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The universe of fluorinated polymers and polymeric substances and potential environmental impacts and concerns

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Abstract

Per- and polyfluoroalkyl substances (PFAS) are a diverse group of surface treatment chemicals falling under non-polymeric and polymeric categories. Polymeric PFAS are comprised of fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers (SCFPs).

Fluorinated polymers and polymeric substances have gained a significant market due to their chemical stability. To date, research and regulatory concern has primarily focused on the environmental occurrence and health effects of non-polymeric PFAS, particularly perfluoroalkyl acids and precursors. Industries consider most fluoropolymers as being “polymers of low concern”, although there is already a considerable environmental burden and widespread contamination resulting from their production, manufacturing and use. For example, SCFPs are widely used, and known to release their perfluorinated side chains. Concerted action is needed to address the dearth of environment-associated information and understanding on polymeric PFAS.

Keywords: Per- and polyfluoroalkyl substances; Fluorinated polymers; Fluoropolymers; Perfluoropolyethers; Side-chain fluorinated polymers; review
Introduction

Perfluoroalkyl substances (PFAS) are a diverse group of surface treatment chemicals although less than 6% of the estimated 4,730 PFAS are reported to be of global commercial relevance and can be divided into non-polymeric and polymeric categories [1]. PFAS have been produced and used for several decades including in electric and electronic devices, fire-fighting foams, photo imaging, hydraulic fluids, metal plating and textiles. Glüge et al. [2] carried out an overview and concluded there are more than 200 use categories and sub-categories for more than 1400 individual PFAS.

To date, research has primarily focused on understanding the identity, life cycle, hazard, and environmental occurrence, monitoring, biotic exposure and health risks of non-polymeric PFAS particularly the perfluoroalkyl acids (PFAA) comprising perfluoroalkylcarboxylic acids (PFCAs), perfluoroalkanesulfonic acids (PFSAs), and some of their well-known non-polymeric precursors derived from fluorotelomers and perfluoroalkanesulfonyl fluorides (PASFs) such as fluorotelomer alcohols (FTOHs) and perfluoroalkanesulfonyl amides/amidoethanols (FASAs/FASeS) [3-7]. These non-polymeric PFAS, in particular PFOS, PFHxS, PFOA and other long-chain (>C7) PFCAs and their related chemistries, have been increasingly phased-out of production and regulated in many global jurisdictions [8, 9].

There are PFAS classified as polymeric, which can be further sub-divided into fluoropolymers, perfluoropolyethers (PFPEs) and side-chain fluorinated polymers (SCFPs) [10, 11] (Figure 1), but environmental studies are far less prevalent than for non-polymeric PFAS. The present minireview discusses the current state of knowledge on fluorinated polymers and polymeric substances and the potential environmental concerns related to their production and use.
Fluoropolymers

There have been a few recent reviews on fluoropolymers. As reviewed in Henry et al. [12], fluoropolymer producers and users summarized that fluoropolymers are high molecular weight polymers (>100 000 Da). Overall, the group of fluoropolymers is dominated by polytetrafluoroethylene (PTFE); together with fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), and other tetrafluoroethylene-copolymers they account for around 75% of the fluoropolymer market. An additional 14 fluoropolymers (e.g. polyvinylidene fluoride (PVDF) homopolymer), include fluoroplastics, fluoroelastomers, and specialty fluoroplastics were considered by Korzeniowski et al. [13] that share extreme stability and other properties with those reviewed by Henry et al. [12] (Figure 2).

To our knowledge, there is a lack of information in the published literature on whether fluoropolymers are thermally, chemically, photochemically, hydrolytically, oxidatively, and biologically stable. Once sufficiently treated, fluoropolymers have negligible residual monomer and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water and not subject to long-range transport, though (fluoro)polymer s can be found across the globe. Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on PTFE, but similar to other microplastics that have been reported in biota. For example, an examination of microparticles in the digestive tracts of farmed gilthead sea bream and common carp at different life stages showed the presence of natural microfibers and microplastics, with microfibers (~ 90%) being the dominant type and for carp 37.5% was PTFE [14]. The total fluoropolymer market, including ionomers and amorphous fluoropolymers was estimated to be
about 330,000 MT in 2021 [13] (see Figure 2). There is also growing use of fluoropolymers in biomedical applications [15]. The fluoropolymer producers have argued that these fluoropolymers fulfil the designations of “polymers of low concern (PLC)”, which results in lower regulatory oversight [12, 13].

As reviewed by Lohmann et al. [16], the designation of PLC-status neglects environmental full life-cycle considerations of fluoropolymers, by only focusing on the ready-for-use stage of production, but neglects the considerable contamination often present during production, manufacturing and disposal of fluoropolymers. A major concern has been the reliance of fluorinated processing aids (such as perfluorooctanoic acid, PFOA, perfluorononanoic acid, PFNA or more recently hexafluoropropylene oxide dimeric acid (HFPO-DA) used in the GenX process) during the production of fluoropolymers, which has resulted in their widespread contamination of the environment. Similar to many other commodity polymers, the extreme stability of fluoropolymers raises concerns given the ubiquitous concern over plastic pollution, in particular of the hydrosphere [17]. Previous studies have already documented that SCFPs (see the following section) can decompose and release non-polymeric PFAS to the environment. A review by Gardiner [18] includes a more complete overview of the different types of fluoropolymers, industry produced 320 300 tonnes of fluoropolymers in 2018, and production is steadily increasing. The production volume of fluoropolymers exceeds those of perfluoro(ether)alkyl acids by approximately two orders of magnitudes [19]. By 2018, the global fluoropolymer industry was expected to be at $10 billion per annum.

**Perfluoropolyethers**
As reviewed recently in Rice et al. [20], perfluoropolyethers (PFPEs) (also known as ether-PFAS) incorporate an ether linkage into their chemical structure and are used as starting materials for the synthesis in polymerization processes, or manufacturing processing aids in the production of other polymeric resins. The most well-known PFPE monomers other than GenX (the ammonium salt of HFPO-DA) are the ammonium salts of dodecafluoro-3H-4,8-dioxanonanoate (AmmoniumDONA), and Difluoro[1,1,2,2,-tetrafluoro-2-(pentafluoro-ethoxy)] ethoxy acetic acid (EEA-NH4). These three PFPEs have similar physicochemical properties, with GenX (HFPO-DA) being branched, while both ADONA and EEA-NH4 are linear. All three are water-soluble, acidic, and hydrolytically stable in aqueous media. All are short-chain (<C6) replacements for long-chain PFOS and PFOA (and other PFAAs >C7).

PFPEs are polymeric PFAS as they are used as starting materials for synthesis of larger PFAS, emulsifiers in polymerization processes, or manufacturing processing aids in the production of other polymeric resins. Common commercial uses reported for PFPEs include the use of HFPO-DA (or Gen-X), DONA, EEA-NH4, and HFPO-TA as replacements for PFOA and perfluorononanoic acid (PFNA) PFOA and perfluorononanoic acid (PFNA) in the manufacture of polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [16, 20].

Rice et al. [20] concluded that there is a dearth of literature publications on the physicochemical properties, presence in the environment, potential toxicological effects, and toxicokinetic profiles of PFPEs. Production volumes of PFPEs are largely unknown but are likely considerable [19]. The growing concern that PFPEs are widespread environmental contaminants is illustrated by GenX (HFPO-DA), which has been reported at a Netherlands fluorochemical production site [21].
In addition to carboxylated PFPEs, there are also sulfonated ones, including those containing a hydrogen, chlorine or double bond [22]. A widely known example is F53B, which is comprised of a major (11-chloroeicosfluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS)) and minor (9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)) components. F53B has been used as a PFOS replacement in metal plating in China, and bioaccumulates more strongly than PFOS [23]. In recent years, F53B in the environment has received increased attention as the major 11Cl-PF3OUdS component has been reported in Arctic air, water, biota and wildlife, thereby also demonstrating long-range Arctic transport potential [24]. For example, F53B has been reported at low levels in wildlife including East Greenland polar bears, killer whales and ringed seals [25].

Side-chain fluorinated polymers

Side-chain fluorinated polymers (SCFPs) are defined as polymers with a non-fluorinated polymer backbone, and with fluorinated moieties on the side chains. They can be sub-divided into acrylate and urethane, oxetane, silicone and ethoxylate SCFPs (Figure 1). In most cases for SCFPs, the generic chemical structure(s) can be identified, ranging from homopolymers to co-polymers with one or more types of non-fluorinated co-monomers. Wang et al. [11] detailed that for SCFPs and other polymers, individual Chemical Abstracts Service Registry Numbers (CASRNs) and chemical names often cover a wide range of substances with different compositions that may have distinct hazardous properties, environmental fates, bioaccessibilities, degradation potentials, and implications for risk management. Chu and Letcher [26] and Fredriksson et al. [27] measured a Scotchgard pre-2002 formulation and a Scotchgard post-2002 formulation, and detected one SCFP different component in each formulation. Similar to PFPEs
and fluoropolymers, such analytical studies on SCFPs are so far limited, partially due to limited access by scientists to commercial formulations and analytical standards.

A very recent OECD report presents a comprehensive overview on SCFPs that have been on the global market, including a non-exhaustive list of 103 SCFPs and 42 monomers [28]. Historically, acrylate and urethane SCFPs were the major SCFPs produced. Until the early 2000s, PASF-based SCFPs were mainly C₈-based (i.e., derived from perfluoroctanesulfonyl fluoride, POSF). Based on the then major producer–3M’s - reporting, it was estimated that prior to 2002, about 55 % of POSF (up to ca. 2400 tonnes in 2000) were used to produce different types of SCFPs; and a majority were made into acrylate (likely up to about 20 % of POSF) and urethane (likely 23–32 % of POSF) SCFPs. For comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000, about 3 % of 3M’s total global production of POSF-derivatives at that time. Based on public records, the same study also estimated that after 2002 following 3M’s global phase out, POSF-based SCFPs were (mostly) discontinued in Japan, Western Europe and the United States (US), while Chinese manufacturers started large-scale production of POSF-based SCFPs in 2002, with a production volume of up to ca. 120 tonnes POSF-equivalent per year, and assumedly discontinued most of this production after 2008. Since 2002, POSF-based SCFPs in many applications such as textiles have largely been replaced by C₄ perfluorobutanesulfonyl fluoride (PBSF)-based SCFPs [28]. The current production volumes of PBSF-based acrylate and urethane SCFPs are largely unknown but are likely still at a substantial level. For example, the production/import of two PBSF-based acrylate SCFP monomers were registered in the EU at the level of ≥110 to <1100 tonnes/year [28]. The 3M company announced its complete phaseout of
fluorochemical production by 2025, likely resulting in at least a temporary decrease in global SCFP (and PFAS) production.

To date, a wide range of commercial SCFP products have been used to treat fabrics, textiles, and apparel articles to impart water- and grease-repellency and soil-resistance, usually applied in combination with hydrocarbon water-repellent adjuvants, resins, and/or monomeric PFAS that demonstrate some synergistic effect [28]. These SCFPs include many acrylate (e.g., CASRN 68298-62-4) and urethane SCFPs. Acrylate and urethane SCFP degradation potentially may follow two main degradation mechanisms (see Figure 1). The first is the direct release of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond). Washington and Jenkins [30] reported half-life estimates of 55–89 years for the neutral abiotic hydrolysis of a commercial fluorotelomer-based polymers (FTPs), whereas base-mediated hydrolysis showed a half-life of ~0.7 years. The second degradation mechanism is via breakdown of the polymer carbon–carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage. Existing degradation studies have shown that the PFAS moieties may be released during abiotic or biotic degradation (i.e., the occurrence of the mechanism A), which can then subsequently further degrade and form PFCAs and/or PFSAs in the environmental and biota following rather well-characterized degradation pathways of non-polymeric PFAS [31, 32]. These studies did not show whether the second type of mechanism also occurred, whereas a recent study by Schellenberger et al. [29] detected release of SCFP-containing microplastic fibers from functional textiles during washing, suggesting the second type of mechanism may occur during certain conditions, which may be learned from the research field of microplastic formation in the future.
Significant amounts of acrylate and urethane SCFPs, and other PFAS impurities present in the commercial formulations, have been and are released via air, wastewater and solid waste along the life cycle of SCFPs: during the application of commercial formulations, during the processing of treated materials into articles, and during the use and disposal of treated articles (e.g., [28, 29]). In the US, regulations allow polymer products to contain up to 2% by mass of the polymer to be present as unreacted monomers, which could quickly leach out of the polymer [33]. 3M estimated that total PFAS losses during textile surface treatment and downstream operations could range between 10 and 25 percent [2]. Further, two studies have investigated and found the presence of target urethane SCFP compositions in two pre- and post-2002 Scotchgard fabric protection formulations in samples of lake sediment, soil samples, and biosolids from wastewater treatment plants [34, 35]. Interestingly, the SCFP compositions could be detected in most of the samples tested, showing that the SCFPs may be directly released and act as a long-term source of perfluoroalkyl acids in the environment. Also, these studies indicate that sludge (biosolids) can be a main source of at least some SCFPs in the environment, particularly when they are subsequently used to treat and augment agricultural land. Another study investigated the releases of SCFP-treated textile fibers during washing, where considerable releases of SCFP-containing fibers were detected in washing and rinsing water [29], many of which may then be retained in sewage sludge at wastewater treatment plants. It was also shown that landfill leachate might be a significant source of some SCFPs [27].

Concluding remarks

Overall, fluorinated polymers and polymeric substances have gained a significant market due to their resistance to harsh conditions and their chemical stability. In particular,
fluoropolymers are durable, stable, and mechanically strong in harsh conditions. The extreme
stability of fluoropolymers has raised concerns with respect to associated plastic pollution.
Fluoropolymer producers are interested in having fluoropolymers treated as “polymers of low
concern (PLC)”, due to their stability and seemingly low environmental impact; it is the use of
fluorinated polymer processing aids that has caused widespread contamination at the production
and manufacturing sites. Regardless, compared to many non-polymeric PFAS, fluoropolymers,
PFPEs and SCFPs have received comparatively little attention from environmental scientists and
regulators, despite their manifold industrial uses and high volumes.

More information is available on fluorinated polymers and polymeric substances in
Material Safety Data Sheets (MSDSs) and patents but is not actively searched and considered in
this mini-review. It also appears that not all information available for fluorinated polymers and
polymeric substances has been made publicly available or has been claimed as confidential
business information. Analysis of commercial mixtures and articles by independent laboratories
and publication of the results in open-access databases and scientific journals would shed further
light on their compositions, and hence their potential environmental hazards and risks.

Despite the large-scale knowledge and data gaps, the following can be concluded from the
information synthesized. A wide range of fluorinated polymers and polymeric substances have
been produced and is being used in many different applications, with some polymeric PFAS
being produced at high volumes (up to tens of thousands of tonnes). Many non-polymeric PFAS
may be present in commercial polymeric PFAS formulations. For example, during the
production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs
and associated non-polymeric PFAS including from degradation (including perfluorinated
sulfonamide precursors that can further degrade to bioaccumulative PFCAs and PFSAs) may be
released into the environment. The current information demonstrates that there is already a
considerable environmental burden of fluorinated polymers and polymeric substances and
potential reservoir of more bioaccumulative degradation products.

De Silva et al. [36] synthesized the current understanding of the magnitudes and methods
for assessing human and wildlife exposures to PFAS, but with a total focus on non-polymeric
PFAS and where most human exposure studies targeted only 2 to 5 legacy PFAS and up to ~30
substances targeted in wildlife studies. However, it was noted that shifts in chemical production
are occurring rapidly including towards the production and use of polymeric PFAS. There is a
small but growing information database of environmental levels such as for F53B in Arctic
environmental compartments. However, for most fluorinated polymers and polymeric substances
there is simply no environmental data to our knowledge. There are continuing challenges to
overcome to address this considerable knowledge gap. New analytical methods remain limited
and authentic analytical standards are lacking for polymeric PFAS. The scientific tools and
analytical approaches (including new analysis methods (NAMs)) for chemical mixtures (target
and non-target, non-polymeric and polymeric) of PFAS and their precursors and degradation
products) in environmental samples is expanding [36]. However, using high-resolution MS for
polymeric PFAS technology currently has some limitations, e.g., high-end mass monitoring
limitations and loss of mass-resolution at high mass. Considerable technological challenges
remain for MS monitoring of oligomers >1000 Da; pyrolysis gas chromatography – mass
spectrometry can help bridge the gap [37]. Finally, total fluorine measurements are
complementing suspect screening using high-resolution mass spectrometry, which needs to be
expanded more to include the study of polymeric PFAS.
Concerted action is needed to address the dearth of environment-associated information and understanding on polymeric PFAS. As Ruan et al. [38] summarized, there are many thousands of PFAS listed in various databases and thus the large PFAS universe remains largely misunderstood including environmental presence, behaviour and impacts. As emphasized in the Helsingør statement PFAS by Scheringer et al. [9], conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing polymeric PFAS and starting with reduction of emissions and release into the environment.

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Papers of special interest (*) or outstanding interest (**)


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future research required to fill in the knowledge gap in PFAS toxicology and to better understand this through real field data and long-term monitoring programs.


that makes the case that basically all fluoropolymers should be classified as polymers of low concern, while adding extensive data on fluoropolymer properties and production volumes.


**Figure captions**

**Figure 1.** Schematic illustration of the three major sub-classes of fluorinated polymers and polymeric substances and major chemical examples including the two main degradation mechanisms of acrylate and urethane SCFPs.

**Figure 2:** Estimated fluoropolymer market and major polymers for 2021 (adopted from Korzeniowski et al. [13]). The fluoroplastics are polytetrafluoroethylene (PTFE); fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers (e.g., perfluoroalkoxy polymer, PFA), polyvinylidene fluoride (PVDF) homopolymer, PVDF copolymer, ethylene-chlorotrifluoroethylene (ECTFE) copolymer, ECTFE terpolymer, polychlorotrifluoroethylene (PCTFE), fluoroethylene-vinyl ether (FEVE), ethylenetetrafluoroethylene-hexafluoropropylene (EFEP) terpolymer, chlorotrifluoroethylene-tetrafluoroethylene (CPT) terpolymer, and tetrafluoroethylene, hexafluoropropylene, vinylidene fluoride (TFE-HFP-VF2 [THV]) terpolymer as well as the specialty fluoroplastics, amorphous fluoropolymers, and fluorinated ionomers, and three fluoroelastomers, namely trifluoroethylene-propylene copolymer (FEPM), HFP-VF2 polymer and HFP-VF2-TFE polymers (FKM), and TFPMVE perfluoroelastomer (FFKM).