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

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

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

3

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24 **Abstract**

25 Per- and polyfluoroalkyl substances (PFAS) are a diverse group of surface treatment
26 chemicals falling under non-polymeric and polymeric categories. Polymeric PFAS are comprised
27 of fluoropolymers, perfluoropolyethers and side-chain fluorinated polymers (SCFPs).
28 Fluorinated polymers and polymeric substances have gained a significant market due to their
29 chemical stability. To date, research and regulatory concern has primarily focused on the
30 environmental occurrence and health effects of non-polymeric PFAS, particularly perfluoroalkyl
31 acids and precursors. Industries consider most fluoropolymers as being “polymers of low
32 concern”, although there is already a considerable environmental burden and widespread
33 contamination resulting from their production, manufacturing and use. For example, SCFPs are
34 widely used, and known to release their perfluorinated side chains. Concerted action is needed to
35 address the dearth of environment-associated information and understanding on polymeric
36 PFAS.

37

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

40 **Introduction**

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

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

57 There are PFAS classified as polymeric, which can be further sub-divided into
58 fluoropolymers, perfluoropolyethers (PFPEs) and side-chain fluorinated polymers (SCFPs) [10,
59 11] (Figure 1), but environmental studies are far less prevalent than for non-polymeric PFAS.
60 The present minireview discusses the current state of knowledge on fluorinated polymers and
61 polymeric substances and the potential environmental concerns related to their production and
62 use.

63

64 **Fluoropolymers**

65 There have been a few recent reviews on fluoropolymers. As reviewed in Henry *et al.*
66 [12], fluoropolymer producers and users summarized that fluoropolymers are high molecular
67 weight polymers (>100 000 Da). Overall, the group of fluoropolymers is dominated by
68 polytetrafluoroethylene (PTFE); together with fluorinated ethylene propylene (FEP), ethylene
69 tetrafluoroethylene (ETFE), tetrafluoroethylene copolymers with perfluoroalkyl vinyl ethers
70 (e.g., perfluoroalkoxypolymer, PFA), and other tetrafluoroethylene-copolymers they account for
71 around 75 % of the fluoropolymer market. An additional 14 fluoropolymers (e.g. polyvinylidene
72 fluoride (PVDF) homopolymer), include fluoroplastics, fluoroelastomers, and specialty
73 fluoroplastics were considered by Korzeniowski *et al.* [13] that share extreme stability and other
74 properties with those reviewed by Henry *et al.* [12] (Figure 2).

75 To our knowledge, there is a lack of information in the published literature on whether
76 fluoropolymers are thermally, chemically, photochemically, hydrolytically, oxidatively, and
77 biologically stable. Once sufficiently treated, fluoropolymers have negligible residual monomer
78 and oligomer content and low to no leachables. Fluoropolymers are practically insoluble in water
79 and not subject to long-range transport, though (fluoro)polymers can be found across the globe.
80 Fluoropolymers are not bioavailable or bioaccumulative, as evidenced by toxicology studies on
81 PTFE, but similar to other microplastics that have been reported in biota. For example, an
82 examination of microparticles in the digestive tracts of farmed gilthead sea bream and common
83 carp at different life stages showed the presence of natural microfibers and microplastics, with
84 microfibers (~ 90 %) being the dominant type and for carp 37.5 % was PTFE [14]. The total
85 fluoropolymer market, including ionomers and amorphous fluoropolymers was estimated to be

86 about 330,000 MT in 2021 [13] (see Figure 2). There is also growing use of fluoropolymers in
87 biomedical applications [15]. The fluoropolymer producers have argued that these
88 fluoropolymers fulfil the designations of “polymers of low concern (PLC)”, which results in
89 lower regulatory oversight [12, 13].

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

106

107 **Perfluoropolyethers**

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

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

124 Rice *et al.* [20] concluded that there is a dearth of literature publications on the
125 physicochemical properties, presence in the environment, potential toxicological effects, and
126 toxicokinetic profiles of PFPEs. Production volumes of PFPEs are largely unknown but are
127 likely considerable [19]. The growing concern that PFPEs are widespread environmental
128 contaminants is illustrated by GenX (HFPO-DA), which has been reported at a Netherlands
129 fluorochemical production site [21].

130 In addition to carboxylated PFPEs, there are also sulfonated ones, including those
131 containing a hydrogen, chlorine or double bond [22]. A widely known example is F53B, which is
132 comprised of a major (11-chloroeicosafluoro-3-oxaundecane-1-sulfonic acid (11Cl-PF3OUdS))
133 and minor (9-chlorohexadecafluoro-3-oxanone-1-sulfonic acid (9Cl-PF3ONS)) components.
134 F53B has been used as a PFOS replacement in metal plating in China, and bioaccumulates more
135 strongly than PFOS [23]. In recent years, F53B in the environment has received increased
136 attention as the major 11Cl-PF3OUdS component has been reported in Arctic air, water, biota
137 and wildlife, thereby also demonstrating long-range Arctic transport potential [24]. For example,
138 F53B has been reported at low levels in wildlife including East Greenland polar bears, killer
139 whales and ringed seals [25].

140

141 **Side-chain fluorinated polymers**

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

153 and fluoropolymers, such analytical studies on SCFPs are so far limited, partially due to limited
154 access by scientists to commercial formulations and analytical standards.

155 A very recent OECD report presents a comprehensive overview on SCFPs that have been
156 on the global market, including a non-exhaustive list of 103 SCFPs and 42 monomers [28].
157 Historically, acrylate and urethane SCFPs were the major SCFPs produced. Until the early
158 2000s, PASF-based SCFPs were mainly C₈-based (i.e., derived from perfluorooctanesulfonyl
159 fluoride, POSF). Based on the then major producer—3M's - reporting, it was estimated that prior
160 to 2002, about 55 % of POSF (up to ca. 2400 tonnes in 2000) were used to produce different
161 types of SCFPs; and a majority were made into acrylate (likely up to about 20 % of POSF) and
162 urethane (likely 23–32 % of POSF) SCFPs. For comparison, 3M reported that its estimated
163 global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000,
164 about 3 % of 3M's total global production of POSF-derivatives at that time. Based on public
165 records, the same study also estimated that after 2002 following 3M's global phase out, POSF-
166 based SCFPs were (mostly) discontinued in Japan, Western Europe and the United States (US),
167 while Chinese manufacturers started large-scale production of POSF-based SCFPs in 2002, with
168 a production volume of up to ca. 120 tonnes POSF-equivalent per year, and assumedly
169 discontinued most of this production after 2008. Since 2002, POSF-based SCFPs in many
170 applications such as textiles have largely been replaced by C₄ perfluorobutanesulfonyl fluoride
171 (PBSF)-based SCFPs [28]. The current production volumes of PBSF-based acrylate and urethane
172 SCFPs are largely unknown but are likely still at a substantial level. For example, the
173 production/import of two PBSF-based acrylate SCFP monomers were registered in the EU at the
174 level of ≥ 110 to < 1100 tonnes/year [28]. The 3M company announced its complete phaseout of

175 fluorochemical production by 2025, likely resulting in at least a temporary decrease in global
176 SCFP (and PFAS) production.

177 To date, a wide range of commercial SCFP products have been used to treat fabrics,
178 textiles, and apparel articles to impart water- and grease-repellency and soil-resistance, usually
179 applied in combination with hydrocarbon water-repellent adjuvants, resins, and/or monomeric
180 PFAS that demonstrate some synergistic effect [28]. These SCFPs include many acrylate (e.g.,
181 CASRN 68298-62-4) and urethane SCFPs. Acrylate and urethane SCFP degradation potentially
182 may follow two main degradation mechanisms (see Figure 1). The first is the direct release of
183 PFAS moieties from the side chains (e.g., hydrolysis of the ester bond). Washington and Jenkins
184 [30] reported half-life estimates of 55–89 years for the neutral abiotic hydrolysis of a commercial
185 fluorotelomer-based polymers (FTPs), whereas base-mediated hydrolysis showed a half-life of
186 ~0.7 years. The second degradation mechanism is via breakdown of the polymer carbon–carbon
187 backbone to form small oligomeric species which subsequently undergo ester bond cleavage.
188 Existing degradation studies have shown that the PFAS moieties may be released during abiotic
189 or biotic degradation (i.e., the occurrence of the mechanism A), which can then subsequently
190 further degrade and form PFCAs and/or PFSAs in the environmental and biota following rather
191 well-characterized degradation pathways of non-polymeric PFAS [31, 32]. These studies did not
192 show whether the second type of mechanism also occurred, whereas a recent study by
193 Schellenberger et al. [29] detected release of SCFP-containing microplastic fibers from
194 functional textiles during washing, suggesting the second type of mechanism may occur during
195 certain conditions, which may be learned from the research field of microplastic formation in the
196 future.

197 Significant amounts of acrylate and urethane SCFPs, and other PFAS impurities present
198 in the commercial formulations, have been and are released via air, wastewater and solid waste
199 along the life cycle of SCFPs: during the application of commercial formulations, during the
200 processing of treated materials into articles, and during the use and disposal of treated articles
201 (e.g., [28, 29]). In the US, regulations allow polymer products to contain up to 2% by mass of the
202 polymer to be present as unreacted monomers, which could quickly leach out of the polymer
203 [33]. 3M estimated that total PFAS losses during textile surface treatment and downstream
204 operations could range between 10 and 25 percent [2]. Further, two studies have investigated and
205 found the presence of target urethane SCFP compositions in two pre- and post-2002 Scotchgard
206 fabric protection formulations in samples of lake sediment, soil samples, and biosolids from
207 wastewater treatment plants [34, 35]. Interestingly, the SCFP compositions could be detected in
208 most of the samples tested, showing that the SCFPs may be directly released and act as a long-
209 term source of perfluoroalkyl acids in the environment. Also, these studies indicate that sludge
210 (biosolids) can be a main source of at least some SCFPs in the environment, particularly when
211 they are subsequently used to treat and augment agricultural land. Another study investigated the
212 releases of SCFP-treated textile fibers during washing, where considerable releases of SCFP-
213 containing fibers were detected in washing and rinsing water [29], many of which may then be
214 retained in sewage sludge at wastewater treatment plants. It was also shown that landfill leachate
215 might be a significant source of some SCFPs [27].

216

217 **Concluding remarks**

218 Overall, fluorinated polymers and polymeric substances have gained a significant market
219 due to their resistance to harsh conditions and their chemical stability. In particular,

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

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

235 Despite the largescale knowledge and data gaps, the following can be concluded from the
236 information synthesized. A wide range of fluorinated polymers and polymeric substances have
237 been produced and is being used in many different applications, with some polymeric PFAS
238 being produced at high volumes (up to tens of thousands of tonnes). Many non-polymeric PFAS
239 may be present in commercial polymeric PFAS formulations. For example, during the
240 production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs
241 and associated non-polymeric PFAS including from degradation (including perfluorinated
242 sulfonamide precursors that can further degrade to bioaccumulative PFCAs and PFSAs) may be

243 released into the environment. The current information demonstrates that there is already a
244 considerable environmental burden of fluorinated polymers and polymeric substances and
245 potential reservoir of more bioaccumulative degradation products.

246 De Silva *et al.* [36] synthesized the current understanding of the magnitudes and methods
247 for assessing human and wildlife exposures to PFAS, but with a total focus on non-polymeric
248 PFAS and where most human exposure studies targeted only 2 to 5 legacy PFAS and up to ~30
249 substances targeted in wildlife studies. However, it was noted that shifts in chemical production
250 are occurring rapidly including towards the production and use of polymeric PFAS. There is a
251 small but growing information database of environmental levels such as for F53B in Arctic
252 environmental compartments. However, for most fluorinated polymers and polymeric substances
253 there is simply no environmental data to our knowledge. There are continuing challenges to
254 overcome to address this considerable knowledge gap. New analytical methods remain limited
255 and authentic analytical standards are lacking for polymeric PFAS. The scientific tools and
256 analytical approaches (including new analysis methods (NAMs)) for chemical mixtures (target
257 and non-target, non-polymeric and polymeric) of PFAS and their precursors and degradation
258 products) in environmental samples is expanding [36]. However, using high-resolution MS for
259 polymeric PFAS technology currently has some limitations, e.g., high-end mass monitoring
260 limitations and loss of mass-resolution at high mass. Considerable technological challenges
261 remain for MS monitoring of oligomers >1000 Da; pyrolysis gas chromatography – mass
262 spectrometry can help bridge the gap [37]. Finally, total fluorine measurements are
263 complementing suspect screening using high-resolution mass spectrometry, which needs to be
264 expanded more to include the study of polymeric PFAS.

265 Concerted action is needed to address the dearth of environment-associated information and
266 understanding on polymeric PFAS. As Ruan et al. [38] summarized, there are many thousands of
267 PFAS listed in various databases and thus the large PFAS universe remains largely
268 misunderstood including environmental presence, behaviour and impacts. As emphasized in the
269 Helsingør statement PFAS by Scheringer *et al.* [9], conducting research on those critical
270 knowledge and data gaps that are most relevant for soundly regulating/managing polymeric
271 PFAS and starting with reduction of emissions and release into the environment.

272

273 **Acknowledgment**

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275

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426 **Figure captions**

427

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

431

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