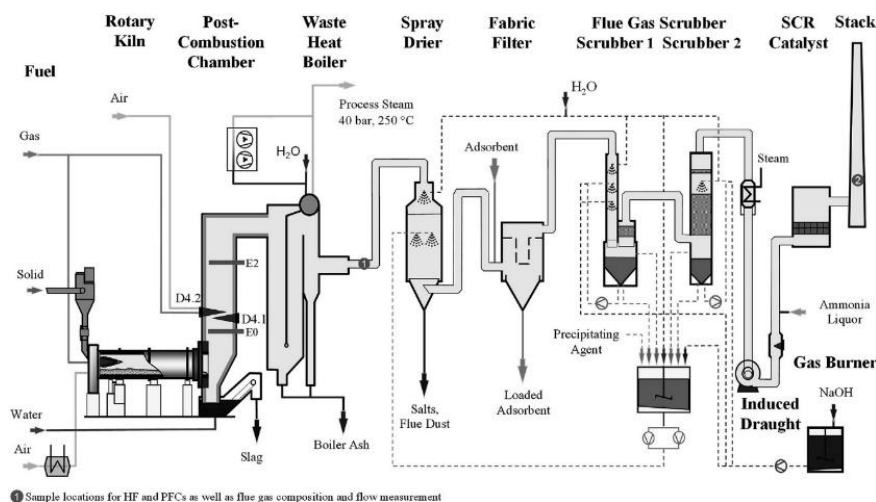


Figure 10: Engineering drawing of the German acronym for “*Brennkammer mit Dampfkessel*” (BRENDa) pilot combustion facility at Karlsruhe Institute of Technology.¹⁷⁴ (Reproduced with permission from Elsevier).

In EU, the overall situation of the fate of collected FP waste involved in recycling, recovery, reuse and landfill, proposed in the Conversio Report, is illustrated in Figure 11¹³⁴⁻¹³⁵ indicating that, globally ca. 23.5 kt of FP waste were collected in 2020 (< 0.01% of the total waste). To compare, ca. 29,450 kt of plastics were gathered in 2020 (<5% of the total collected waste excluding mineral fractions). Moreover, about 84% (20.4 kt) of the total FP collected waste in Europe in 2020 is either thermally or (co-)incinerated destroyed while 3.1 kt (13.1%) were landfilled. Finally, 0.81 kt were gathered separately for recycling whereas a significant amount was exported for recycling (e.g., to Asian countries).¹³⁰

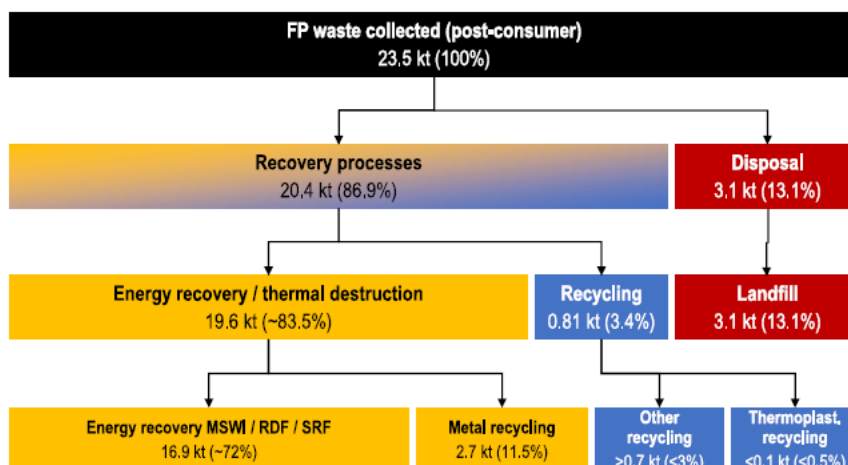


Fig. 11: Fate of collected FP waste and tonnages (percentages) involved in recycling, recovery, reuse and landfill in EU.¹³⁵

Beside incineration, more severe degradation of FPs can be obtained by various methods including smoldering, pyrolysis. These are efficient to treat fluorinated waste,¹³⁶ the first one being self-sustaining. As a high-temperature process used for thermal decomposition, pyrolysis is similar to incineration except it is achieved in an inert atmosphere. For an efficient degradation, a temperature greater than 900 °C is preferred. These techniques enable to lead to total destruction of released hazardous PFASs. Several studies have tested the efficiency of these methods to determine if they reach temperatures high enough for a sufficient duration enabling a complete degradation.¹⁷⁴⁻¹⁷⁵ Other techniques of incineration¹³⁶ such as mineralization (vide infra) of FPs during thermal treatment, or a plasma-based water treatment, are also being investigated as they may be safer and more efficient to treat waste.

4.2.2.7. End-of-life

Several authors have studied the end of life of FPs.¹³⁶ Actually, when a FP has fulfilled its intended use and will be disposed of, the fate of FPs must be investigated. Many reports have concluded that FPs such as PTFE do not degrade in the environment and do not release any hazardous compounds toward mammals, human beings and for environment.^{102,123,165,176,177} Thus, the downstream, end-of-life process of incineration should lead to more studies.

In addition, though FPs match the PLC criteria (section 4.2.2.3.), circular economy of FPs deserves more interest, and to our knowledge, Wahlström et al.¹⁶⁵ have comprehensively proposed an overall situation including several flows (Fig. 12) ranging from the manufacture of FPs to their use and their recycling (also analyzing the depolymerization of PTFE into TFE as explained in sections above).

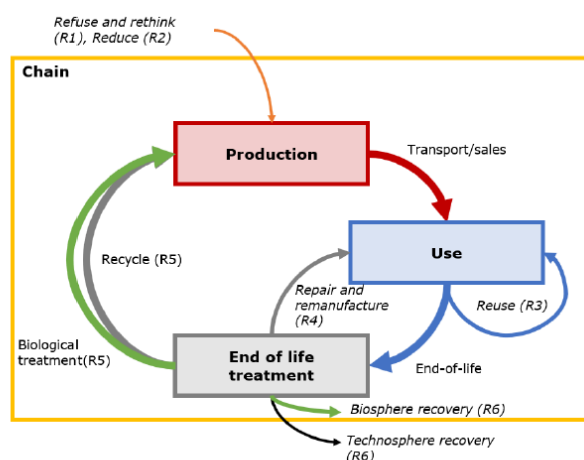


Fig. 12: Sketch of flows of materials in a circular economy¹⁶⁵ (reproduced with permission from the European Topic Centre Waste and Materials in a Green Economy).

The Conversio report¹³⁴ extensively provided the results of the treatment of FP waste by industry segments (automotive, aerospace, semiconductors, electronics⁷⁶ and chemical industries) in the EU in 2020 regarding collected waste, energy recovery, landfill and recycling as well as co-treatment of FP and associated waste streams. Figure 13 represents the overall circular economy situation of FPs in EU, involving pre-consumer processing losses during the manufacturing of FP products and applications.¹³⁴⁻¹³⁵ Most FP are (co-)incinerated in MSWI plants or dedicated hazardous waste incineration plants which are treating different wastes from chemical waste producers. Indeed, two main ways of recycling have been used (Figure 13): the mechanical and the chemical ones enabling to recycle melt processible FPs (such as PVDF or PFA) or non-melt processible ones (as achieved at Dyneon¹⁴⁵⁻¹⁴⁶ or Karlsruhe Institute of Technology¹⁷⁴) or virgin raw FPs.

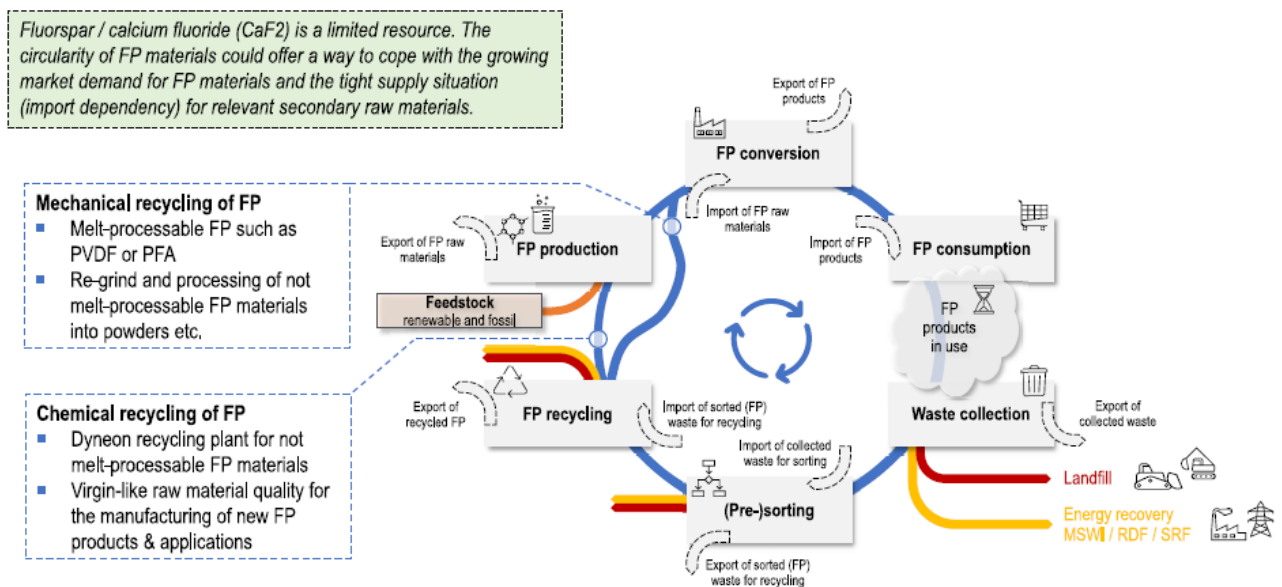


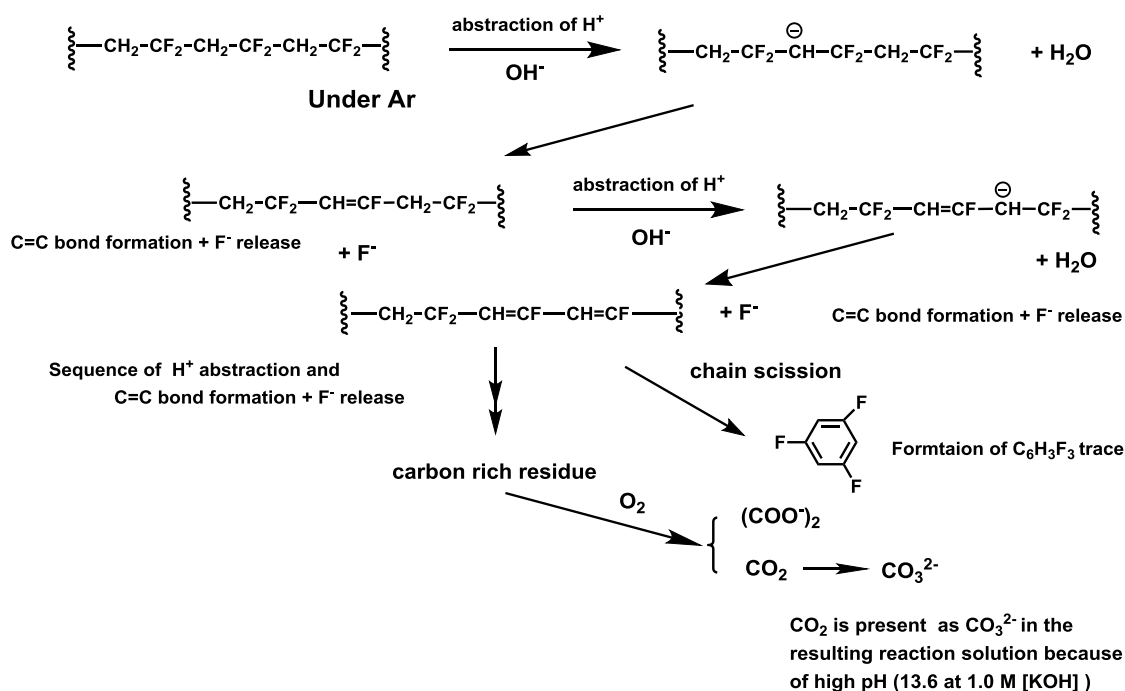
Figure 13: Circular economy situation of FPs: lifecycle of FPs from feedstocks extraction to end of life in EU¹³⁴

The processing of FP materials such as the machining of PTFE rods and cubes for the manufacturing of various milled and drilled parts results pre-consumer FP processing losses. Actually, ca. 20 - 25% of FP producers claim to get their own internal re-processing steps for their process losses. These are the cases for Dyneon,¹⁴⁵⁻¹⁴⁶ Arkema¹⁴⁷⁻¹⁴⁸ and other companies. Then, 30 - 35% report to send their pre-consumer FP waste to external material re-processing companies while 15% exported their pre-consumer wastes to other companies inside the EU. 5 - 10% mention that their FP processing losses are exported outside the EU for re-processing,

e.g., to Asian countries.¹³⁰ Finally, 5% of them state that they do not have any information on their process losses. These companies usually sub-contract waste companies.

4.2.2.8. Mineralization

A totally degradation of FPs is desired to avoid any release of oligomers that imparts severe persistent and toxic issues. The mineralization, that yields to fluoride anions, appears as an attractive and environmentally friendly method. As reported for low molar mass-PFASs,⁴⁴ the mineralization of FPs has been deeply studied by Hori's group since more than 10 years, by means of subcritical (or superheated) water.¹⁷⁸ These conditions can be reached at the critical temperature (374 °C) and pressure (> 22.1 MPa) of water¹⁷⁸⁻¹⁸⁴ for which this fluid displays low viscosity, high diffusivity, and ability to hydrolyze and mineralize many organic compounds. Indeed, reactions requiring subcritical water are considered environmentally benign with the goal at recycling the fluorine element. In the case of FPs, from this technique, Hori's team mineralized PVDF,¹⁷⁹⁻¹⁸⁰ (decomposed into F⁻ and CO₂) as well as VDF copolymers: poly(VDF-*co*-HFP),¹⁸⁰ poly(VDF-*co*-CTFE),¹⁷⁹ poly(VDF-*co*-PMVE)¹⁸¹ and poly(VDF-*co*-MAF)¹⁸² copolymers (where MAF stands for methacrylic acid) and poly(VDF-*ter*-HFP-*ter*-TFE) terpolymer¹⁸³. This led to a *quasi*-complete mineralization of PVDF performed at 250 °C as well as for poly(VDF-*co*-HFP) and poly(VDF-*co*-CTFE) copolymers.¹⁷⁹⁻¹⁸⁰



Reaction under Ar: Efficient F^- formation + carbon rich residue

Reaction under O_2 : Efficient F^- formation + no residue

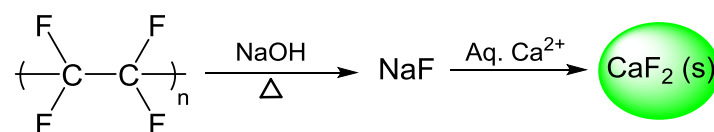
Scheme 3: Proposed mechanism for the H_2O_2 -induced decomposition of PVDF.¹⁸⁰ Reproduced with permission from Elsevier.

Scheme 3 supplies a suggested mechanism of the decomposition of PVDF. Advantageously, by reacting Ca^{2+} cations (from $Ca(OH)_2$) onto such released fluoride anions, these authors examined the CaF_2 formation¹⁸⁰⁻¹⁸³ to close the loop on the fluorine element, since CaF_2 is the source for all fluorinated compounds.

These authors also extended that strategy to the mineralization of poly(VDF-*co*-HFP) and ETFE copolymers¹⁸⁰ and PFSA membranes¹⁸⁴ in much more attractive conditions than those reporting the degradation of PFSA membranes generating perfluoroalkanoic acids¹⁵¹ and perfluoroalkane sulfonic acids.¹⁸⁵

A different approach from another Japanese team¹⁸⁶ involved molten alkaline metal hydroxide at 400-600 °C to mineralize PTFE. This two step-process allowed an efficient mineralization by chemical recycling. However, that process appears surprising since PTFE can be etched by liquid sodium and also degrades from 500 °C as seen in section 4.2.2.4. First, PTFE (as well as PVDF, PCTFE, and poly(VDF-*co*-HFP) copolymer) was decomposed into soluble alkaline fluorides *via* a degradation in such molten hydroxides at high temperatures and atmospheric pressure. Then, CaF_2 , considered the main source of the organofluorine chemistry, was produced by treatment of the former aqueous solution with

CaCl₂. When PTFE was heated with a large excess of NaOH at 500 °C, 74% yield of CaF₂ was obtained (Scheme 4) with respect to the initial PTFE amount.



Scheme 4: Proposed procedure for the mineralization of PTFE by molten NaOH¹⁸⁶ (readapted from Royal Society of Chemistry).

Indeed, such high temperatures are not far from thermal conditions to favor the unzipping depolymerization of PTFE^{102,137-144,157} and, consequently, for other less thermostable FPs than PTFE, the degradation should also happen, even without any base. These authors noted that i) there was no decomposition with molten NaOH below 400 °C whereas ii) from 600 °C yields of CaF₂ fell down to 46% (from 67% and 74% at 450 and 500 °C, respectively).

More recently, Sheldon et al.¹⁸⁷ reported that a nucleophilic magnesium reagent (Figure 14 and Scheme 5) could enable defluorination of PTFE powder under mild conditions (room temperature and 1 atm), releasing a molecular soluble magnesium fluoride coordination product (2) that was separated from the surface-modified FP. This kinetically stabilized species could be utilized as fluoride carrier and appeared more reactive than inorganic metal fluorides, MF(s) or MF₂(s), which suffer from high lattice enthalpies and high stability. This proof-of-concept evidences that the Fluorine atoms in PTFE can be harvested and reused in coordination synthesis.

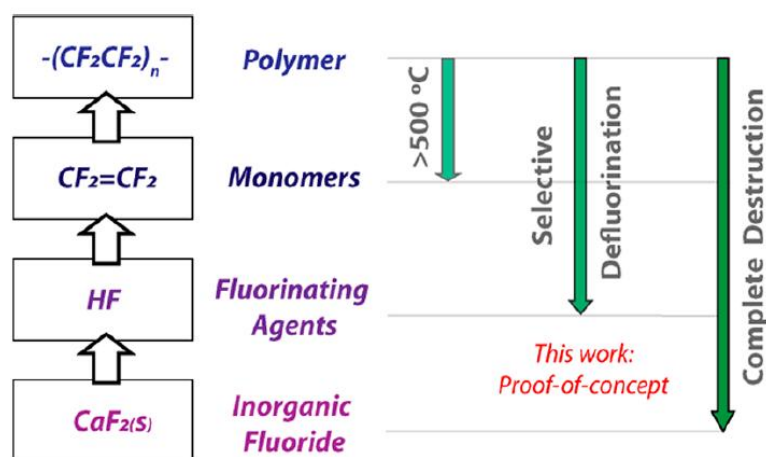
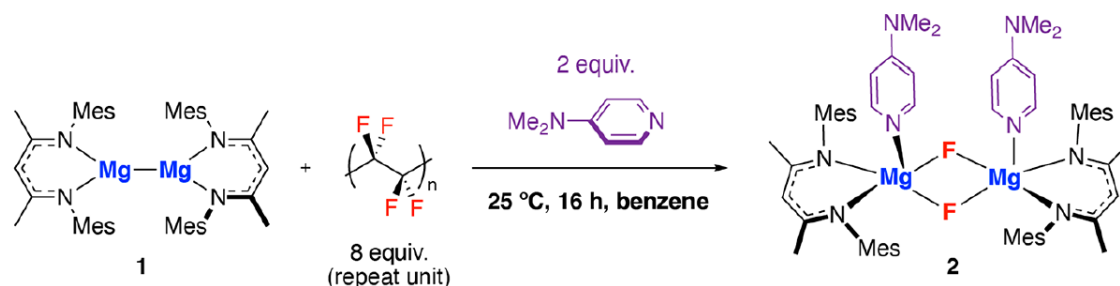


Figure 14: Cycle of Fluorine Chemistry from Fluorspar (CaF₂) to PTFE, along with potential routes for recycling, including the thermal depolymerization (above 500 °C), the selective

defluorination¹⁸⁷ to form fluorinating agents, and complete destruction back to inorganic metal fluoride. (Reproduced with permission from Amer. Chem. Soc.)



Scheme 5: Room temperature reaction of a nucleophilic magnesium reagent (1) with PTFE to generate an organometallic fluorinated magnesium complex (2).¹⁸⁷ (Reproduced with permission from Amer. Chem. Soc.).

Conclusions and Discussion

PFASs cover more than 12,000 synthetic compounds containing a carbon-fluorine bond. With such a broad scope, all PFASs are not the same and it is likely that the impact on the global industry of a possible restriction on PFASs will be a shocking prospect, particularly since the recent proposal does not differentiate between substances that may have different toxicity profiles, and applications. Indeed, the justification to launch a restriction on PFAS as a group is based on ‘persistence and other concerns’ related to these chemicals, and the fact that previous initiatives to regulate PFAS chemicals individually has resulted in substitution of one PFAS molecule by another molecule that also matches the PFAS definition, and may exhibit similar toxicological properties.

While most PFASs have not yet undergone toxicology assessments or been linked to health harms, many efforts have been devoted to the detection and remediation in both solid and aqueous media to ensure that contamination is limited to safe levels.

Because of their chemical composition, structure, and much higher molar masses, fluoropolymers are significantly different from other substances in the PFAS family. The only main reason for concern associated to FPs deals with the use of non-polymeric PFASs as polymerization aids during the manufacturing process (the radical polymerization in aqueous medium requires a hydrocarbon surfactant used since a couple of years).

With so high molar masses (several million for PTFE), FPs can not migrate through the cellular membrane, hence displaying their non-bioavailability and non-toxicity. Furthermore, since recent improvements in their manufacturing without any use of fluorinated surfactants

in addition to their high chemical, thermal and aging stabilities, they contain no or quite tiny oligomer or organic leachables. In addition, their physico-chemical properties prevent from bioaccumulation and degradation. Advantageously, as most FPs, PTFE is insoluble in water and, therefore, is not mobile in the environment. Consequently, the outcomes of such features (in addition to others of the 13 requirements) are that ca. 96% of the global commercial FPs satisfy the accepted OECD PLC criteria.

Actually, FPs exhibit exceptional properties while preserving their high performance even in aggressive chemical and thermal conditions. These niche technical polymers are stable to hydrolysis, UV, oxidation and to biodegradation. Their applications encompass health, safety, performance and functioning of the society and are used in strategic sectors and High-Tech industries (e.g., aerospace, electronics, energy, optics, medicine). Their relevant combinations of outstanding features are not observed by any of the alternative hydrocarbon polymers^{9,63,83-84} hence making them so unique and valuable. Presently, alternatives to FPs, which should be assessed based on the criteria such as *performance, safety, accessibility, resource efficiency, waste generation, cost, availability, stability and lifetime*, do not exist. Furthermore, various reports indicate that FPs (especially PTFE) have been extensively tested to fulfil the Japanese¹³⁰, US and EU food contact and global medical device regulations (e.g., Japan Pharmaceutical and Medical Device Agency, US Food and Drug Administration, Korea Ministry of Food, China Food and Drug Administration, and Drug Safety, including ISO 10993 biocompatibility testing and preclinical animal testing).

As presented throughout this review, FPs could potentially present environmental challenges across international borders. Since their inception and widespread commercial and industrial utilizations, these materials have become essential for many everyday applications and are not considered to be a health hazard during their typical life cycle. At end-of-life, possible low molar mass compounds which are dependent upon conditions may become an issue that needs to be easily detected and removed from the environment. Many techniques on remediation of PFASs have already been achieved.

FPs and the Stockholm Convention persistent organic pollutant (POP) criteria meet the persistence criterion only, but not the bioaccumulative, toxic, or mobile criteria.

Furthermore, the main concerns have been recently addressed, both in using NFPA and controlling >99 % PFAS emissions linked to appropriate abatement technology of the industrial FP productions. As a result, FPs produced with NFPA technology has led to a commercial success and further motivates the industry to work harder in this direction. In addition, various solutions are searched for recycling, reuse, circular economy and life cycle

analysis. In this vein, several occidental companies have already found strategies to depolymerize, recycle (“close the loop” even on pilot plant) or reuse FPs. Among the annual plastic production of more than 460 million tons,¹³¹ only 9 % has been recycled while the data fall down to 3.4% for FPs (for a yearly production of 330,300 tonnes⁶⁴). Further efforts on the recycling of clean FPs (e.g., PTFE), FEP, PFA and PVDF waste or scraps generated in the production has already been achieved (e.g., by Dyneon on PTFE, FEP and PFA at a pilot scale¹⁴⁵⁻¹⁴⁶, by Arkema company on PVDF^{147,148} and at Karlsruhe Institute of Technology¹⁷⁴), the recycling of FPs in consumer articles is not well-clarified because they are usually contaminated by several (inorganic) fillers and substances, which hamper that process.

Various studies have shown, on small and pilot (500 tonnes/year¹⁸⁸) scales, the ability to upcycle FPs back to their monomers (*via* the recycling to monomer) and to use the generated fluoromonomers (e.g., TFE) for further (co)polymerizations. Though such an approach to a closed loop economy for FPs has already been scaled up, it is expected that additional studies on recycling and reuse of FPs are currently continuing.

To overcome limitations of incineration (especially HF release), recent alternative processes regarding the thermal treatment (mineralization to release fluoride anions, precursor of CaF₂ as the starting point of the Fluorine Chemistry chain) of FPs either under subcritical water or with molten sodium or a Magnesium complex are quite relevant to close the loop and deserves to be further scaled up.

Research is needed to determine the possible emissions from thermal disposal of FPs. Furthermore, methods of the thermal degradation and waste treatment of polymers containing PFASs can be greatly expanded on to enable environmentally safe and conscientious processes. In addition, PTFE is known to undergo a quite low decomposition above the application temperature of 260 °C for months while 400 °C is requested to favor a major degradation. Hence, incineration may potentially degrade FPs and from 850 °C, a total decomposition is observed without releasing any PFAS. Such a growing topic allows evaluating efficient degradation temperatures, the potential to release compounds of incomplete combustion, deposition onto land, stack gas analyses and other risk factors. In addition, reactive extrusion processing has been reported as a versatile technology to recycle melt processible polymers,¹⁸⁹ and could be extended to FPs (except PTFE).

Though many reports evidence that FPs i) do not degrade in the environment or ii) do not generate harmful compounds, the incineration requires further innovations. Labelling should comply with eco-labelling standards and thus help the EoL managers in identifying and sorting the hazardous fluoropolymer waste from other plastic waste during the EoL process.

Though the demand of FPs is still increasing,¹⁹⁰ future works should deal with FP manufacture highlighting the safety, health, and environmental management practices, under applicable regulations.

FPS could be impacted by the upcoming restriction on PFASs under the EU REACH Regulation, the proposal of which was published on February 2023.³³ Much progress has been made in industry over the last years in relation to control of PFAS emissions due to their use in fluoropolymer production. The FP representative industry¹⁹¹, the *FluoroProducts and PFAS for Europe* group (which represent producers, importers, and users of fluorinated products and PFASs across Europe) have issued a six-point action plan, which includes derogations in key applications which are not time limited.

In addition, the FP industry in Europe¹⁹²⁻¹⁹³ evaluated the contribution brought by the FP manufacturers regarding revenue, investment and employments, while many more significant benefits can be released along the value chain via the use of FPS in many High-Tech applications.

For these reasons and because of their usefulness, inertness, non-toxicity, non-bioaccumulation, non-mobility and growing interest even in coming-up technologies, FPS cannot be in the scope of the PFAS restriction. Moreover, the main concerns linked to the industrial productions of FPS have been addressed (improvement of abatement techniques, removal of PFAS polymerization aids and introducing alternative technologies). They show that these high value-added polymers must be separated from conventional PFASs, are essential for everyday life and are irreplaceable materials.

Hence, the data presented demonstrate that the FP class of PFAS is well-defined, safe and an essential subset of PFAS. Though the dossier is still under evaluation³³ after more than 3000 answers to the consultation, the restriction of FPS under REACH regulations may significantly slow down the EU strategic sustainability ambition¹⁹⁴ as well as the Ecological transition. For example, in the hydrogen sector, such a PFAS ban without granting any exemption, would have catastrophic consequences on the industry's €30-billion worth of investment in a decade¹⁹⁵ (only including electrolyzers and fuel cells). Such a ban would also jeopardize up to 200,000 direct jobs and over 260,000 indirect ones within 10 years in a market with a potential value of € 820 billion employing 5.4 million people by the middle of the century.

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ACKNOWLEDGMENTS

The author thanks coworkers cited in the list of references below, the French Fluorine Network (Groupement d'Intérêt Scientifique, GIS) and [Programmes et équipements prioritaires de recherche \(PEPR\)](#) (Nouvelles Technologies de l'Energie).

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