

# Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle



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# **Synthesis Report on Understanding Side-Chain Fluorinated Polymers and Their Life Cycle**



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# IOMC

INTER-ORGANIZATION PROGRAMME FOR THE SOUND MANAGEMENT OF CHEMICALS

A cooperative agreement among FAO, ILO, UNDP, UNEP, UNIDO, UNITAR, WHO, World Bank and OECD

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# Executive Summary

Per- and polyfluoroalkyl substances (PFASs) comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence, hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure, and risk of non-polymeric PFASs. This has informed development of many risk management measures at the national and international level. To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric PFASs, which include side-chain fluorinated polymers (SCFPs), fluoropolymers and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019).

This report summarizes efforts by the OECD/UNEP Global PFC Group, between July 2021 and April 2022, in synthesizing publicly available scientific and technical information on the life cycle of SCFPs, which are polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition (hereafter referred to as “PFAS moieties”) on the side chains.

The report provides a comprehensive overview on the chemical identities of SCFPs that have been on the global market, including a non-exhaustive list of 103 SCFPs and 42 monomers (Chapter 2). Based on the generic chemical structures identified, these SCFPs can be categorized according to the types of PFAS moieties present on the side chains, including n:2 fluorotelomers ( $C_nF_{2n+1}CH_2CH_2-$ ), perfluoroalkanesulfonyl fluoride (PASF)-derivatives [ $C_nF_{2n+1}S(O)_2-$ ], perfluoroalkanoyl fluoride (PACF)-derivatives [ $C_nF_{2n+1}C(O)-$ ;  $C_nF_{2n+1}CH_2-$ ] and perfluoropolyethers (PFPEs; containing a moiety such as  $-CF_2-O-CF_2-$  in the fluorinated side chains), with varied fluorinated carbon chain lengths. Another way of categorizing the SCFPs can be according to the structural repeating units in the polymer backbone, with some simplifications, including acrylates {e.g.,  $[-CH_2-CH(C(O)OR_F)-]_n$ }, ethoxylates {e.g.,  $[-O-CH_2-CH_2-]_n$ }, oxetanes {e.g.,  $[-CH_2-C(CH_3)(CH_2OCH_2R_F)-CH_2-O-]_n$ }, silicones {e.g.,  $[-Si(CH_2CH_2R_F)-O-Si(CH_2CH_2R_F)-]_n$ } and urethanes {e.g.,  $[-NH-C(O)-O-]_n$ }, where  $R_F$  is used to represent a fluorinated carbon chain moiety. In this report, the four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6). In each chapter, the analysis focuses on the production and use of respective SCFPs, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, environmental releases of SCFPs, and other PFASs present in the commercial formulations, followed by a summary of critical knowledge and data gaps and options for a way forward. Chapter 7 focuses on overarching conclusions and recommendations. The key messages of chapters 3-6 are summarized at the start of each chapter. The report comes with an Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAs.

Concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in safety data sheets and patents (but was not actively searched and considered in this analysis due to time and resource constraints); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

# List of Acronyms

CAS	Chemical Abstracts Service
CASRN	CAS Registry Numbers
CDR	Chemical Data Reporting
EU	European Union
FASAs	Perfluoroalkanesulfonyl amides
FASEs	Perfluoroalkanesulfonyl amidoethanols
FCN	Inventory of Effective Food Contact Substance Notifications
FTAc	Fluorotelomer acrylates
FTCA	Fluorotelomer carboxylic acids
FT-ethers	Fluorotelomer ethers
FTOs	Fluorotelomer olefins
FTOHs	Fluorotelomer alcohols
FTOH-aces	Fluorotelomer alcohols acetates
FTUCAs	Fluorotelomer unsaturated carboxylic acids
ICCM	International Conference on Chemicals Management
IUR	Inventory Update Reporting
$M_n$	Number-average molecular weight
$M_w$	Weight-average molecular weight
N.A.	Not available
OECD	Organisation of Economic Co-operation and Development
PACF	Perfluoroalkanoyl fluoride
PASFs	Perfluoroalkanesulfonyl fluorides
PDMS	Polydimethylsiloxane



PFAIs	Perfluoroalkyl iodides
PFASs	Per- and polyfluoroalkyl substances
PFCAs	Perfluoroalkylcarboxylic acids
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PFPEs	Perfluoropolyethers
PFSAs	Perfluoroalkanesulfonic acids
PMTFPS	Polymethyltrifluoropropylsiloxane
POSF	Perfluorooctanesulfonyl fluoride
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SCFPs	Side-chain fluorinated polymers
SDS	Safety data sheets
SPIN	Substances in Preparations in Nordic Countries
t	Tonnes
UN	United Nations
UNEP	United Nations Environment Programme
US	United States
US EPA	US Environmental Protection Agency
US FDA	US Food & Drug Administration
yr	Year

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# 1 Background, motivation and scope

The OECD/UNEP Global PFC<sup>1</sup> Group was established to respond to the Resolution II/5 adopted at the second session of the UN International Conference on Chemicals Management (ICCM 2) in 2009, which calls upon intergovernmental organizations, governments and other stakeholders to “consider the development, facilitation and promotion in an open, transparent and inclusive manner of national and international stewardship programmes and regulatory approaches to reduce emissions and the content of relevant perfluorinated chemicals of concern in products and to work toward global elimination, where appropriate and technically feasible”. Further work on this resolution was reaffirmed in Resolution III/3 adopted at ICCM 3 in 2012 noting that a significant need remains for additional work to support implementation of Resolution II/5. This report is prepared within the framework of the Group. For more details on the Group and its work, see the OECD PFAS web portal (<https://oe.cd/2M9>).

This report summarizes recent efforts by the Group between July 2021 and April 2022 in synthesizing publicly available scientific and technical information on side-chain fluorinated polymers (SCFPs), a subset of per- and polyfluoroalkyl substances (PFASs)<sup>2</sup>. It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations. In brief, this report provides a comprehensive overview on the identities of SCFPs that have been on the global market (Chapter 2), on the life cycle of acrylate and urethane SCFPs (Chapter 3), of oxetane SCFPs (Chapter 4), of silicone SCFPs (Chapter 5), and of ethoxylate SCFPs (Chapter 6), and a brief summary (Chapter 7). The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

PFASs comprise a class of synthetic compounds that have attracted much public attention since the early 2000s, when the persistence hazards and ubiquitous occurrence of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) started to be reported and recognized. Since then, research and risk management measures have expanded from these two PFASs to a wide range of PFASs.

In general, PFASs can be divided into two categories: non-polymeric and polymeric ones. To date, research has primarily focused on understanding the identity, life cycle, hazard, occurrence and exposure,

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<sup>1</sup> “PFCs” here refer to “per- and polyfluorinated chemicals”, and not to “perfluorocarbons”. As stated below, “per- and polyfluorinated chemicals” was a term commonly used before the term “per- and polyfluoroalkyl substances” was recommended by Buck et al. (2011). As it is part of the Group official name, it remains unchanged.

<sup>2</sup> Following OECD (2021), this report uses the acronym “PFASs” for “per- and polyfluoroalkyl substances” as stated in Buck et al. (2011), and its corresponding singular form “PFAS” refers to either a perfluoroalkyl or polyfluoroalkyl substance. It is noted that there is a notion of using “PFAS” as the acronym for both the singular and plural forms. This report does not make any recommendation to address this notion. Readers may decide which acronym they would use.

and risk of non-polymeric PFASs, particularly perfluoroalkylcarboxylic acids (PFCAs), perfluoroalkanesulfonic acids (PFSA), 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)<sup>3</sup>. This has informed development of many risk management measures at the national and international levels.<sup>4</sup>

To ensure the sound management of the entire class of PFASs, it is equally important to understand polymeric ones, which include SCFPs, fluoropolymers, and perfluoropolyethers (Buck et al., 2011; Fiedler et al., 2019). In this spirit, the Global PFC Group have identified understanding of the life cycle of polymeric PFASs as a work priority. This is a first synthesis report on polymeric PFASs, focusing on SCFPs—defined as polymers with a non-fluorinated polymer backbone and with substructures that meet the OECD PFAS definition<sup>5</sup> (hereafter referred to as “PFAS moieties”) on the side chains.<sup>6</sup>

SCFPs are of particular interest because many of them can act as a long-term significant source of non-polymeric PFASs such as PFCAs and/or PFSA in the environment as a result of the following three factors: historical and likely ongoing high production volumes and widespread use, presence of (high levels of) other non-polymeric PFASs in the commercial formulations, and ability of releasing PFAS moieties on the side chains over time (these three factors are elaborated below). This has resulted in the inclusion of related SCFPs in regulatory actions in many jurisdictions when addressing some PFCAs and PFSA.<sup>7</sup> For example, the recent listing of PFOA, its salts and PFOA-related compounds under the Stockholm Convention includes SCFPs that meet the definition, “PFOA-related compounds which, for the purposes of the Convention, are any substances that degrade to PFOA, including any substances (including salts and polymers) having a linear or branched perfluoroheptyl group with the moiety (C<sub>7</sub>F<sub>15</sub>)C as one of the structural elements” (Stockholm Convention, 2019; POPRC, 2021).

In addition, certain SCFP formulations have been applied in a way that can result in direct human exposure to monomers and their reaction products, causing adverse effects on human health. For example, upon inhalation of sprays containing 6:2 fluorotelomer silanes for surface treatment during application, the hydrolysis products of 6:2 fluorotelomer silanes may cause serious acute lung injury (e.g., Nørgaard et al. 2010, 2014). This has led to the restriction of (3,3,4,4,5,5,6,6,7,7,8,8-tridecafluorooctyl)silanetriol and its

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<sup>3</sup> These well-known non-polymeric PFCA/PFSA precursors are also common degradation intermediates of many other PFASs including certain SCFPs, which are elaborated in the sections below.

<sup>4</sup> <https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/riskreduction/>

<sup>5</sup> PFASs are defined as fluorinated substances that contain at least one fully fluorinated methyl or methylene carbon atom (without any H/Cl/Br/I atom attached to it), i.e., with a few noted exceptions, any chemical with at least a perfluorinated methyl group (–CF<sub>3</sub>) or a perfluorinated methylene group (–CF<sub>2</sub>–) is a PFAS (OECD, 2021).

<sup>6</sup> This is derived from the commonly accepted SCFP definition in Buck et al. (2011)—polymers that “do not have perfluorinated or polyfluorinated polymer backbones, but are composed of variable composition backbones with polyfluoroalkyl (possibly perfluoroalkyl) side chains”. Other definitions of SCFP exist, e.g., “side-chain fluorinated polymers contain a nonfluorinated polymer backbone, off of which fluorinated side chains branch.” by ITRC ([https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/#2\\_2\\_3\\_1](https://pfas-1.itrcweb.org/2-2-chemistry-terminology-and-acronyms/#2_2_3_1)). The definitions agree with each other, but only have some different wordings for describing the PFAS moieties on the side chains.

<sup>7</sup> Note that degradation intermediates themselves may be toxic and have long lifetime in biota and humans, see, e.g., Kabadi et al. (2020) and Rice et al., (2020).

mono-, di- or tri-O-(alkyl) derivatives from their use in spray products under the European Union (EU) REACH regulation<sup>8</sup> and in Switzerland.<sup>9</sup>

This report aims to provide an overview of existing scientific and technical information on SCFPs, focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps. It builds primarily on a review of peer-reviewed scientific literature, regulator reports and databases, and technical documents published by companies. It is intended to be comprehensive, but not exhaustive. For instance, due to time and resource constraints, an active search and analysis of patents and safety data sheets (SDS) was not conducted for this report. Also, not all critical knowledge and data gaps are captured in this report, particularly unknown ones.

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<sup>8</sup> Annex XVII to REACH, Entry 73 (<https://echa.europa.eu/documents/10162/2906fed0-12ab-9593-23a1-72efd611fe70>), including the following condition of restriction: *1. Shall not be placed on the market for supply to the general public after 2 January 2021 individually or in any combination, in a concentration equal to or greater than 2 ppb by weight of the mixtures containing organic solvents, in spray products.*

<sup>9</sup> [https://www.fedlex.admin.ch/eli/cc/2005/478/en#lvl\\_d4e267/lvl\\_d4e268/lvl\\_3](https://www.fedlex.admin.ch/eli/cc/2005/478/en#lvl_d4e267/lvl_d4e268/lvl_3)

# 2 Identities of Side-Chain Fluorinated Polymers on the Global Market

## Chapter summary:

- A wide range of SCFPs and their monomers have been commercialized since the 1950s. Many of them have information on their generic chemical structures in the public domain, whereas for some others, only ambiguous descriptions are identified.
- The generic chemical structures of SCFPs allow for grouping them according to the types of PFAS moieties present on the side chains and/or the structural repeating units in the polymer backbone. Such grouping can, to a certain extent, inform about, e.g., their possible impurities, use patterns, and degradation mechanisms, which are elaborated in the following chapters.
- CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution).
- However, limited to no information is available on additional structural details of most commercial SCFPs, e.g., molecular-weight ranges and distribution, molecule parts other than the monomers or structural repeating units, and percentage compositions of individual monomers. This impedes the ability to more precisely assess environmental behavior and thus risks of individual SCFPs.
- Nevertheless, existing information shows that chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.
- Future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to have in-depth understanding of the chemical identities of commercial SCFPs, including by making existing measurements publicly available and by measuring commercial formulations. Such efforts can start with the SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner (including development of unique identifiers other than CASRNs and CAS names).



A wide range of SCFPs have been commercialized since the 1950s. Aiming to capture a comprehensive overview of the SCFP diversity on the market, Table S1 in the Annex (an Excel sheet file provided separately) provides a non-exhaustive list of 103 SCFPs and 42 monomers, including information sources, Chemical Abstracts Service Registry Numbers (CASRN), CAS names, synonyms (if available), molecular formula (if available), previously used CASRN (if relevant), types of PFAS moieties and structural repeating units, fluorinated carbon chain length, CASRN of the related PFAS monomers, and registration status in various national/regional chemical inventories. They were identified by a brief search of the OECD 2018 PFAS List, regulatory databases,<sup>10</sup> scientific literature,<sup>11</sup> technical documents published by companies and SciFinder.<sup>12</sup> These identities served as a basis for the search of production and use information discussed in the later sections.

## 2.1. General categorization of SCFPs

In most cases, the generic chemical structure(s) can be identified, ranging from homopolymers to copolymers with one or more types of non-fluorinated co-monomers. In several other cases, the generic chemical structure(s) cannot be identified or cross-referenced from multiple sources because only ambiguous trade/trivial names or descriptions are available. For example, the substance with EC No. 458-200-2 is registered with the name “[No public or meaningful name is available]” under the EU REACH, while its Substance Infocard<sup>13</sup> provides a figure of some vague structures without explanation.

Based on the generic chemical structures identified, these SCFPs can be categorized in different ways. One way is according to the types of PFAS moieties present on the side chains, including primarily n:2 fluorotelomers ( $C_nF_{2n+1}CH_2CH_2-$ ),<sup>14</sup> PASF-derivatives [ $C_nF_{2n+1}S(O)_2-$ ], perfluoroalkanyl fluoride (PACF)-derivatives [ $C_nF_{2n+1}C(O)-$ ;  $C_nF_{2n+1}CH_2-$ ]<sup>15</sup> and perfluoropolyethers (PFPEs; containing a perfluorinated ether moiety such as  $-CF_2-O-CF_2-$  in the fluorinated side chains),<sup>16</sup> with varied fluorinated carbon chain lengths.

<sup>10</sup> Sources: the Inventory of Effective Food Contact Substance (FCS) Notifications by the United States Food & Drug Administration (<https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN>); EU REACH registered substances (<https://echa.europa.eu/information-on-chemicals/registered-substances>); US EPA CDR database (<https://chemview.epa.gov/chemview/>)

<sup>11</sup> Sources: Dinglasan-Panlilio and Mabury (2006; <https://pubs.acs.org/doi/10.1021/es051619%2B>), Frömel and Knepper (2010; <https://www.sciencedirect.com/science/article/pii/S0045653510006491>), Wang et al. (2013; <https://doi.org/10.1016/j.envint.2013.08.021>), Wang et al. (2014A; <https://doi.org/10.1016/j.envint.2014.04.013>).

<sup>12</sup> Sources: two Solvay’s presentations on Fluorolink®, a search of the brand names “PolyFox” (provided in Buck et al., 2011), “Zonyl” and “Capstone” in SciFinder.

<sup>13</sup> <https://echa.europa.eu/substance-information/-/substanceinfo/100.104.618>

<sup>14</sup> Historically, fluorotelomer manufacturers have also produced other types of fluorotelomers, such as  $[(CF_3)_2CF-(CF_2CF_2)_n-CH_2CH_2-]$  (Wang et al., 2014A), which might have also been made into SCFPs.

<sup>15</sup> For example, one monomer CASRN 3934-23-4 (2-Propenoic acid, 2-methyl-, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctyl ester,  $C_7F_{15}CH_2OC(O)C(CH_3)=CH_2$ ) was synthesized by 3M from PFOA that was derived from perfluorooctyl fluoride (Bank et al. 1994); therefore, such compounds are categorized as PACF-based derivatives here. Despite not being derived from the telomerization process, such PFASs have sometimes been termed as “n:1 fluorotelomers” in literature for readability. Future work may consider to identify more proper terminology for this PFAS group.

<sup>16</sup> Other types of PFAS moieties present on the side chains include perfluoroalcohols ( $C_nF_{2n+1}O-$ ) (see Table S1) or a vinylene-intercepted polyfluorinated side chain [e.g.,  $-(CF_2)_6-CH=CH-(CF_2)_5CF_3$ ] (Shirai et al. 2021).

The SCFPs can also be categorized according to the structural repeating units in the polymer backbone, with some simplifications, including acrylates<sup>17</sup> {e.g.,  $[-\text{CH}_2-\text{CH}(\text{C}(\text{O})\text{OR}_F)-]_n$ }, ethoxylates {e.g.,  $[-\text{O}-\text{CH}_2-\text{CH}_2-]_n$ },<sup>18</sup> oxetanes {e.g.,  $[-\text{CH}_2-\text{C}(\text{CH}_3)(\text{CH}_2\text{OCH}_2\text{R}_F)-\text{CH}_2-\text{O}-]_n$ }, silicones {e.g.,  $[-\text{Si}(\text{CH}_2\text{CH}_2\text{R}_F)-\text{O}-\text{Si}(\text{CH}_2\text{CH}_2\text{R}_F)-]_n$ } and urethanes<sup>19</sup> {e.g.,  $[-\text{NH}-\text{C}(\text{O})-\text{O}-]_n$ }, where  $\text{R}_F$  is used to represent a fluorinated carbon chain moiety.

Examples of different types of SCFPs are illustrated in Figure 2.1. The two categorization methods bring different benefits. For example, categorization according to the types of PFAS moieties present on the side chains can inform about synthesis routes, possible impurities, and PFAS degradation products, whereas categorization according to structural repeating units in the polymer backbone can inform about possible use areas, possible impurities, degradation mechanisms, and so on. Depending on the exact purposes, readers may select either way of categorization, or a combination of both. In this report, the following four chapters on the life cycle of different SCFPs are separated according to structural repeating units in the polymer backbone, specifically: acrylates and urethanes (Chapter 3), oxetanes (Chapter 4), silicones (Chapter 5), and ethoxylates (Chapter 6).

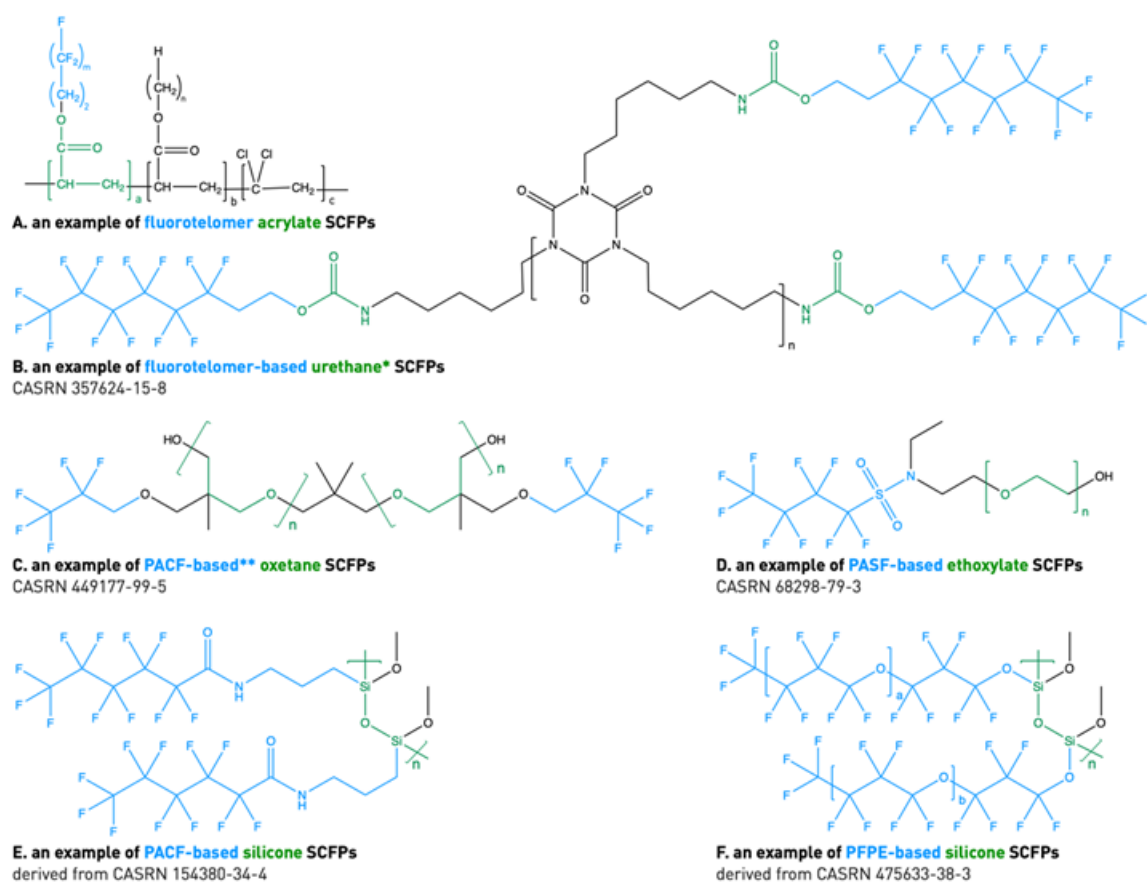
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<sup>17</sup> The term “acrylates” here also include methacrylates.

<sup>18</sup> Note that ethoxylates are different from other SCFPs, with often only one PFAS side chain connecting to the end of the polymer backbone. Given their polymer backbones  $[-\text{OCH}_2\text{CH}_2-]_n$  are non-fluorinated, they are listed as SCFPs here.

<sup>19</sup> The term “urethanes” here include polyurethanes and related chemistry (such as polyallophanates and polyisocyanurates).

Figure 2.1. Examples of different types of side-chain fluorinated polymers. Blue colour highlights PFAS moieties, and green colour highlights structural repeating units in the polymer backbone.



**Notes:**

- \* The term "urethane" here is a simplification of polyurethanes and related chemistry (such as polyallophanates and polyisocyanurates).
- \*\* In this example, the fluorinated oxetane monomer is derived from  $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ , which is derived from  $\text{CF}_3\text{CF}_2\text{COOH}$ .

## 2.2. Detailed structural information for individual SCFPs

As highlighted in Wang et al. (2021), for SCFPs and other polymers, individual CASRNs and chemical names often cover a wide range of substances with different compositions (such as different molecular-weight ranges, and numbers and types of functional groups) that may have distinct hazardous properties, environmental fate, bioaccessibility, degradation potential and implications for risk management. Therefore, it is important to have additional structural details of individual SCFPs such as molecular weight-ranges and distribution, molecule parts other than monomers or structural repeating units, and percentage compositions of individual monomers.

Currently, such additional structural details are sometimes available in the public literature (including technical datasheets provided by companies), but are scattered and often with limitations. For example, two biodegradation studies reported additional information on the chemical compositions of two commercial acrylate and urethane SCFPs, respectively (see Table 2.1; Russell et al., 2008 and 2010); however, due to a lack of CASRNs or other identifiers, such information cannot be linked to the SCFPs in Table S1. Further, the structural details of two commercial fluorotelomer-based ethoxylate SCFPs have

been reported by an analytical study and a biodegradation study: Zonyl FSO-100—with the perfluorocarbon chain length being between 2 and 14 carbon atoms and the degree of ethoxylation being between 0 and about 15 (Dinglasan-Panlilio and Mabury, 2006); and Zonyl FSH—with the perfluorocarbon chain length being at least between 4 and about 12 carbon atoms and the degree of ethoxylation being between 0 and at least 18 (Frömel and Knepper, 2010). In addition, Solvay reported the structural details of three PFPE-based ethoxylate SCFPs in one presentation (Solvay, no date (n.d.)), which were coincidentally identified during the preparation of this synthesis report.

Additional structural details can be identified in patents, but possibly in wide ranges. For example, Washington et al. (2015A) looked into two patents of fluorotelomer-based acrylate polymers and noted that the mass % of fluorotelomer in the polymers ranged from 79% to 85% in one patent and from 40% to 75% in the other. It is generally unknown how individual patents are translated into commercial practices (Freilich and Ouellette, 2019).

Further efforts have also been made by scientists to analytically determine compositions in commercial SCFPs. For example, Chu and Letcher (2014) measured a Scotchgard pre-2002 formulation and a Scotchgard post-2002 formulation, and detected one composition<sup>20</sup> in each formulation. Later, this analytical information was used to detect the presence of these compositions in different environmental media as an indicator of environmental fate and releases of the corresponding formulations (more details are elaborated in Section 3.4 below). Such analytical studies are so far limited, partially due to limited access by scientists to commercial formulations and analytical standards (Ng et al. 2021).

Therefore, it is generally challenging to capture an overview of the data availability of structural details for commercial SCFPs on the global market. Nevertheless, based on existing information, the chemical identities, including molecular weight and PFAS moiety content in the molecular structure, can vary considerably across different types of SCFPs and across different SCFPs within the same type.

Table 2.1. Additional structural details on the chemical compositions in commercial SCFP formulations reported in peer-reviewed scientific studies. N.A. = not available

References	Russell et al. (2008)	Russell et al. (2010)
<b>SCFP type</b>	Fluorotelomer-based acrylate polymer (Figure 2.1 A)	Fluorotelomer-based urethane polymer
<b>Molecular weight</b>	$M_n = 40\,000$ Daltons*	$M_n$ or $M_w = 3\,500$ Daltons**
<b>Fluorine content</b>	10.095 weight%	10 weight%
<b>SCFP weight% in the formulation</b>	23–24%	23%
<b>SCFP particle size in the formulation</b>	100–300 nm	100–300 nm

\* Here the authors used a number-average molecular weight ( $M_n$ ), which is defined as the total weight of the molecules divided by the total number of molecules.

\*\* Here it is not clear whether the authors referred to a number-average molecular weight ( $M_n$ ) or a weight-average molecular weight ( $M_w$ ), as both terms were mentioned for the same value in the Supporting Information of the study. A weight-average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule. It can be calculated as  $\sum w_i M_i$ , where  $w_i$  is the weight fraction of polymer with molecular weight  $M_i$ . A

<sup>20</sup> They were able to detect mass spectral peaks at  $m/z$  1315.0591 and 1634.3120 in each formulation, respectively. However, the authors did not report more details, except that the former mass peak contains a  $[C_8F_{17}SO_2N(C_2H_5)]^-$  ion and the latter contains a  $[C_4F_9SO_2N(CH_3)]^-$  ion.

weight-average molecular weight is larger than or equal to the corresponding number-average molecular weight for any given polymer.

### 2.3. Summary of critical knowledge and data gaps related to the chemical structure of SCFPs

**A)** In multiple cases in Table S1, the generic chemical structures of a given SCFP or its monomer(s) cannot be identified, even though their corresponding CASRNs were identified; such information gap impedes our understanding of these SCFPs (e.g., which non-polymeric PFASs may be released). Ways in which the information is lacking include: (i) Only the trade names were assigned to the CASRNs without further details, e.g., CASRNs 949581-65-1 (Scotchgard PM-3622), 940891-99-6 (Scotchgard PM-490), 923298-12-8 (Scotchgard PM-930) and 1224842-54-2 (Unidyne TG-5521); and (ii) the assigned CAS name is ambiguous, e.g., CASRN 328389-91-9 [Propanoic acid, 3-hydroxy-2-(hydroxymethyl)-2-methyl-, polymers with 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane and reduced Me esters of reduced polymd. oxidized tetrafluoroethylene, compds. with triethylamine].

**B)** CASRNs and CAS names alone cannot be used to identify unique SCFPs (in other words, the same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such molecular-weight ranges and distribution). Therefore, apart from the generic chemical structures of any given SCFPs, additional structural information is needed for studies and assessments of their hazardous properties, environmental fate, bioaccessibility, degradation potential, and implications for risk management, such as the molecular-weight range and distribution of the SCFP, the fluorine content, the molecular percentage of individual co-monomers, and how the co-monomers are connected (e.g., by providing a reaction scheme if available). In the public literature, additional structural information was identified for some commercial SCFPs; however, such information is scattered and often with limitations (e.g., due to a lack of CASRNs or other identifiers, reported information cannot be linked to specific SCFPs listed in Table S1). Analytical studies can help to measure the structural details of individual SCFPs, but such studies are generally challenging due to a lack of access by scientists to commercial formulations and analytical standards.

### 2.4. Options for a way forward

To address these two gaps, future efforts may further investigate technical datasheets from companies and patents, and work with manufacturers to better understand the chemical identities of commercial SCFPs, including by making existing measurement results publicly available and by measuring commercial formulations. To increase efficiency, priorities may be first given to those SCFPs that are still in commerce and with high production volumes. Efforts are also needed to collect and make such information publicly available in an easily accessible manner, e.g., via the OECD PFAS Web Portal, the OECD eChemPortal and/or work under the Stockholm Convention<sup>21</sup>; such efforts may engage the cheminformatics community, as unique identifiers other than CASRNs and CAS names would be needed for identifying unique SCFPs. This can greatly enable a better understanding of the environmental fate and degradation behaviour of

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<sup>21</sup> The Secretariat of the Stockholm Convention, in consultation with the POPs Review Committee, has developed an indicative list for PFOA, its salts and PFOA-related compounds, including PFOA-related SCFPs, covered under the listing under the Stockholm Convention. It is expected that an indicative list of PFHxS, its salts and PFHxS-related compounds will be prepared if those chemicals are listed under the Stockholm Convention. For more details, see the Stockholm Convention webpage ([www.pops.int](http://www.pops.int)).

individual SCFPs (which can vary greatly, given the large range of molecular weights and the mass percentage of PFAS moieties in the polymer reported for a few commercial SCFPs as outlined above), and estimation of generation and releases of non-polymeric PFASs from individual SCFPs. In parallel, a logical maximum percentage of PFAS moieties could be developed based on literature review (including patents) and stakeholder consultation, as a precautionary approach for estimating non-polymeric PFAS releases from SCFPs.

# 3 The Life Cycle of Acrylate and Urethane SCFPs

## Chapter summary:

- Historically, many acrylate and urethane SCFPs containing *long-chain* PFAS moieties on the side chains (hereafter referred to as “*long-chain*” SCFPs) were produced in significant amounts, jointly on the scale of thousands of tonnes or more per annum (which were at least one order of magnitude higher than the production volumes of many non-polymeric PFASs including those used in fire-fighting foams). Currently, many long-chain acrylate and urethane SCFPs have been replaced by short-chain ones, while some long-chain ones may still be used (details unknown due to confidentiality). Despite limited information (due to no reporting requirements, confidentiality, etc.), it can be concluded that short-chain acrylate and urethane SCFPs are still being produced jointly on the scale of thousands of tonnes or more per annum.
- Acrylate and urethane SCFPs have been mainly used as surface protectors to impart water- and oil-repellency and soil-resistance to fabrics, textiles, and apparel articles (both for industrial pre-market treatment, or professional/consumer aftermarket treatment), and food contact paper and paperboard. Some acrylate and urethane polymers may also be used as fluorosurfactants in products such as fire-fighting foams, inks, and paints, lacquers and varnishes.
- Considerable amounts (up to 5 weight%) of other non-polymeric PFASs may be present in commercial formulations. They may originate from unreacted starting materials and reaction intermediates, contaminants from the raw materials, degradation products, and reaction byproducts. They may also be monomeric PFASs intentionally left in the formulations to keep the acrylate and urethane particles suspended in the formulations.
- Acrylate and urethane SCFP degradation may follow two main degradation mechanisms: direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond), and breakdown of the polymer carbon-carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage.
- While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives, ranging from less than 1 year to over a thousand years. Some of these large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two commercial fluorotelomer-based acrylate SCFPs were measured to be several decades).

Meanwhile, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including molecular size of SCFPs, specific surface area of SCFP particles, substrate, temperature, pH values, and humidity. Such variability cannot be minimized/eliminated. Therefore, degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain. Nevertheless, it can be concluded that these SCFPs will degrade and thus serve as a long-term source of non-polymeric PFASs once released in the environment.

- In contrast to abiotic and biotic degradation, little is known about the fate of SCFPs during municipal waste incineration of SCFP-treated articles, and whether this would be a significant source of non-polymeric PFASs into the environment.
- Upon application for surface treatment, both SCFPs and other PFASs present in the formulations may partially be released via air, wastewater and/or solid waste, and partially transferred onto treated articles, which may be released during the subsequent processing, use and disposal. Due to various uncertainties and unknowns, the contribution of acrylate and urethane SCFPs to PFASs in the environment and biota is unclear. But it is likely significant, particularly in the long term, given the large volumes produced and used. Future efforts may collect further information and reduced the uncertainties to reach more precise estimates.

Given the similarities between acrylate and urethane SCFPs in many aspects in terms of use patterns, presence of other PFASs in the commercial formulations, and degradation mechanisms, they are jointly analysed and described in this chapter.

### 3.1. Historical and ongoing production and uses

Most acrylate and urethane SCFPs and acrylate SCFP monomers identified in Table S1 have been registered for production and use in many jurisdictions, but mostly with unknown commercial status<sup>22</sup>. Table 3.1 summarizes the production/import volumes of various acrylate and urethane SCFPs, containing various types of PFAS moieties with varied chain length on the side chains, as reported in the EU, in the United States (US), and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and sealed from the public. Therefore, these data are discussed together with other information identified in peer-reviewed scientific literature as follows.

Historically, acrylate and urethane SCFPs were the major SCFPs produced. Until the early 2000s, PASF-based SCFPs were mainly derived from perfluorooctanesulfonyl fluoride (POSF), i.e., long-chain C<sub>8</sub>-based SCFPs.<sup>23</sup> Based on the then major producer—3M's reporting, it was estimated that prior to 2002, about

<sup>22</sup> The listing in most national/regional chemical inventories indicate whether the substances have been produced or used in the respective jurisdiction, but do not indicate whether they are currently being produced or used.

<sup>23</sup> Long-chains refer to perfluorocarboxylic acids (PFCAs) with carbon chain lengths C<sub>8</sub> and higher, including perfluorooctanoic acid (PFOA); perfluoroalkane sulfonic acids (PFASs) with carbon chain lengths C<sub>6</sub> and higher,



55% of POSF (up to ca. 2400 tonnes in 2000) were used to produce different types of SCFPs (see Figure S8 in the Supplementary Data of Wang et al. 2014A); and a majority were made into acrylate (likely up to about 20% of POSF) and urethane (likely 23–32% of POSF) SCFPs. As a 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 POSF-derivatives at that time (3M, 2000). 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 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 presumably discontinued most of this production after 2008. However, it is possible that some POSF-based acrylate SCFPs are still being produced and used. For example, the use of CASRNs 68298-62-4 and 68867-62-9 in some Nordic countries in 2019 has been reported, though it is unclear at what levels and for which purposes due to confidentiality (see Table 3.1).

Since 2002, POSF-based SCFPs in many applications such as textiles have largely been replaced by C<sub>4</sub> perfluorobutanesulfonyl fluoride (PBSF)-based SCFPs, i.e., short-chain ones (Wang et al. 2013, 2014A). The current production volumes of PBSF-based acrylate and urethane SCFPs are largely unknown, but are still on a significant level. For example, two PBSF-based acrylate SCFP monomers are registered in the EU with the production/import tonnage band of ≥110 to <1100 tonnes/year (see Table 3.1).

Similarly to PASF-based derivatives, most (80%) of the n:2 fluorotelomers manufactured by Asahi, Clariant, Daikin and Dupont were made into SCFPs (up to 7200 tonnes PFAI-equivalent in 2006), as reported by the “Telomer Research Program” in 2002 to the US Environment Protection Agency (EPA). At that time, n:2 fluorotelomers were produced as mixtures of different chain lengths with long-chain 8:2 and 10:2 as main components (Wang et al. 2014A). Since 2006, the major global fluorotelomer manufacturers have stepwise replaced mixture fluorotelomers with predominantly short-chain 6:2 fluorotelomer (>99%) and the transition was completed by 2015 (Wang et al., 2013; US EPA, n.d.). However, the use of two long-chain fluorotelomer-based acrylate SCFPs (CASRNs 142636-88-2 and 70969-47-0) and one long-chain fluorotelomer-based acrylate monomer (CASRN 27905-45-9) in some Nordic countries in 2019 has been reported (see Table 3.1). It is possible that CASRN 70969-47-0 was produced before the transition, given the long shelf-life of fire extinguish agents, in which it is used (see below). For CASRNs 142636-88-2 and 27905-45-9, it is unclear whether they were produced before or after the industrial transition, as no details are provided in the SPIN database.

Unlike for PASF-based derivatives, a break-down of the production of n:2 fluorotelomer SCFPs on the basis of SCFP types is not publicly available, but at least n:2 fluorotelomer acrylate SCFPs have been and are still being produced in large quantities, on the scale of hundreds to thousands of tonnes per annum (for examples, see acrylate SCFP monomers–n:2 fluorotelomers in Table 3.1).

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including perfluorohexanesulfonic acid (PFHxS) and perfluorooctanesulfonic acid (PFOS); and, precursors of these substances (<https://www.oecd.org/chemicalsafety/portal-perfluorinated-chemicals/aboutpfass/>).

Table 3.1. Production/import volumes of acrylate and urethane SCFPs and their monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. n.d. = no date; t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import mass reported
<i>Acrylate SCFPs</i>			
101896-32-6	n:2 fluorotelomers	unclear	EU: confidential (n.d.)
817203-49-9	n:2 fluorotelomers	6	EU: confidential (n.d.)
1071022-26-8	n:2 fluorotelomers	6	SPIN: 0.6 t + confidential (2012–2019)
1793072-86-2	n:2 fluorotelomers	6	SPIN: confidential (2016)
142636-88-2	n:2 fluorotelomers	8;10;12	US: <454 t/yr in 2012–2015 SPIN: confidential (2011–2019)
70969-47-0	n:2 fluorotelomers	6;8;10;12;14;16;18	US: <227 t in 2005, 57.9 t in 2011, <454 t/yr in 2012–2015 SPIN: 64.7 t + confidential (2001–2019)
304012-61-1	n:2 fluorotelomers	6;8;10;12	SPIN: confidential (2008–2016)
479029-28-2	n:2 fluorotelomers	6;8;10;12	SPIN: confidential (2004–2011)
1078712-88-5	n:2 fluorotelomers	2;4;6;8;10;12;14;16;18	US: 15.6 t in 2011
53515-73-4	PACF-derivatives	7	SPIN: confidential (2000–2003)
1017237-78-3	PASF-derivatives	4	US: <454 t/yr in 2012–2015 SPIN: confidential (2011, 2014–2019)
425664-29-5	PASF-derivatives	4	SPIN: confidential (2008–2019)
819069-72-2	PASF-derivatives	4	SPIN: confidential (2006–2007)
162568-17-4	PASF-derivatives	8	SPIN: confidential (2000–2015)
68298-61-3	PASF-derivatives	7;8	SPIN: confidential (2000)
68298-62-4	PASF-derivatives	7;8	SPIN: confidential (2000–2019)
68555-90-8	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
68329-56-6	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
68555-92-0	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2017)
68586-13-0	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
68586-14-1	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
68649-26-3	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
68867-62-9	PASF-derivatives	4;5;6;7;8	US: >4.54 to <227 t in 2001 SPIN: confidential (2000–2019)
127133-66-8	PASF-derivatives	4;5;6;7;8	SPIN: confidential (2000–2003)
<i>Acrylate SCFP monomers</i>			
1228350-17-1	n:2 fluorotelomers	6	EU: =1 to =10 t/yr (n.d.)
17527-29-6	n:2 fluorotelomers	6	EU: =100 to <1000 t/yr (n.d.) US: >4.54 to <227 t/yr in 1989, 1997 & 2001, confidential in 2011, <454 t in 2012, >454 to <908 t/yr in 2013–2015 SPIN: confidential (2000, 2004–2010)
2144-53-8	n:2 fluorotelomers	6	EU: =1000 to <10000 t/year (n.d.) US: >4.54 to <227 t in 1985, confidential in 2011, >454 to <4540 t in 2012, >272 to <454 t in 2013, >454 to <4540 t/yr in 2014 and 2015 SPIN: confidential (2003–2019)
27905-45-9	n:2 fluorotelomers	8	US: >4.54 to <227 t/yr in 1989 and 1997, >227 to <454 t in 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 SPIN: confidential (2000, 2004–2019)

17741-60-5	n:2 fluorotelomers	10	<b>US:</b> >4.54 to <227 t/yr in 1989, 1997 and 2001, >454 to <4540 t in 2005, confidential in 2011, >45.4 to <227 t in 2012, <454 t/yr in 2013–2015 <b>SPIN:</b> confidential (2000, 2004–2005)
34395-24-9	n:2 fluorotelomers	12	<b>US:</b> >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 <b>SPIN:</b> confidential (2000, 2004–2005)
34362-49-7	n:2 fluorotelomers	14	<b>US:</b> >4.54 to <227 t/yr in 1989, 1997 and 2001, <227 t in 2005, <454 t/yr in 2012–2015 <b>SPIN:</b> confidential (2004–2005)
85631-54-5	n:2 fluorotelomers	6;8;10;12	<b>EU:</b> =10 to <100 t/yr (n.d.) <b>SPIN:</b> confidential (2000–2012)
352-87-4	PACF-derivatives	1	<b>EU:</b> =1 to <10 t/yr (n.d.) <b>SPIN:</b> confidential (2008–2009, 2015–2017)
355-93-1	PACF-derivatives	4(1H)	<b>EU:</b> =10 to <100 t/yr (n.d.)
67584-55-8	PASF-derivatives	4	<b>EU:</b> =100 to <1000 t/yr (n.d.) <b>US:</b> >4.54 to <227 t/yr in 1985, 1989, 1993 and 1997, confidential in 2011, <454 t/yr in 2012–2015 <b>SPIN:</b> confidential (2000–2019)
67584-59-2	PASF-derivatives	4	<b>EU:</b> =10 to <100 t/yr (n.d.) <b>SPIN:</b> confidential (2000–2017)
212335-64-3	PASF-derivatives	4	<b>US:</b> confidential in 2011, <454 t/yr in 2012–2015
3063-94-3	Unclear*	1	<b>EU:</b> =0 to <10 t/yr (n.d.)
<i>Urethane SCFPs</i>			
357624-15-8	n:2 fluorotelomers	6	<b>SPIN:</b> confidential (2011–2014)
118102-37-7	n:2 fluorotelomers	6;8;10;12	<b>SPIN:</b> confidential (2000–2014)
118102-38-8	n:2 fluorotelomers	6;8;10;12	<b>SPIN:</b> confidential (2000–2014)
68990-40-9	n:2 fluorotelomers	2;4;6;8;10;12;14;16	<b>SPIN:</b> confidential (2000–2003)
135228-60-3	n:2 fluorotelomers	4;6;8;10;12;14;16;18	<b>SPIN:</b> confidential (2003–2016)
144468-32-6	n:2 fluorotelomers	4;6;8;10;12;14;16;18	<b>SPIN:</b> confidential (2000–2010)
162491-88-5	n:2 fluorotelomers	Unclear	<b>SPIN:</b> confidential (unclear)

Both acrylate and urethane SCFPs have been used in a wide range of applications, which are divided into several major use areas and separately described below. Similar to the production volumes, use information reported to the SPIN database has mostly been claimed as confidential business information (see Table S2). Furthermore, although some data were reported by 3M in the past (see Figure S8 in the Supplementary Data of Wang et al. 2014A), it is generally unknown how much acrylate and urethane SCFPs have been used in which applications.

### ***Fabrics, textiles, and apparel articles***

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 PFASs that demonstrate some synergistic effects (Bank et al., 1994). These SCFPs include many acrylate (e.g., CASRN 68298-62-4) and urethane<sup>24</sup> (e.g., 3M Scotchgard Fabric Protector; 3M, 2018) SCFPs. They can also be a mixture containing both acrylate and urethane SCFPs (e.g., Teflon Advance Carpet Protector), as reported by Dinglasan-Panlilio and Mabury (2006). In these SCFPs, nonfluorinated co-monomers serve the functions of extending fluorine efficiency, providing functionality to enhance durability, and/or modifying the hand feel of the treated fabric (Bank et al. 1994). The treatments of textiles can be done both pre-market by manufacturers,

<sup>24</sup> Urethane SCFPs, typically based on the reaction of fluorinated diol intermediates with diisocyanates, were particularly used for the treatment of 100% cotton and cotton-blend textiles (Bank et al., 1994).

and aftermarket by professional services and consumers (3M, 1999). For more examples and technical details, see Table S1, 3M (1999) and Bank et al. (1994).

### ***Food-contact paper and paperboard***

Many acrylate and urethane SCFPs have been used as an oil- and water-resistant agent in paper and paper board. As such, these SCFPs can prevent the paper material from soaking up fats and water, with the applications particularly targeting fatty foods especially those intended to be heated in packaging or stored for an extended period, and as moisture barriers (OECD, 2020). These SCFPs can be used either by the addition to the pulp during paper production (internal sizing), or as a surface treatment to the paper (external sizing) (Uehara et al., 2021; OECD, 2020). More technical details on the internal and external sizing, including respective advantages and disadvantages can be found in OECD (2020).

Currently, 15 fluorotelomer-based acrylate<sup>25</sup> and 1 PFPE-based urethane SCFPs are listed on the US Food & Drug Administration (FDA)'s Inventory of Effective Food Contact Substance Notifications (FCN) database<sup>26</sup> for such uses. Additional information on the concentration limits for using SCFPs in making the food-contact paper and paperboard in the US can be found in the US FDA FCN database.<sup>27</sup> Furthermore, several major manufacturers have reached agreement with the US FDA to voluntarily phase out their sales of 6:2 fluorotelomer-based SCFPs for use in food contact applications in the US by 2023 (see Table S2; US FDA, n.d.).

### ***Others***

One acrylate SCFP (CASRN 70969-47-0) has been reported as fluorosurfactants in fire-fighting foam formulations (e.g., Solberg 1x3 ATC, Sigma AFFF; Solberg, n.d.; Sigma, n.d.) that are used in extraction of crude petroleum and natural gas, manufacture of coke and refined petroleum products, and wholesale trade (except of motor vehicles and motorcycles) (see Table S2; US EPA, 2016; SPIN, n.d.). CASRN 68298-62-4 has been reported for use in the following application areas with no further details available (likely as fluorosurfactants): paints, lacquers and varnishes; reprographic agents; adhesives and binding agents; printing inks; and glossing agents (see Table S2; SPIN, n.d.).

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<sup>25</sup> The number here counts different salts of a SCFPs as different SCFPs. If different salts of a SCFP would be counted as one SCFP, there would be 11 distinct fluorotelomer-based acrylate SCFPs.

<sup>26</sup> <https://www.cfsanappsexternal.fda.gov/scripts/fdcc/?set=FCN>

<sup>27</sup> Further US-FDA generated documents on the chemistry and exposure, toxicology, and environmental impacts of the PFASs that were approved by US FDA for food contact substances between 2002 and 2016 can be found at <https://www.edf.org/sites/default/files/EDF-PFAS-FOIA-FCN-Chemistry-Memos.pdf>.

### 3.2. Presence of other PFASs in the commercial formulations

Commercial acrylate and urethane SCFP formulations are generally available in the form of aqueous dispersion of SCFP particles (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). A range of non-polymeric PFASs have been detected in several fluorotelomer-based commercial acrylate and urethane SCFP formulations (see Table S3), including perfluoroalkyl iodides (PFAIs), PFCAs, and fluorotelomer acrylates (FTAcS), alcohols (FTOHs), alcohol acetates (FTOH-aces), carboxylic acids (FTCAs), ethers (FT-ethers), olefins (FTOs) and unsaturated carboxylic acids (FTUCAs).

The levels of non-polymeric PFASs may vary considerably across commercial formulations (see Table S3). One study reported residuals at the level of over 5 weight % of the solids in one fluorotelomer-based commercial formulation tested (see Table S1 of Washington et al. 2014). 3M reported that most of its PASF-based formulations for industrial applications typically contain monomer residuals at 1 percent or lower levels, though it is not clear whether the 1 percent or lower levels referred to the ratio of non-polymeric PFAS residuals to the SCFP content in dispersions or to the total dispersion mass (3M, 1999). In another two PASF-based commercial urethane SCFP formulations, no non-polymeric PFASs were detected (Chu et al. 2014; Letcher et al. 2020); however, this result may be an artefact.<sup>28</sup>

The detected non-polymeric PFASs can be grouped into four categories based on origins (by comparing to the general synthesis routes of SCFPs; see Figure 3.1), with some belonging to more than one category: (i) unreacted raw materials and reaction intermediates used in the synthesis (e.g., PFAIs, FTOHs, FTAcS); (ii) impurities from the starting materials (e.g., PFOA)<sup>29</sup>; (iii) degradation products of the unreacted raw materials and reaction intermediates (e.g., FTAcS → FTOHs → FTCAs, FTUCAs, and PFCAs; Young and Mabury, 2010, Liu and Avendaño, 2013, and Evich et al., 2022) and SCFPs (see Section 3.3 below); and (iv) reaction byproducts of PFASs in the previous three categories (e.g., 8:2 FTOH → 8-8 ether; 8:2 FTOH + PFOA → 8-2-8 ester)<sup>30</sup>.

In addition to being impurities from the starting materials and synthesis in the formulations, some non-polymeric PFASs (e.g., FTOHs) can also be intentionally left at significant levels in commercial formulations as dispersants to keep the SCFP particles suspended in the aqueous phase.

Commercial formulations are applied to materials such as textiles and pulp whereby the SCFP particles are strongly adsorbed and, in some cases, chemically bound to the material surface, and the rest application suspension is discharged to wastewater (Russell et al. 2008, 2010; Uehara et al. 2021; Washington et al. 2014). Thus, during application of commercial formulations, PFAS impurities therein are partially released (via air, wastewater and/or solid waste; Heydebreck et al., 2016), and partially transferred onto products (for examples of the detection of some non-polymeric PFASs in SCFP-treated products, see Table S3). The levels of PFAS impurities released and remaining in treated products may be highly

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<sup>28</sup> The non-detection could be due to several reasons: (i) the dilution that the concentration of SCFPs was estimated to be <3% in the formulations (i.e., at least about an order of magnitude lower than the other studies), resulting in the PFAS impurity levels below the detection limit; (ii) possible key compounds such as FASEs (Wang et al., 2014A) were not monitored; and/or (iii) the analytical methods used in that particular study are not effective for capturing non-polymeric PFASs, particularly those that are still co-associated with the polymer (Larsen et al. 2006; Washington et al. 2009, 2014). Washington et al. (2014) provides a solid analytical workflow for measuring levels of PFAS other than the SCFPs in the commercial formulations.

<sup>29</sup> PFOA was detected in the perfluoroalkyl iodides (PFAIs) starting material for synthesizing fluorotelomers; for more details, see the Supplementary Data of Wang et al. (2014A).

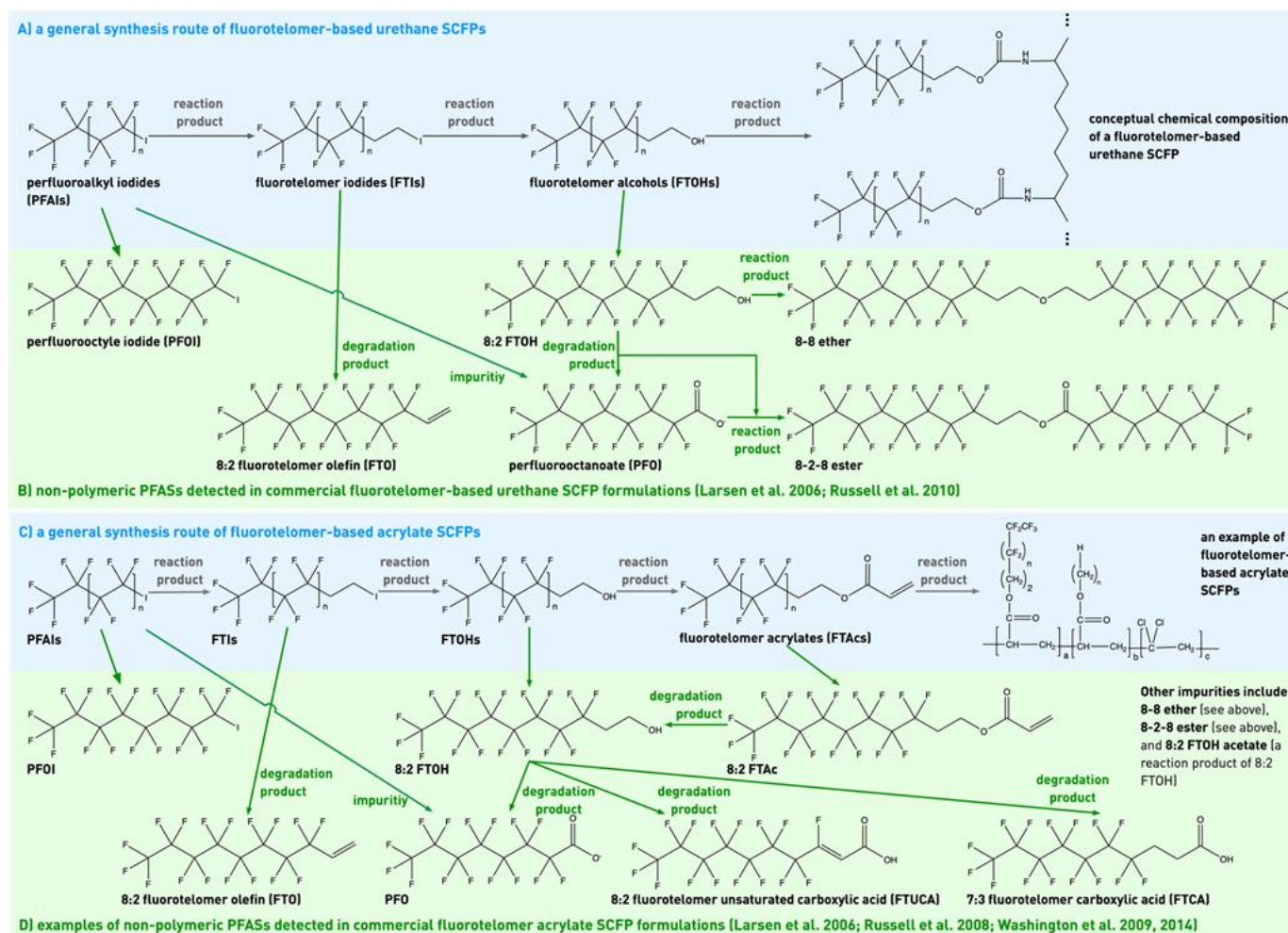
<sup>30</sup> The acronyms “8-8 ether” and “8-2-8 ester” are taken from the original publications. Future terminology may harmonized them in the same manner as “8:2 FTOH” for “8:2 fluorotelomer alcohol”.

variable, depending on the processes and control measures.<sup>31</sup> No mass balance studies of the fate and distribution of non-polymeric PFAS during application of commercial SCFPs are identified.

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<sup>31</sup> Some patents describe flash drying, e.g., at 127 °C, is included in the application of SCFPs. When Washington et al. (2014) dried a commercial SCFP at 127 °C, the PFAS impurities dropped 2- to 3-orders of magnitude to constant concentrations within about 10 minutes.

Figure 3.1. A comparison of detected non-polymeric PFASs to the general synthesis routes of commercial fluorotelomer acrylate and urethane SCFPs.



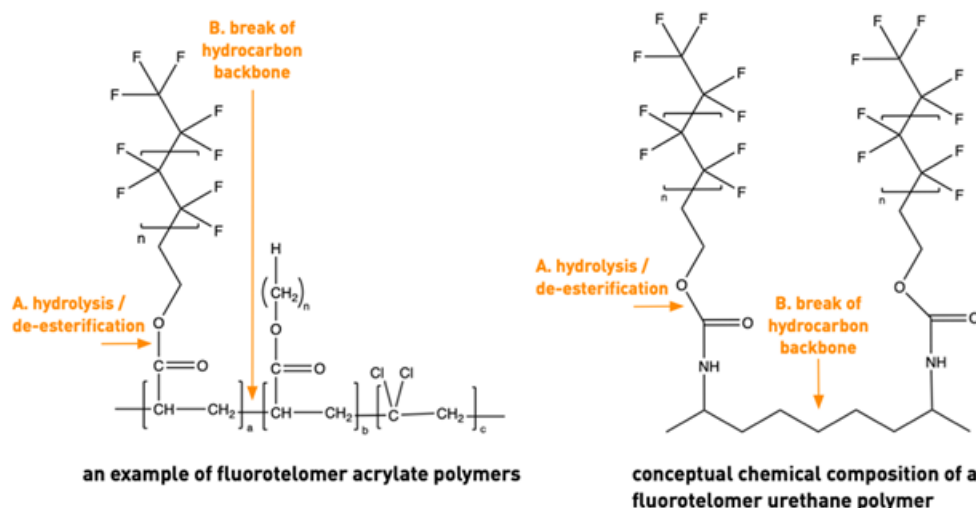
### 3.3. Degradation of SCFPs during use and after end-of-life

Acrylate and urethane SCFP degradation may follow two main degradation mechanisms (see Figure 3.2): A) direct cleavage of PFAS moieties from the side chains (e.g., hydrolysis of the ester bond); and B) breakdown of the polymer carbon-carbon backbone to form small oligomeric species which subsequently undergo ester bond cleavage (Russell et al. 2008, 2010).

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 PFSA in the environmental and biota following rather well-characterized degradation pathways of non-polymeric PFASs [which have been well synthesized in Young and Mabury (2010), Liu and Avendaño (2013) and Evich et al. (2022)].

These studies did not show whether the mechanism B also occurred, whereas a recent study by Schellenberger et al. (2022) detected release of SCFP-containing microplastic fibres from functional textiles during washing, suggesting the mechanism B may occur during certain conditions (which may be learned from the research field of microplastic formation in the future).

Figure 3.2. Schematic illustration on two main degradation mechanisms of acrylate and urethane SCFPs.



While existing degradation studies agree well on the degradation mechanisms, historical studies have reported a wide range of degradation half-lives<sup>32</sup> (see Table 3.2), ranging from less than 1 year, to a couple of years, to decades to roughly a century, to over a thousand years. These large variations are partially caused by limitations in the experimental design of some previous studies (e.g., whether non-polymeric PFAS residues were all removed; Larsen et al., 2006, Washington et al., 2009, Washington et al. 2015B). In other words, some of the large variations observed are caused by experimental artefacts, which can be and were minimized/eliminated in more recent studies (where the degradation half-lives of two fluorotelomer-based acrylate SCFPs were measured to be several decades; Washington et al., 2015A and

<sup>32</sup> Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone.



2015B). More technical details and discussion on this possible source of error, as well as a recommended analytical workflow to minimize/eliminate it, can be found in Washington et al. (2014).

At the same time, the variations observed also partially reflect the true variability of several parameters that may impact degradation, including 1) molecular size of SCFPs (only three studies reported, with the number/weight-average molecular weight ranging from nearly 3000 Dalton to 40,000 Dalton, which can influence, e.g., bioavailability); 2) specific surface area of SCFP particles (which can influence areas available for degradation; Washington et al. 2009); 3) substrate (as hydrophobicity may well be diminished when water can come through the substrate and result in hydrolysis / de-esterification without or with less interference from the side chains, see Figure 3.2); 4) temperature, 5) pH values (shorter degradation half-lives with increasing alkalinity above pH = 8; Washington et al. 2015B), and 6) humidity (the same SCFP degraded more slowly when it was dry in comparison to when it was water-submerged; Washington et al. 2015A,B). Such variability cannot be minimized/eliminated.

Therefore, the degradation half-lives of acrylate and urethane SCFPs in the environment and biota will remain to some extent uncertain, in part reflecting real-world variability associated with the factors described above. Still, more of this uncertainty is because the characterization of many of these parameters are not available in the public domain (e.g., molecular size and specific surface areas of SCFP particles in commercial formulations) and may change over time (e.g., molecular size decreases when the degradation mechanism B occurs). Nevertheless, it can be concluded that these SCFPs generally will degrade under environmental conditions, with half-lives often falling roughly at a century or less, and thus serve as a long-term source of non-polymeric PFASs in the environment and biota.

In contrast to abiotic and biotic degradation, little is known about the fate of acrylate and urethane SCFPs during municipal waste incineration of SCFP-treated articles.<sup>33</sup> Yamada et al. (2005) investigated the thermal degradation of a polyester/cellulose fabric substrate treated with a fluorotelomer acrylate SCFP (that was described in the US Patents 4742140 and 5344903) under laboratory conditions with an average temperature of 1000 °C or greater<sup>34</sup> over approximately 2 seconds of residence time. The results observed thermal degradation of the SCFP started at ca. 600 °C and increased with increasing temperature (90% sample destruction at ca. 850 °C, and 99.9% sample destruction at 1000 °C), with no formation of PFOA. Fluorinated radicals such as  $\bullet\text{CF}_3$  and  $\bullet\text{CF}_2\text{CH}=\text{CH}_2$  were major extracted species at 600 °C, and their levels decreased with increasing temperature (they still existed at 1000 °C, but the relative amount remaining was  $\leq 0.1\%$ ). It is currently unknown whether other non-polymeric PFASs would be generated during incineration, as they were not monitored in the study.

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<sup>33</sup> More is known about incineration of other PFASs including fluoropolymers. For more details, see, e.g., Olsavsky et al., 2020 (<https://doi.org/10.3390/app10196921>) and Winchell et al., 2020 (<https://doi.org/10.1002/wer.1483>).

<sup>34</sup> Note that in Europe, the flue gases from municipal waste incinerators are meant to run at a temperature of 850 °C for at least two seconds, see <https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=LEGISSUM:l28072&from=EN>.

Table 3.2. Reported experimental degradation half-lives of commercial acrylate and urethane polymers.\*

Reference	SCFP type (characterization)	Degradation half-life [years]	Notes
Russell et al. 2008	A commercial n:2 fluorotelomer acrylate SCFP (number-average molecular weight of 40000 Dalton and 10.095 weight% fluorine)	Alfisol soil: 217 (SAS calculations) / 1140 (Excel calculations) Inceptisol soil: 95 (SAS calculations) / 637 (Excel calculations) Mollisol soil: 202 (SAS calculations) / 1270 (Excel calculations) Ultisol soil: >2000 (SAS calculations & Excel calculations)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2009	A commercial n:2 fluorotelomer acrylate SCFP that is pre-treated by the manufacturer to minimize non-polymeric residue level (unknown)	870–1400 for coarse-grained test polymer in soil 10–17 for more-finely grained polymers in soil (based on modelling, assuming degradation is surface-mediated)	The specific area of the test SCFP was about 0.05 m <sup>2</sup> /g, lower than the specific area of a typical commercial acrylate SCFP at about 14 m <sup>2</sup> /g.
Russell et al. 2010	A commercial n:2 fluorotelomer urethane SCFP (number/weight-average molecular weight of 3500 Dalton and 10 weight% fluorine)	Alfisol soil: 241 Inceptisol soil: 72 Mollisol soil: 219 Ultisol soil: 28 (use data through day 273) to 79 (use all data)	These degradation half-lives may be an overestimate, as the study did not follow the recommendation by Larsen et al. (2006) to capture all non-polymeric residues remained in the polymer – an issue that was detailed in Washington et al. (2009).
Washington et al. 2015A	Two commercial n:2 fluorotelomer acrylate SCFPs – FTP3 and FTP4 (unknown)	Quantitative rate-constant treatment: Applying (ultisol) soil (FTP4, driving at 127 °C, soil moisture saturated, endogenous microbial community, 7 sampling rounds, 5 microcosms per sample rounds) = 65 (use C <sub>8</sub> data and 80% recovery)–112 (first-order sum of all analytes and 100% recovery); Semi-quantitative range-finding treatments: 5 sample media (2 ultisol soils, 1 alfisol soil, 1 commercial soil, and 1 water); 2 moisture states (moist and saturated): FTP3 and FTP4; 2 FTP dispersion driving temperatures (22 °C and 127 °C); 2 assumed recoveries (80% and 100%) = 30–77; Best composite estimate: 33–112	Abiotic hydrolysis control unexpectedly degraded to form FTOHs roughly at the same rate as soil treatments.
Washington et al. 2015B	A commercial n:2 fluorotelomer acrylate SCFP – FTP3 (unknown)	Abiotic hydrolysis at 25 °C ca. 55 (based on C <sub>8</sub> data) / 89 (based on C <sub>10</sub> data) at pH = 5–8 34 (based on C <sub>8</sub> data) / 34 (based on C <sub>10</sub> data) at pH = 9 15 (based on C <sub>8</sub> data) / 18 (based on C <sub>10</sub> data) at pH = 10 4.9 (based on C <sub>8</sub> data) / 5.1 (based on C <sub>10</sub> data) at pH = 11 0.7 (based on C <sub>8</sub> data) / 0.66 (based on C <sub>10</sub> data) at pH = 12	Half-lives for pH>8 not expected to represent common environmental conditions, but these data aid elucidation of hydrolysis mechanism.

\* Note that the degradation half-lives here refer to the initial degradation step(s) of cleaving PFAS moieties from the polymer backbone. Additionally, Rankin et al. (2014) studied two non-commercial, custom-synthesized homopolymeric n:2 fluorotelomer acrylate SCFPs and observed degradation half-lives of 8–111 years. It should be noted that the number-average molecular weight in this study were 3000–3800, roughly an order of magnitude less than common commercial acrylate SCFPs.

### 3.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

As stated above, significant amounts of acrylate and urethane SCFPs, and other PFAS impurities present in the commercial formulations, have been and are released via air, waste water and solid waste along the life cycle of SCFPs: during the application of commercial formulations (e.g., Heydebreck et al., 2016), during the processing of treated materials into articles (e.g., 3M, 1999; Liu et al., 2009, 2014), and during the use and disposal of treated articles (e.g., Freriksson et al., 2020; Schellenberger et al., 2022; van der Veen et al., 2022).

3M estimated that total PFAS losses during surface treatment of uncut fibre, textile or leather raw materials using POSF-based SCFPs and downstream industrial operations (e.g., drying, cutting, shearing, packaging and shipping) could range between 10 and 25 percent (3M, 1999);<sup>35</sup> it is unclear how the reported levels are relevant for the SCFPs and processes being used today.

Further, three studies have investigated the presence of target urethane SCFP compositions in two pre- and post-2002 Scotchgard fabric protection formulations in lake sediment, soil samples, sludge from wastewater treatment plants and landfill leachates (see Table S5) (for more analytical details, see, e.g., Chu and Letcher, 2017). 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, the three studies indicate that sludge can be a main source of at least some SCFPs in the environment, particularly when they are subsequently used as biosolids to treat agricultural land. This is in line with another study investigating releases of SCFP-treated textile fibres during washing, where considerable releases of SCFP-containing fibres were detected in washing and rinsing water (Schellenberger et al., 2022), many of which may then be retained in sewage sludge at wastewater treatment plants (Wu et al. 2021). It was also shown that landfill leachate might not be a significant source of some SCFPs themselves (Fredriksson et al. 2020). Nevertheless, landfill leachates can be a significant source of other non-polymeric PFASs (e.g., Lang et al., 2017; Masoner et al. 2020), which may partially originate from SCFP-related sources.

### 3.5. Summary of critical knowledge and data gaps

It can be qualitatively concluded that production, use and disposal of acrylate and urethane SCFPs are significant sources of non-polymeric PFASs in the environment, particularly in the long term, as also demonstrated in several simplified modelling simulation studies (Wang et al., 2014B; Wang et al., 2017; Li et al. 2017). This is because of historical and ongoing high production volumes, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle.

However, due to presence of the following critical knowledge and data gaps, it is currently not possible to more precisely estimate the contribution of acrylate and urethane SCFPs to non-polymeric PFASs in the environment: (i) a lack of detailed information on the production and use volumes of individual acrylate and

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<sup>35</sup> The levels were calculated using material flow analyses, based on 3M's internal sales data, knowledge of product handling and use practices from field sales and technical personnel, best estimates of end-use applications from known customer activities, and knowledge of worldwide activities (where applicable) by St. Paul-based personnel. Calculation details are provided in the original document submitted to the US EPA, but are to a large extent redacted in the publicly accessible version of the document.

urethane SCFP (with many not reported in the public domain due to confidentiality or no reporting requirements), (ii) a lack of a comprehensive overview of acrylate and urethane SCFPs on the market, particularly in terms of their structural details and thus degradation potential, (iii) a lack of understanding of their fate in municipal waste incinerators.

### 3.6. Options for a way forward

A better understanding of the production, use and releases of acrylate and urethane SCFPs can inform a better understanding of the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots, particularly as the current analytical and monitoring capability and capacity of PFASs are limited due to various reasons. Future action may include addressing both existing information and current information gaps. Addressing existing information may include: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, and harmonizing reported structural and use information (in terms of, e.g., the level of details, terminologies, and data format), and (ii) exploring ways to make publicly available the structural and use information that has been reported to regulators, but has not been claimed as confidential business information. Addressing current information gaps may include further research on their fate in municipal waste incinerators.

# 4 The Life Cycle of Oxetane SCFPs

## Chapter summary:

- Limited information is available on the historical and current production of oxetane SCFPs.
- They have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants.
- Little is known about other PFASs present in commercial oxetane SCFPs, but likely include at least two types of other PFASs: unreacted raw materials and intermediates, and reaction by-products (e.g., cyclic oligomers of the oxetane monomers).
- Also, little is known about the degradability of oxetane SCFPs. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs, the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs.
- No studies on the releases of oxetane SCFPs and other PFASs present in the formulations were identified. However, it is likely that oxetane SCFPs and other PFASs present in the formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment.
- Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

## 4.1. Historical and ongoing production and uses

In comparison to acrylate and urethane SCFPs, limited public information is identified on the production of oxetane SCFPs. A range of PACF-based oxetane SCFPs with varied fluorinated carbon chain lengths have been marketed under the brand name “PolyFox” (see Table S1). At least four of them are registered in the EU under REACH; however, the production/import volumes of three have been claimed as confidential, whereas the production/import volume of one monomer is reported to be  $\geq 1$  to  $< 10$  tonnes/year (see Table 4.1). The oxetane SCFP monomer<sup>36</sup> has also been registered for production in or import into Japan, Vietnam and the US with unknown amounts (see Table S1).

According to the manufacturer, oxetane SCFPs have been primarily used as wetting, flow and levelling agents in different use areas such as coatings, electronic applications, floor finish, and inks, and some may also be used as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants (see Table S2).

Table 4.1. Production/import volumes of oxetane SCFPs and monomers in the EU reported in the REACH dossiers. n.d. = no date

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
<i>oxetane SCFPs</i>			
449204-80-2	PACF-derivatives	1	EU: confidential (n.d.)
1182261-26-2	PACF-derivatives	1	EU: confidential (n.d.)
449204-81-3	PACF-derivatives	2	EU: confidential (n.d.)
<i>Oxetane SCFP monomer</i>			
449177-94-0	PACF-derivatives	2	EU: $\geq 1$ to $< 10$ tonnes/year (n.d.)

## 4.2. Presence of other PFASs in the commercial formulations

From the limited public information identified, at least two types of other PFASs can be present in the commercial formulations: unreacted raw materials and intermediates, and reaction by-products. The former is deduced from Dinglasan-Panlilio and Mabury (2006): the authors detected several FTOHs ( $C_nF_{2n+1}CH_2CH_2OH$ ) – the likely starting materials – in a non-commercialized fluorotelomer-based oxetane SCFP that was specially prepared by the oxetane SCFP manufacturer (who produces commercial oxetane SCFPs from  $C_nF_{2n+1}CH_2OH$ ; Buck et al., 2011).

Reaction by-products have been reported by Wesdemiotis et al. (2006); the authors observed that during the polymerization of an oxetane monomer and other co-monomers/reactants (like other commercial oxetane SCFPs; Kausch et al., 2002), cyclic oligomers of the oxetane monomers were formed in small yields (about 5%), with the tetramer being predominant (at least one order of magnitude more abundant than other oligomers).

Commercial oxetane SCFPs are available both in the form of aqueous dispersion (e.g., PolyFox PF-2003; Synthomer, 2020A) and in pure form (e.g., PolyFox PF-656; Synthomer, 2020B). It is unknown whether

<sup>36</sup> Oxetane (or 1,3-propylene oxide) is a heterocyclic organic compound with the molecular formula  $C_3H_6O$ , and has a four-membered ring. Oxetanes are highly reactive as they are strained cyclic ethers, and frequently used as reactive intermediates for further organic molecular synthesis.

the impurities mentioned above would be removed from the commercial products before being put on the market.

### 4.3. Degradation of oxetane SCFPs during use and after end-of-life

No studies on the degradation of oxetane SCFPs during use and after end-of-life are identified.<sup>37</sup> It is also challenging to theoretically project the degradation behaviour of oxetane SCFPs from the chemical structures. On one side, in comparison to the ester bonds in acrylate and urethane SCFPs (see point A in Figure 3.2), the ether bonds (–O–) in oxetane SCFPs are more stable. On the other side, many commercial oxetane SCFPs appear to have lower average molecular weight (e.g., about 1500 Dalton for PolyFox PF-136A, PF-656 and PF-2003; Synthomer, 2020A,B,C), which may indicate higher bioavailability than many commercial acrylate and urethane SCFPs. Future studies investigating the degradation of oxetane SCFPs during use and after end-of-life are needed.

### 4.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

No studies on the environmental releases of oxetane SCFPs and other PFASs present in the commercial formulations are identified.<sup>38</sup> However, it is likely oxetane SCFPs and other PFASs present in the commercial formulations are released during use (given their use patterns as wetting, flow and levelling agents in open applications such as coatings, floor finish, and inks) and end-of-life treatment. Future studies investigating their releases during use and after end-of-life and environmental presence are needed.

### 4.5. Summary and options for a way forward

Overall, little is known about oxetane SCFPs. Future action may first make the current production and use volumes of oxetane SCFPs publicly available and accessible, and then the priority level of investigating oxetane SCFPs in comparison to other SCFPs can be determined by relevant stakeholders.

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<sup>37</sup> Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “stability”, “degradation”, “thermolysis” and/or “pyrolysis” did not return relevant results.

<sup>38</sup> Google Scholar searches using the combination of keywords “fluoro”, “oxetane”, “polyfox”, “environmental”, “presence”, “occurrence” and/or “release” did not return relevant results.

# 5 The Life Cycle of Silicone SCFPs

## Chapter summary:

- Various silicone SCFPs and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been and are being produced and used. Ultrashort-chain silicone SCFPs (where fluorinated carbon chain length = 1) have been produced at the scale of tens of thousands tonnes per annum, whereas less is known about longer-chain silicone SCFPs (due to confidentiality, no reporting requirements, etc.).
- Commercial silicone SCFPs are available in a wide range of different forms, including different polymers that are manufactured at the industrial scale, and commercial formulations (e.g., spray) containing monomers of silicone SCFP which can then form silicone SCFPs on the material surface upon application.
- Silicone SCFPs have been used in a wide range of applications, including as surface protectors to treat different materials, in medical applications, in personal care products, as antiformers, as lubricants, and in rubber applications.
- Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels: unreacted raw materials and intermediates, and reaction byproducts. For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application.
- Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains and/or at the silicone polymer backbone, thus releasing various PFAS degradation products including cyclic PFAS siloxanes and PFCAs during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions. Once released, cyclic PFAS siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.
- Significant amounts of SCFPs and other PFASs present in the commercial formulations may be and are released from the production, use and disposal, via air, wastewater and solid waste, with elevated levels of ultrashort-chain monomers detected close to the manufacturing sites in China, and in sewage sludge and sediments in several parts of the world.
- Similar to acrylate and urethane SCFPs, given the high production volumes and wide use of silicone SCFPs, possible presence of high levels of other PFASs in the commercial formulations, and their ability to degrade to non-polymeric PFASs including PFCAs, silicone SCFPs are very likely significant sources of non-polymeric PFASs in the environment. Future efforts may collect further information and reduce the uncertainties to reach more precise estimates.



## 5.1. Historical and ongoing production and uses

Various silicone SCFPs<sup>39</sup> and monomers, belonging to different categories of PFAS moiety types with varied fluorinated chain lengths, have been registered for production/import in many jurisdictions (see Table S1). Table 5.1 summarizes the production/import volumes of various silicone SCFPs and monomers reported in the EU, in the US, and in the Nordic Countries (Denmark, Finland, Norway and/or Sweden). Many are available in large tonnage ranges (e.g., >454 to <4540 tonnes/year), and many others have been claimed as confidential business information and not made public.

Nevertheless, it can be concluded that significant amounts of silicone SCFPs have been and are being produced, from the numbers reported in Table 5.1. Furthermore, in 2016, the total global production of trifluoropropyl-based silicone SCFPs (i.e., fluorinated carbon chain length = 1) was reported to be about 43600 tonnes, with the demand from China being about 3000 tonnes (Xiang et al., 2021).

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<sup>39</sup> They are often called “polysiloxanes” in the technical literature.

Table 5.1. Production/import volumes of silicone SCFPs and monomers in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting); and in the EU reported in the REACH dossiers. t = tonnes; yr = year; n.d. = no date.

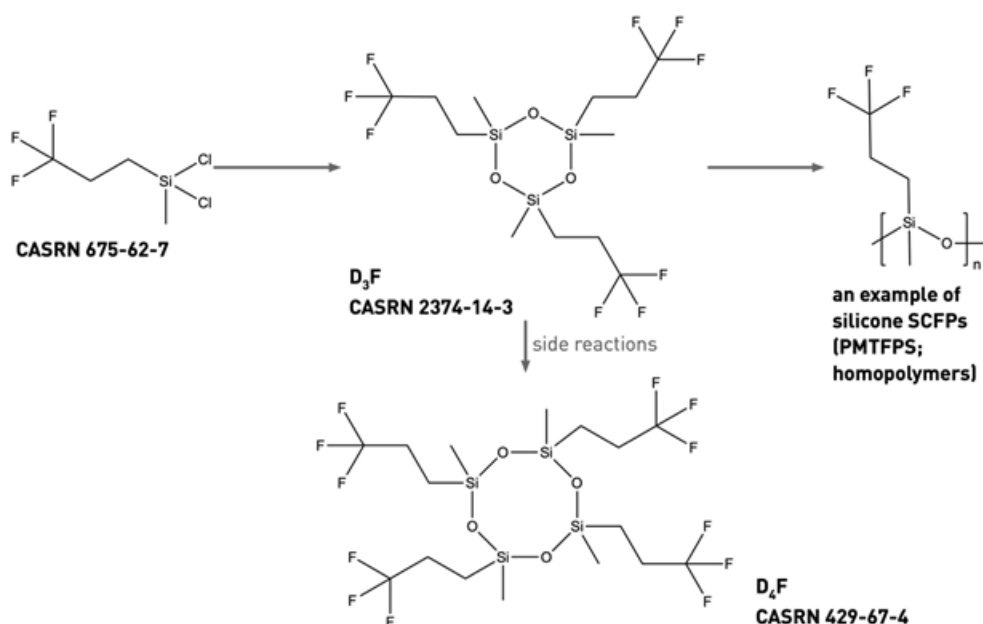
CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported [tonne; t]
<i>silicone SCFPs</i>			
104780-70-3	n:2 fluorotelomers	6	SPIN: confidential (2000–2019)
115340-95-9	n:2 fluorotelomers	6	SPIN: confidential (2000–2019)
262292-17-1	n:2 fluorotelomers	6	SPIN: confidential (2001–2019)
273737-91-0	n:2 fluorotelomers	6	SPIN: 0.3 t + confidential (2007–2019)
125476-71-3	n:2 fluorotelomers	8	US: confidential in 2011, <454 t/yr in 2012–2015 SPIN: confidential (2013–2019)
143372-54-7	n:2 fluorotelomers	8	SPIN: confidential (2000–2019)
146632-08-8	PASF-derivatives	8	SPIN: confidential (2001–2017)
162567-79-5	Perfluoroalcohol	8;9;10;11;12;13;14	SPIN: confidential (2000–2019)
<i>silicone SCFP monomers</i>			
429-60-7	n:2 fluorotelomers*	1	SPIN: confidential (2018–2019)
675-62-7	n:2 fluorotelomers*	1	EU: =100 to <1000 t/yr (n.d.) US: >454 to <4540 t/yr in 1985 and 1989, >227 to <454 t/yr in 1993, >454 to <4540 t/yr in 1997, 2001, 2005 and 2011, >454 to <908 t/yr in 2012–2015
2374-14-3	n:2 fluorotelomers*	1	EU: =100 to <1000 t/yr (n.d.) US: >454 to <4540 t in 1985, >227 to <454 t/yr in 1989 and 1993, >454 to <4540 t/yr in 1997 and 2001, <227 t in 2005, confidential in 2011, >454 to <4540 t/yr in 2012–2015 SPIN: confidential (2001–2019)
85877-79-8	n:2 fluorotelomers	4	EU: confidential (n.d.)
85857-16-5	n:2 fluorotelomers	6	EU: =10 to <100 t/yr (n.d.) SPIN: confidential (2017–2019)
51851-37-7	n:2 fluorotelomers	6	EU: =10 to <100 t/yr (n.d.) SPIN: confidential (2003–2019)
73609-36-6	n:2 fluorotelomers	6	EU: =10 to <100 t/yr (n.d.)
78560-45-9	n:2 fluorotelomers	6	EU: =10 to <100 t/yr (n.d.)
96383-55-0	n:2 fluorotelomers	6	EU: =10 to <100 t/yr (n.d.)
101947-16-4	n:2 fluorotelomers	8	EU: confidential (n.d.)
137606-16-7	n:2 fluorotelomers	8	EU: confidential (n.d.)
83048-65-1	n:2 fluorotelomers	8	SPIN: confidential (2015–2019)
475644-38-3 358750-76-2	PFPEs	Unclear	EU: confidential (n.d.)
EC 458-200-2	Unclear	Unclear	EU: confidential (n.d.)
EC 429-350-6	Unclear	Unclear	EU: confidential (n.d.)
EC 442-180-7	Unclear	Unclear (likely 1)	EU: confidential (n.d.)
EC 442-330-1	Unclear	Unclear	EU: confidential (n.d.)

\* Strictly speaking, these are not n:2 fluorotelomers, as the synthesis of the starting material, trifluoropropene, does not involve fluorotelomerization. Rather, trifluoropropene has been used in telomerization with other telogens/reagents (Boschet et al., 2012). For the purpose of simplification, they are included here in the category of n:2 fluorotelomers.

Commercial silicone SCFPs are available in a wide range of different forms. Industrially, PFAS silanes are first converted into cyclotrisiloxanes, which are then polymerized alone (into high molecular weight polymers, or so-called fluorosilicone gums with about 5000 monomer units), with end-blocking agents (into lower molecular weight polymers, or so-called fluorosilicone fluids/oils; Gelest, n.d.), or with co-monomers (into co-polymers); for an example, see Figure 5.1. The different forms are for different applications. For example, fluid polymers are used as is, or formulated for specific applications. If a reactive end blocking group is incorporated during polymerization, the fluid polymer is then useful for making a coating, a sealant, or a liquid rubber product. Gums can be further processed to produce various rubber products. More details on industrial polymerization of PFAS silanes and subsequent processing can be found in Kirk-Othmer (2006) and Yang et al. (2022).

In addition, commercial products (e.g., sprays) are also available in the form of formulations containing PFAS silane monomers [e.g.,  $C_nF_{2n+1}CH_2CH_2Si-(R)_3$ ,  $R = Cl, OCH_3$  or  $OC_2H_5$ ]. The active terminal groups  $R$  attached to silicon in the molecular structures can be easily hydrolysed to form reactive silanol ( $Si-OH$ ) groups. Upon application, mono, double or triple functional silanol groups can either react with the hydroxyl groups on the material surface (e.g.,  $SiO_2/Si$  surface) to form siloxane ( $Si-O-Si$ ) linkages, or form intermolecular polysiloxane network, i.e., silicone SCFPs directly on the material surface (ECHA 2016; Zhu et al. 2019; Adamopoulos et al. 2021).

Figure 5.1. An example of synthesis routes of silicone SCFPs from PFAS silanes and side reactions



Different forms of silicone SCFPs have been used in a wide range of applications, including the following several major use areas (more uses and additional technical details can be found in Kirk-Othmer, 2006). It should be noted that much of the use information reported to the SPIN database has been claimed as confidential business information (see Table S2).

### Surface protection

Solutions of silicone SCFPs can be used to impart oil and water repellent finishes to nylon-cotton fabrics (Kirk-Othmer, 2006). Furthermore, as stated above, PFAS-based silanes have been incorporated into commercial/consumer impregnation spray products for surface treatment of a wide range of materials with

non-absorbing surfaces such as stone, glass and enamels and with absorbing surfaces such as leather and textiles, providing water- and oil-repellency (ECHA, 2016). For instance, Dynasylan F 8261 has been used for treatment of automotive glass, coating of float glass, easy-to-clean coatings on ceramics and other silicate substrates including silica, quartz powder, sand, sandstone, cristobalite, wollastonite, mica, kaolin, and talc (ECHA, 2016). Fluowet ETC 100 and ETC 140 (likely fluorotelomer-based) have been specifically marketed for ceramic tiles in kitchens, glass doors of shower cabins, ceramic sanitary ware, wash basins, bath tubs and enamel (ECHA, 2016). Protectosil® Antigrffiti has been applied to surfaces of concrete, brick, concrete masonry units and natural stone to allow easy removal of a wide variety of graffiti (ECHA, 2016). X-Shield FluroSil 100 (likely based on PFAS-based silanes) has been marketed for protection of reinforced concrete structures, e.g., highways, bridge structures, parking decks, commercial buildings, marine structures and industrial facilities (X-Calibur, n.d.). Previously, a perfluorohexanoic acid (PFHxA)-derivative [CASRN 154380-34-4;  $\text{CF}_3(\text{CF}_2)_4\text{CONH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ] was marketed by the then Miteni as a surface treatment for glasses, natural stones, metals, wood, cellulose, cotton, leather and ceramics (Wang et al. 2013).

### ***Medical applications***

Different silicone SCFPs are used in many medical applications (Kirk-Othmer, 2006). For example, medical devices such as gastric feeding tubes use silicone SCFP-based rubber balloons for feeding tube retention while resisting gastric fluids. The low permeability of silicone SCFPs versus dimethylsilicone is utilized to control the rate of release in drug devices and in medical tubing to stop the migration of active ingredients into the tubing. Silicone SCFP fluids are used in the treatment of detached retina and other eye diseases. It is reported that from 1982 to 1993, Dow Corning produced polydimethylsiloxane (PDMS) implants with a total content of 2% PMTFPS (Kählig et al., 2009).

### ***Personal care products***

Silicone SCFP fluids and copolymers are used in a variety of personal care products, e.g., cosmetic foundations (where silicone SCFPs can provide durable water- and oil-repellency) (Kirk-Othmer, 2006). In addition, the low permeation of silicone SCFPs provides a degree of protection as a hand lotion.

### ***Antifoams***

Silicone SCFP fluids and copolymers are effective antifoams in nonaqueous systems (Kirk-Othmer, 2006). Successful application in the petroleum industry allows the full capacity of gas–oil separators to be used on offshore production platforms. Diesel fuels also require fluorosilicone antiforms due to the profoaming nature of dimethylsilicones in nonaqueous systems.

### ***Lubricants***

Silicone SCFP fluids are used as lubricants for pumps and compressors in harsh chemical service, such as those using acids, bases, and halogenated compounds and solvents (Kirk-Othmer, 2006). Silicone SCFP fluids are also found in many automotive and aerospace lubrication applications, since they are not easily leached by fuels from mechanical joints (Gelest, n.d.). In addition, silicone SCFPs, particularly the co-polymers, have been employed as lubricants for electrical contacts and precision timing devices (Gelest, n.d.). Greases formulated from silicone SCFPs and solid fluoropolymer thickeners have been used in sealed transmission and other extreme pressure applications (Gelest, n.d.).

## Rubber applications

The majority of silicone SCFPs is used in elastomers/rubber applications (Kirk-Othmer, 2006). Silicone SCFP elastomers can be formulated to provide specific durometer (hardness), tear strength, modulus, and solvent resistance properties. It is used as O-rings for fuel lines containing gasoline and aviation fuels, particularly for low temperature sealing.

## 5.2. Presence of other PFASs in the commercial formulations

Similar to acrylate, oxetane and urethane SCFPs, at least two types of other PFAS impurities can be found in the silicone SCFPs, at likely significant levels (Fei et al., 2014): unreacted raw materials and intermediates (e.g., D<sub>3</sub>F is often present as an impurity in PMTFPS; see Figure 5.1), and reaction by-products (e.g., the synthesis of PMTFPS from D<sub>3</sub>F could form its other cyclic homologues such as the tetramer homologue–D<sub>4</sub>F; see Figure 5.1). The levels of impurities may vary considerably among commercial silicone SCFP products depending on the actual synthesis conditions (Fei et al., 2014) and whether purification process may take place. A market overview could not be found using Google Scholar searches of keywords “PMTFPS”, “fluorosilicones”, “poly[methyl(3,3,3-trifluoropropyl)siloxane]”, “impurities”, and/or “residuals”.

For PFAS silane-based commercial formulations, presence of non-polymeric PFASs on the final treated products depends not only on the compositions in commercial formulations, but also the reactions that take place on the material surface upon application. For the former, Zhu et al. (2019) investigated several commercial antifingerprint formulations with a focus on fluorotelomer silanes, and detected, in addition to 6:2, 8:2 and 10:2 fluorotelomer silanes as expected, also 7:2 fluorotelomer silanes and perfluorooctyl vinyl ether (C<sub>8</sub>F<sub>17</sub>OCH=CH<sub>2</sub>)<sup>40</sup> in some formulations. The origin of 7:2 fluorotelomer silanes is unclear, whereas perfluorooctyl vinyl ether was likely intentionally added as a co-monomer for generating a highly ordered copolymer thin film (Zhu et al., 2019). Future work may investigate the mass balance of different compositions on the material surface after application.

## 5.3. Degradation of silicone SCFPs during use and after end-of-life

Similar to acrylate and urethane SCFPs, degradation of silicone SCFPs may occur at the side chains (similarly to point A in Figure 3.2) and/or at the silicone polymer backbone (similarly to point B in Figure 3.2), thus releasing various PFAS degradation products during use and after end-of-life. The dominant degradation half-lives, mechanisms and products depend on the PFAS moieties and conditions.

- Degradation of anti-sticking layers based on Optool DSX [R–(CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O)<sub>n</sub>–Si(OCH<sub>3</sub>)<sub>3</sub>] and F<sub>13</sub>-TMS [C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>–Si(OCH<sub>3</sub>)<sub>3</sub>] in UV nanoimprint lithography was observed during use and at the side chains (Truffier-Boutry et al., 2010).
- PMTFPS products suffer from poor thermal stability and tend to degrade when exposed to temperatures over 200 °C for extend periods of time, with cyclic siloxanes such as D<sub>3</sub>F and D<sub>4</sub>F being the primary products (You et al., 2020). When thermolysis was carried out at a relatively high temperature (600 °C), an additional decomposition product, trifluoropropene, was observed (You et al., 2020). Such thermolysis mechanisms, i.e., re-arrangement of the silicone backbone (causing

<sup>40</sup> In this case, the unique formula [C<sub>10</sub>H<sub>4</sub>F<sub>17</sub>O]<sup>+</sup> was assigned within the mass error of 5 ppm, which was tentatively identified as perfluorooctyl vinyl ether through database search (e.g., PubChem CID 54096250).

formation of D<sub>3</sub>F and D<sub>4</sub>F in the example) and removal of the side chains (causing formation of trifluoropropene in the example), might occur for other silicone SCFPs as well, though possibly at different temperatures and with different yields.

- Photodegradation of the self-assembled monolayer derived from a 8:2 fluorotelomer silane [C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>], which contained likely 8:2 fluorotelomer silicone SCFP, was observed after UV–visible light exposure. After a 10-day exposure, the authors observed the formation of PFCAs (a mean molar yield of 0.2%), 8:2 fluorotelomer carboxylic acid (8:2 FTCA; a mean molar yield of 0.06%) and 8:2 fluorotelomer unsaturated carboxylic acid (8:2 FTUCA; a mean molar yield of 0.009%) (Zhu et al., 2019). However, the study did not investigate the degradation mechanisms.

Once released, PFAS cyclic siloxanes can further degrade under different mechanisms, and possibly form highly stable PFCAs as the end products.

- They may undergo hydrolysis, and yield various transformation products including homologues (e.g., D<sub>3</sub>F → D<sub>4</sub>F) and breakdown products [e.g., D<sub>3</sub>F and D<sub>4</sub>F → CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>MeSi(OH)<sub>2</sub>] (Zhi et al., 2018). Zhi et al. (2018) further reported that under the laboratory conditions, the hydrolysis half-lives of D<sub>3</sub>F and D<sub>4</sub>F at different pH values (5.2, 6.4, 7.2, 8.3, and 9.2) varied from 80.6–154 h and from 267–533 h, respectively.
- They may also undergo biodegradation, e.g., in sludges. Their biodegradation half-lives are likely longer than their hydrolysis half-lives, with one study reported 41.1 d for D<sub>3</sub>F and about 55 days for D<sub>4</sub>F (Huang et al., 2020). The same authors also reported, from the degradation of D<sub>3</sub>F and D<sub>4</sub>F, the formation of CF<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>MeSi(OH)<sub>2</sub> (similarly to hydrolysis) and MeSi(OH)<sub>3</sub> (which was not observed in the hydrolysis study by Zhi et al., 2018). The latter means that PFAS moieties were released, which may be further transformed into highly stable of PFCAs; a recent study shows that n:2 fluorotelomer silanes [e.g., C<sub>8</sub>F<sub>17</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub>] can be easily oxidized to corresponding PFCAs using the total oxidizable precursor assay (Zhu et al., 2019).

#### 5.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

Given the high levels of historical and ongoing production as well as the myriad of uses, significant amounts of silicone SCFPs and other PFASs present in the commercial formulations are expected to have been released from production, use and disposal, via air, wastewater and solid waste. For example, Zhi et al. (2018) reported elevated levels of D<sub>3</sub>F and D<sub>4</sub>F in surface water (up to 291 ng/L for D<sub>3</sub>F and up to 168 ng/L for D<sub>4</sub>F) and sediment (up to 5478 ng/g for D<sub>3</sub>F and up to 6277 ng/g for D<sub>4</sub>F) near a fluorinated methylsiloxane manufacturing plant in Weihai, China. In addition, both Truffier-Boutry et al. (2010) and Zhu et al. (2019) provide evidence of significant levels of non-polymeric PFASs present in the silicone SCFP layer after applying PFAS silanes, which can be released during use and disposal. Furthermore, van Bavel et al. (2016) detected D<sub>3</sub>F and D<sub>4</sub>F in the leachates from the ISI and Lindum landfills in Norway, showing releases from solid waste treatment.

Several other studies have also detected elevated levels of D<sub>3</sub>F and/or D<sub>4</sub>F in the sewage sludge from Sweden and sediment from some lakes in Sweden and Norway (McLachlan et al., 2014), in the effluents of two WWTPs in Norway (van Bavel et al., 2016), and in about 20% of the sludge samples from 29 WWTPs at 25 cities distributed over seven geographic regions of China (Huang et al., 2020). These studies did not report the likely sources of these observations.

## 5.5. Summary and options for a way forward

Silicone SCFPs share many similarities to acrylate and urethane SCFPs. They are likely significant sources of non-polymeric PFASs in the environment, particularly in the long term because their high production volumes and wide use, possible presence of high levels of non-polymeric PFASs in the formulations, ability to degrade and form non-polymeric PFASs in the environment and biota, and multiple release pathways along the life cycle. Also, due to the presence of many critical knowledge and data gaps such as on the production volumes, use patterns, levels of other non-polymeric PFAS impurities in the formulations, and degradation potential, it is currently not possible to more precisely estimate the contribution of silicone SCFPs to non-polymeric PFASs in the environment.

A better understanding of the production, use and releases of silicone SCFPs can better inform the sources, human and environmental exposure routes, true environmental and human body burden of PFASs. Thus, it can assist in the identification of possible overlooked hotspots/blindspots. Future action may include addressing both existing information and current information gaps. Addressing existing information may include the following activities: (i) more in-depth research and analysis of additional information sources such as companies' individual technical handbooks and brochures, SDS and patents, (ii) harmonizing reported structural and use information to the same level, and (iii) exploring ways to make public available the structural and use information that has been reported to regulators but has not been claimed as confidential business information. Addressing current information gaps may include further research on their material flows and degradation behaviour.

# 6 The Life Cycle of Ethoxylate SCFPs

## Chapter summary:

- Limited information is available on the production of ethoxylate SCFPs, with several that may have been produced up to hundreds of tonnes per annum.
- Ethoxylate SCFPs have mainly been used as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. Some ethoxylate SCFPs may also be used to treat certain material surfaces (e.g., glasses) to impart water- and oil-repellency.
- Significant presence of unreacted residuals (up to 4%) has been reported in fluorotelomer- and PASF-based ethoxylate SCFPs.
- The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time.
- The use pattern of ethoxylate SCFPs will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill leachates, etc.
- Future action may look into the current production and use volumes of ethoxylate SCFPs, as well as longer-term degradation behaviour, and thus provide a better understanding of PFASs releases from the production, use and disposal of ethoxylate SCFPs.

## 6.1. Historical and ongoing production and uses

Limited information on the historical and ongoing production of ethoxylate SCFPs was identified in the national/regional chemical inventories. Reporting to the US EPA by manufacturers/importers via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act is summarized in Table 6.1. In addition, at least 12 ethoxylate SCFPs were identified on the SPIN database, but their production or import volumes (and uses) have been mostly claimed as confidential business information and thus sealed from the public. For more details, see Table S1, Table S2, and the corresponding entries in the national/regional chemical inventories.



Table 6.1. Production/import volumes of ethoxylate SCFPs in the US reported to the US EPA via the Chemical Data Reporting (CDR; formerly Inventory Update Reporting or IUR) under the Toxic Substances Control Act; and in Denmark, Finland, Sweden and/or Norway reported in the SPIN database (data in the brackets indicating the time period with reporting). t = tonnes; yr = year.

CASRN	PFAS moiety type	Fluorinated carbon chain length	Production/import volume reported
68298-79-3	PASF-derivatives	4	SPIN: confidential (2000–2011)
68298-80-6	PASF-derivatives	5	SPIN: confidential (2000–2011)
56372-23-7	PASF-derivatives	6	SPIN: confidential (2000–2011)
68298-81-7	PASF-derivatives	7	SPIN: confidential (2000–2011)
68958-60-1	PASF-derivatives	7	SPIN: confidential (2000–2006)
68958-61-2	PASF-derivatives	8	US: >4.54 to <227 t in 2001* SPIN: confidential (2000–2006)
29117-08-6	PASF-derivatives	8	US: >4.54 to <227 t in 2001* SPIN: confidential (2000–2011)
52550-44-4	n:2 fluorotelomers	6	SPIN: confidential (2013–2019)
65545-80-4	n:2 fluorotelomers	6;8;10;12;14;16**	US: >4.54 to <227 t in 2001, >11.3 to <45.4 t/yr in 2012–2015 SPIN: confidential (2000–2019)
200013-65-6	PFPEs	unclear	US: <454 t/yr in 2012–2015 SPIN: confidential (2015–2017)
162492-15-1 1000390-73-7	PFPEs	Unclear	SPIN: confidential (2008–2019)
56467-05-1	Perfluoroalcohol	6	SPIN: confidential (2000–2006, 2017)

\* According to another reporting by 3M to the US EPA, it produced >10.6 tonnes of CASRN 68958-60-1 and about 10–30 tonnes of CASRN 29117-08-6 in the US in 1997 (US EPA Administrative Record 226, #580, #582, and #600).

\*\* The fluorinated carbon chain length of CASRN 65545-80-4 is retrieved from the SDS of DuPont's Zonyl FSN fluorosurfactant (e.g., <https://www.yumpu.com/en/document/view/10055541/zonyl-fsn-fluorosurfactant-msds-dupont>) and the patent US 8367756 B2 (<https://patentimages.storage.googleapis.com/88/07/2a/6fc07e409a037c/US8367756.pdf>).

On the use side, more information is available, showing a wide range of use areas for ethoxylate SCFPs, particularly as surfactants/surface active agents in industrial processing, commercial applications and consumer uses. For example, Zonyl FSO-100 (CASRN 122525-99-9) is described as a non-ionic surfactant able to impart low aqueous surface tensions at low concentrations, and thus has been incorporated into applications such as caulks, paints, coatings and adhesives (Dinglasan-Panlilio and Mabury, 2006). Similar surfactant use has also been reported for other PASF-, fluorotelomer- and PFPE-base ethoxylate SCFPs, though in some cases incorporated into formulations for broader application areas including ink, oil and gas drilling, soap and cleaning products, automotive care products, lubricants, food packaging (e.g., CASRN 200013-65-6) and fire-fighting foam agents (e.g., CASRN 65545-80-4). For more details, see Table S2.

In a recent study, fluorotelomer-based ethoxylate SCFPs have also been detected as the major fluorinated components in several anti-fog sprays and cloths purchased from Amazon.com (Herkert et al. 2022). This is in line with 3M's reporting that PASF-based ethoxylate SCFPs were "used as received or diluted with water or butyl acetate to impart soil or water repellency to surfaces (including printed circuit boards or photographic film)" (3M, 1999). 3M also reported that some formulators used PASF-based ethoxylate SCFPs as a thickener to aqueous coatings used to protect tile, marble and concrete.

## 6.2. Presence of other PFASs in the commercial formulations

Significant presence of unreacted residuals (i.e., n:2 FTOHs) in two commercial fluorotelomer-based ethoxylate SCFPs has been reported (see Table S3): Zonyl FSO 100 contained 6:2, 8:2 and 10:2 FTOHs (1.03% of dry weight; Dinglasan and Mabury, 2006), and Zonyl FSH contained 6:2 FTOH (0.54%) and 8:2 FTOH (0.29%) (Frömel and Knepper, 2010).<sup>41</sup> These levels are also in line with recent measurements of 6:2 FTOH in two anti-fog sprays primarily based on 6:2 fluorotelomer-based ethoxylate SCFP formulations (Herkert et al. 2022).<sup>42</sup> Further, 3M reported that PASF-based ethoxylate SCFPs typically contained 4% or less PFAS residuals (3M, 1999). Due to the high volatility of FTOHs, they may be released during the production, use and disposal of commercial ethoxylate SCFPs. Similar levels of unreacted residuals might be expected to be present in other commercial ethoxylate SCFPs unless they were purified.

## 6.3. Degradation of SCFPs during use and after end-of-life

The ethoxy part in ethoxylate SCFPs can likely undergo biotic degradation and release the PFAS moieties over time, as concluded by an assessment of Capstone FS-30—a n:2 fluorotelomer-based ethoxylate SCFP—by NICNAS that “over time, the notified polymer is expected to ultimately degrade into perfluorohexanoic acid (PFHxA)” (NICNAS, 2018). However, such degradation may take a long time and thus ethoxylate SCFPs themselves may be persistent in the environment. For example, Frömel and Knepper (2010) studied biodegradation of a n:2 fluorotelomer-based ethoxylate SCFP. The authors observed that the alcohol group at one end of the polymer chain can be oxidized and form a carboxylic group, i.e.,  $C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_mOH \rightarrow C_nF_{2n+1}CH_2CH_2(OCH_2CH_2)_{m-1}OCH_2COOH$ . The authors further hypothesized that the ether bond can be cleaved, as observed for non-fluorinated ethoxylate polymers, and such chain-shortening continues until the ethoxylate SCFP is transformed to the corresponding n:2 FTOHs, which are precursors to PFCAs. The authors noticed that the ethoxylates did not further degrade once the chain length was shortened to a certain degree (where  $m < 9$ ), but the authors noted the limited testing time period (48 days) might be too short to observe full transformation. In another biodegradation study of  $C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$  following the OECD guideline 301C, the ethoxy unit profile hardly changed during the 28-day test (Yamamoto et al., 2014).

## 6.4. Environmental releases of SCFPs and other PFASs present in the commercial formulations

The use pattern of ethoxylate SCFPs (see Section 5.1 above) will likely result in (uncontrolled) releases of the ethoxylate SCFPs themselves, other PFASs present in the commercial formulations, and their degradation products into the environment during use and after disposal, via air, wastewater, landfill

<sup>41</sup> The results from the two studies cannot be directly compared due to the use of different methods.

<sup>42</sup> The authors also screened for 4:2, 8:2, 10:2, 12:2, 14:2 and 16:2 FTOHs in all sampled anti-fog spray and cloth products, but did not detect them in any of the products except one (this specific product is likely based on an old formulation, with 8:2 and 10:2 fluorotelomers being the dominant species).

Furthermore, the authors also tested another two anti-fog sprays and reported higher levels of 6:2 FTOH, up to ca. 40%; however, in these two products, 6:2 FTOH and 6:2 fluorotelomer ethoxylates could explain only ca. 60% of the total organic fluorine. It is likely that other 6:2 fluorotelomer-based substances were added in the two anti-fog sprays, interfering the data interpretation. Therefore, the levels of 6:2 FTOH in these two anti-fog sprays are not considered in the comparison here.

leachates, etc. For example, the presence of a fluorotelomer-based ethoxylate SCFP [ $C_9F_{19}CH_2CH_2O(CH_2CH_2O)_nH$ ] in the leachates from a disposal facility located in the Kansai area in 2010 was reported by Yamamoto et al. (2014).

## 6.5. Summary and options for a way forward

Their historical and current production and use volumes, as well as degradation half-lives, are key parameters that need to be improved in order to better understand the contribution of ethoxylate SCFPs to PFASs in the environment.

# 7 Conclusions

Compared to many non-polymeric PFAS, SCFPs and their known and unknown degradation products have received comparatively little attention from scientists and regulators, despite their manifold industrial uses and high volumes, their propensity to release non-polymeric PFAS, and their potential environmental and health impacts.

Overall, a wide range of information on the chemical identities of SCFPs, other PFASs present therein, historical and ongoing production and use, degradation of SCFPs, and release of SCFPs and associated non-polymeric PFASs is identified in the public domain and has been synthesized in this report.

Despite the many knowledge and data gaps identified in the respective chapters above, the following can be concluded from the information synthesized here: A wide range of SCFPs have been produced and used in many different applications, with at least some SCFPs at high volumes (up to tens of thousands of tonnes/year); as a comparison, 3M reported that its estimated global production of POSF-derivatives for fire-fighting foams was about 150 tonnes in 2000 (3M, 2000). Many non-polymeric PFASs may be present in the commercial SCFP formulations, sometimes at percentage levels. During the production, use and disposal of SCFPs and SCFP-treated products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released. It is well expected that SCFPs can degrade and form non-polymeric PFASs, including PFCAs and/or PFSAAs, in the environment and biota. Thus, many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs including PFCAs and PFSAAs.

Therefore, concerted action by all stakeholders is needed to address SCFPs in an efficient and effective manner. This includes identifying, making funding available and conducting research on those critical knowledge and data gaps that are most relevant for soundly regulating/managing SCFPs in different jurisdictions, building on the gaps identified in the respective chapters above. When addressing critical knowledge and data gaps, to increase efficiency, the following concerted action may be taken: (i) investigating additional information that is available in SDSs and patents (but was not actively searched and considered in this analysis due to time and resource constraints<sup>43</sup>); (ii) working with manufacturers to enable open access to information that has been generated by them (and made available to specific regulators), but has not been made publicly available; and (iii) regularly gathering newly available public information and synthesizing them to further increase the knowledge base on SCFPs.

In parallel to action on critical knowledge and data gaps, concerted action may be taken to develop, facilitate and promote national and international stewardship programmes and regulatory approaches to reduce emissions of SCFPs and related PFASs and to work toward global elimination, where appropriate and technically feasible.

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<sup>43</sup> It should also be noted that SDS often contain inaccurate or missing information; and the listed chemical(s) could be found at higher concentrations than what the SDS listed. Thus, the information would need to be evaluated during review.

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This report provides an overview of existing scientific and technical information on side-chain fluorinated polymers (SCFPs), focusing on their identities and life cycle, and with a particular goal to map the existing landscape and highlight critical knowledge and data gaps.

It focuses on the life cycle of SCFPs, including production and use, presence of other PFASs in the commercial formulations, degradation of SCFPs during use and end-of-life treatment, and environmental releases of SCFPs and other PFASs present in the commercial formulations.

The report comes with a separate Annex comprising five spreadsheets providing information on: substances identities, use information, PFAS-impurity studies, degradation studies and SCFP release.

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