



Selected physicochemical aspects of poly- and perfluoroalkylated substances relevant to performance, environment and sustainability—Part one



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HIGHLIGHTS

- Highly thermally and chemically stable PFASs form sturdy, repellent protecting films.
- Perfluorinated chains are both extremely hydrophobic and lipophobic.
- Performances of PFASs decrease strongly with fluorinated chain length.
- Surprisingly little reliable data is available on the physical chemistry of PFASs.
- Such data are needed for understanding the environmental and health impact of PFASs.

GRAPHICAL ABSTRACT

A global Dr. Jekyll and Mr. Hyde case, or outstanding performances unleashed



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ABSTRACT

The elemental characteristics of the fluorine atom tell us that replacing an alkyl chain by a perfluoroalkyl or polyfluorinated chain in a molecule or polymer is consequential. A brief reminder about perfluoroalkyl chains, fluorocarbons and fluorosurfactants is provided. The outstanding, otherwise unattainable physicochemical properties and combinations thereof of poly and perfluoroalkyl substances (PFASs) are outlined, including extreme hydrophobic and lipophobic character; thermal and chemical stability in extreme conditions; remarkable aptitude to self-assemble into sturdy thin repellent protecting films; unique spreading, dispersing, emulsifying, anti-adhesive and levelling, dielectric, piezoelectric and optical properties, leading to numerous industrial and technical uses and consumer products. It was eventually discovered, however, that PFASs with seven or more carbon-long perfluoroalkyl chains had disseminated in air, water, soil and biota worldwide, are persistent in the environment and bioaccumulative in animals and humans, raising serious health and environmental concerns. Further use of long-chain PFASs is environmentally not sustainable. Most leading manufacturers have turned to shorter four to six carbon perfluoroalkyl chain products that are not considered bioaccumulative. However, many of the key performances of PFASs decrease sharply when fluorinated chains become shorter. Fluorosurfactants become less effective and less efficient, provide lesser barrier film stability, etc. On the other hand, they remain as persistent in the environment as their longer chain homologues. Surprisingly little data (with considerable discrepancies) is accessible on the physicochemical properties of the PFASs

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under examination, a situation that requires consideration and rectification. Such data are needed for understanding the environmental and in vivo behaviour of PFASs. They should help determine which, for which uses, and to what extent, PFASs are environmentally sustainable.

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1. Introduction and scope

Chemistry analyses and transforms matter. It has been practiced ever since man invented beer, fired pottery and cooked his stew. Nowadays, chemistry touches essentially every facet of human life and activity. Man has created molecules and materials that do not (sometimes cannot) exist in nature and that are bestowed with properties unfound or unmatched by natural products and materials. Highly fluorinated organics are among these anthropogenic creations. The first perfluoroalkanoic acid, trifluoroacetic acid CF_3COOH , was synthesized in 1920 by Swartz (Banks et al., 1994), and the first perfluorocarbon, CF_4 , was isolated in 1926 (Lebeau and Damien, 1926). Commercial exploitation started, with little regulation, in the early 1950' following Plunkett's fortuitous discovery (1938) of poly(tetrafluoroethylene) (PTFE, e.g. Teflon). Thousands of per- and polyfluoroalkyl substances (PFASs)¹ (Buck et al., 2011) have since been synthesized and their outstanding properties have generated hundredths of valuable technical advances, uses and markets (Banks et al., 1994; Howe-Grant, 1995; Baasner et al., 2000; Banks, 2000; Kissa, 2001; Krafft and Riess, 2007; OECD, 2014).

Then, in the late 1970', two to three orders of magnitude higher than normal levels of organic fluorine were detected in the blood of workers at a perfluorochemical production factory. Perfluorooctanoic acid (PFOA, Table 1 compound **20**) was identified in their urine (Ubel et al., 1980). PFASs were subsequently found in air, water, soil, animals and humans worldwide, and were identified as global, persistent and bioaccumulative, potentially harmful pollutants (Giesy et al., 2001; Hansen et al., 2001; Prevedouros et al., 2006; Calafat et al., 2007; Lau et al., 2007; Conder et al., 2008; Parsons et al., 2008; Olsen et al., 2009; van Leeuwen and de Boer, 2007; Pistocchi and Loos, 2009; D'Hollander et al., 2010; Frömel and Knepper, 2010; Ahrens, 2011; Houde et al., 2011; Lindstrom et al., 2011; OECD, 2014).

A turning point was reached in 2000 when concerns about environmental and toxicological impact led the 3M Company, in association with the US Environmental Protection Agency (USEPA), to start phasing out its perfluorooctane sulfonates (PFOS **5**), perfluorooctanoic acid (PFOA **20**) and related compounds product lines.

This review is Part one of a Project that examines the physico-chemical properties of perfluoroalkyl chains and PFASs that underlie both their widespread usages and the environmental concerns they raise. Part Two will review the reasons why long perfluoroalkyl chain substances are now being phased out as much as technically possible; discuss their shorter chain alternatives' performances and whether the specific functional properties of fluorosurfactants and fluoropolymers can be obtained without recourse to long perfluoroalkyl chains; outline some perspectives for future developments, and address the question whether sustainable use of highly fluorinated material is achievable.²

The literature on the subject has become colossal, with over 400 papers published per year (Buck et al., 2011); only a limited number of references can be provided here.

2. Some fundamentals about fluorine, perfluoroalkyl chains, and fluorosurfactants

Replacing hydrogen atoms by fluorine atoms in an organic molecule is not a benign operation. Fluorine, "the enabler" (Banks et al., 1994), has a much higher ionisation potential (1676 vs. 1312 kJ mol⁻¹), electron affinity (328 vs. 73 kJ mol⁻¹) and electronegativity (3.98 vs. 2.20), and lower polarisability ($\alpha = 0.557 \cdot 10^{-24}$ vs. $0.667 \cdot 10^{-24}$ cm³) than hydrogen (and all the other Second Row elements of the Periodic Table (Table 2)). Its covalent radius is 0.57 Å versus 0.31 Å for hydrogen. The exact value of its van der Waals radius (which reflects the atom's space requirements) is still controversial (Schlosser and Michel, 1996). Published values range from 1.35 Å (Pauling, 1960) to 1.47 Å (vs. 1.20 Å for H), probably meaning that the space occupied by an individual fluorine atom in a molecule depends largely on its neighbourhood, which can cause some electron density anisotropy. In *F*-chains, the value of 1.43–1.47 Å (Bondi, 1964) appears realistic in view of the difference in cross-sections measured between *F*-alkyl and alkyl chains. Fluorine's radius would then be close to that of oxygen (1.52 Å). Difluorine F_2 has a much higher oxidation potential than H_2 ($1/2 \text{X}_2 \rightarrow \text{X}^-$: 2.87 eV) (Rosen, 1978; Tiddy, 1985; Smart, 1994; Howe-Grant, 1995; Kissa, 2001).

2.1. Perfluoroalkyl chains versus alkyl chains

Perfluoroalkyl chains ($\text{C}_n\text{F}_{2n+1}-$, *F*-alkyl)³ differ from alkyl chains ($\text{C}_n\text{H}_{2n+1}-$) in many important ways (Fig. 1) (Banks et al., 1994; Howe-Grant, 1995; Krafft and Riess, 2009). For a given number of carbon atoms, a linear *F*-alkyl chain has a ~50% larger cross-section area than an alkyl chain (27–30 Å², vs. 18–21 Å²). The van der Waals diameters are ~5.6 Å for *F*-alkyl chains and ~4.2 Å for alkyl chains (Barriet and Lee, 2003). *F*-alkyl chains are thus more space demanding than alkyl chains. Structurally, the larger size of fluorine as compared to hydrogen forces long *F*-chains to adopt an all-trans helical conformation rather than the trans-planar zig-zag conformation of alkyl chains (Bunn and Howells, 1954; Clark, 1999; Ellis et al., 2004b; Krafft and Riess, 2009; Zenasni et al., 2013).

The volumes occupied by CF_2 and CF_3 groups are ~38 Å³ and ~92 Å³, as compared to 27 Å³ and 54 Å³ for CH_2 and CH_3 groups, respectively. They are also much more rigid, have lesser conformational freedom and present fewer conformational defects than hydrocarbon chains, which facilitates ordered packing of *F*-chain, including in one molecule-thick (1–3 nm) two-dimensional films. The helical conformation (and helical/planar interchanges) and dense electron coating also provide a smoother, streamlined dynamic molecular shape that may facilitate movement of the *F*-chain along its axis, a feature reflected macroscopically by lubricant properties.

The standard C—F bond (av. ~485 kJ mol⁻¹, as compared to ~413 kJ mol⁻¹ for C—H bond in hydrocarbons) is the strongest sin-

¹ The terminology and acronyms used here (see Table 1) are those recommended by Buck et al. (2011).

² This paper is largely based on lectures (MPK) presented at the 5th International Workshop on Per- and Polyfluorinated Alkyl Substances in Helsingør, Denmark (October 2013) and at the Society for Analytical Chemistry, Copenhagen University.

³ The common chemist's italicized notation *F*- for "perfluoro" will be used throughout the paper; *F*-chains, for short, means *F*-alkyl chain.

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