Empa
Materials Science and Technology

# Understanding Side-Chain Fluorinated Polymers and Their Life Cycle

## Zhanyun Wang

# Background, Motivation and Scope

- PFASs can be divided into non-polymers and polymers.

  - Attention has primarily focused on non-polymeric PFASs.

  - It is equally important to understand polymeric PFASs, including side-chain fluorinated polymers (SCFPs), fluoropolymers and perfluoropolyethers.

- A first synthesis report, focusing on the life cycle of SCFPs

  - defined as polymers with a non-fluorinated polymer backbone and with PFAS moieties on the side chain(s).

# Report Structure

- Chapter 2. Identities of SCFPs on the Global Market

- Chapters 3–6 The life cycle of various SCFPs

    - Production and uses

    - Presence of other PFASs in the commercial formulations

    - Degradation of SCFPs

    - Environmental releases of SCFPs and other PFASs

    - Summary and options for a way forward

- Chapter 7. Conclusions

- Annex: five spreadsheets on substance identities, use information, PFAS-impurity studies, degradation studies and SCFP release

# SCFPs on the Market

- Table S1: A non-exhaustive list of 103 SCFPs and 42 PFAS monomers
  - In most cases, the generic chemical structure(s) can be identified



**A. an example of fluorotelomer acrylate SCFPs**

**B. an example of fluorotelomer-based urethane* SCFPs**
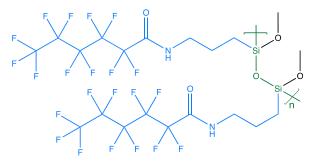CASRN 357624-15-8

\* The term "urethane" here is a simplification of polyurethanes and related chemistry (e.g., polyallophanates and polyisocyanurates).
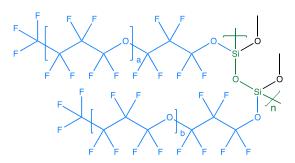
# SCFPs on the Market

**C. an example of PACF-based\*\* oxetane SCFPs**
CASRN 449177-99-5



**D. an example of PASF-based ethoxylate SCFPs**
CASRN 68298-79-3



**E. an example of PACF-based silicone SCFPs**
derived from CASRN 154380-34-4



**F. an example of PFPE-based silicone SCFPs**
derived from CASRN 475633-38-3

\*\* In this example, the fluorinated oxetane monomer is derived from $CF_3CF_2CH_2OH$, which is derived from $CF_3CF_2COOH$

# SCFPs on the Market

- Additional structural details are available in limited cases

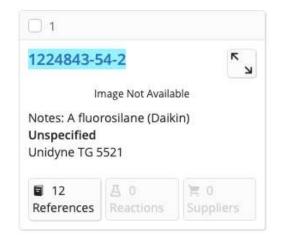| References | Russell et al. (2008) | Russell et al. (2010) |
|---|---|---|
| SCFP type | Fluorotelomer-based acrylate polymer (Figure 2.1 A) | Fluorotelomer-based urethane polymer |
| Molecular weight | $M_n$ = 40 000 Daltons* | $M_n$ or $M_w$ = 3 500 Daltons** |
| Fluorine content | 10.095 weight%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

- The chemical identities, including molecular weight and PFAS moiety content, can vary considerably across different types of SCFPs and across different SCFPs within the same type → Possibly different behavior

# SCFPs on the Market: Critical Data Gaps

- In multiple cases, the generic chemical structures or its monomer(s) cannot be identified, due to

  - Confidential business information

  - Only the trade name were assigned to the CASRNs

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⊖ CAS Registry Number: 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

# SCFPs on the Market: Critical Data Gaps

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- The same CASRN and CAS name can be used for different SCFPs with the same generic chemical structures, but different structural details such as molecular-weight ranges and distribution …

# Acrylate and Urethane SCFPs: Production



A. an example of fluorotelomer acrylate SCFPs

B. an example of fluorotelomer-based urethane* SCFPs
CASRN 357624-15-8

# Acrylate and Urethane SCFPs: Production

- Large production in the past
  - In 2000, up to about 50% of POSF used for acrylate and urethane SCFPs vs. ca. 3% of POSF for producing fire-fighting foams
  - In 2006, 80% of the n:2 fluorotelomers manufactured (including all SCFPs)
- Now, a shift to shorter-chain PFASs
  - Limited information is available on the volumes, but likely still significant
  - However, some long-chain SCFPs, CASRNs 68298-62-4, 68867-62-9 (POSF-based), 142636-88-2 and 70969-47-0 (fluorotelomer-based), were still used in some Nordic countries at least until 2020.
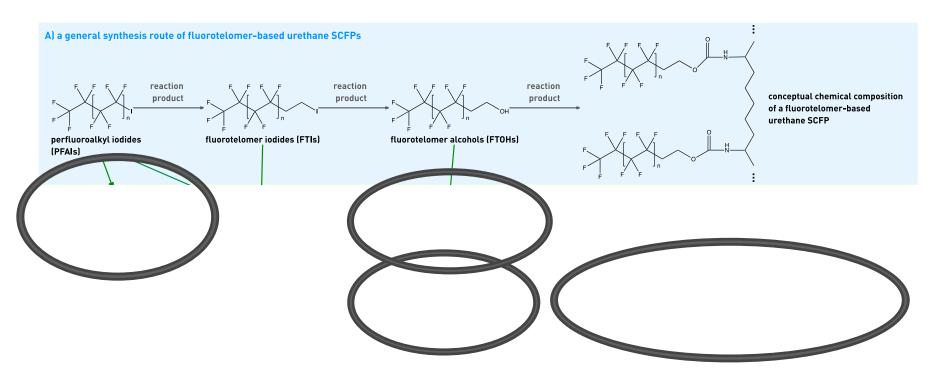
# Acrylate and Urethane SCFPs: Use

- Surface treatment, e.g.,

  - Fabrics, textiles and apparel articles

  - Food-contact paper and paperboard

- Fluorosurfactants, e.g.,

  - Fire-fighting foam formulations

- Other applications areas (likely also as fluorosurfactants)

  - Paints, laquers and varnishes; reprographic agents; adhesives and binding agents; printing inks; and glossing agents

# Presence of other PFASs in Urethane SCFPs



A) a general synthesis route of fluorotelomer-based urethane SCFPs

perfluoroalkyl iodides (PFAIs) → reaction product → fluorotelomer iodides (FTIs) → reaction product → fluorotelomer alcohols (FTOHs) → reaction product → conceptual chemical composition of a fluorotelomer-based urethane SCFP

→ The levels vary considerably across formulations, up to about 5% of the solids.

# Presence of other PFASs in Acrylate SCFPs



C) a general synthesis route of fluorotelomer-based acrylate SCFPs
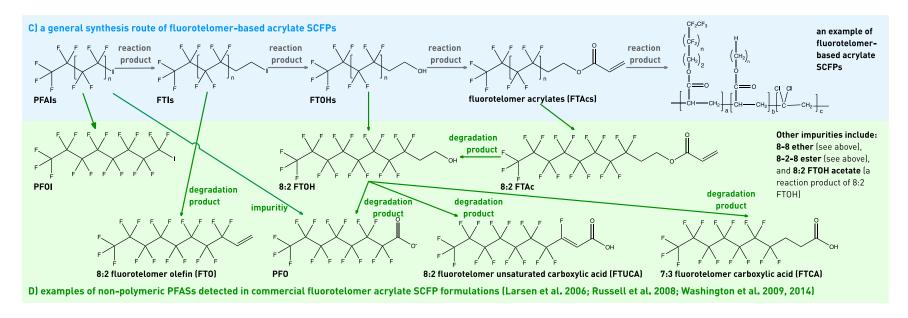
PFAIs → FTIs → FTOHs → fluorotelomer acrylates (FTACs) → an example of fluorotelomer-based acrylate SCFPs

PFOI

8:2 FTOH — degradation product → 8:2 FTAc

Other impurities include: 8-8 ether (see above), 8-2-8 ester (see above), and 8:2 FTOH acetate (a reaction product of 8:2 FTOH)

8:2 fluorotelomer olefin (FTO)

PFO

8:2 fluorotelomer unsaturated carboxylic acid (FTUCA)

7:3 fluorotelomer carboxylic acid (FTCA)

D) examples of non-polymeric PFASs detected in commercial fluorotelomer acrylate SCFP formulations (Larsen et al. 2006; Russell et al. 2008; Washington et al. 2009, 2014)
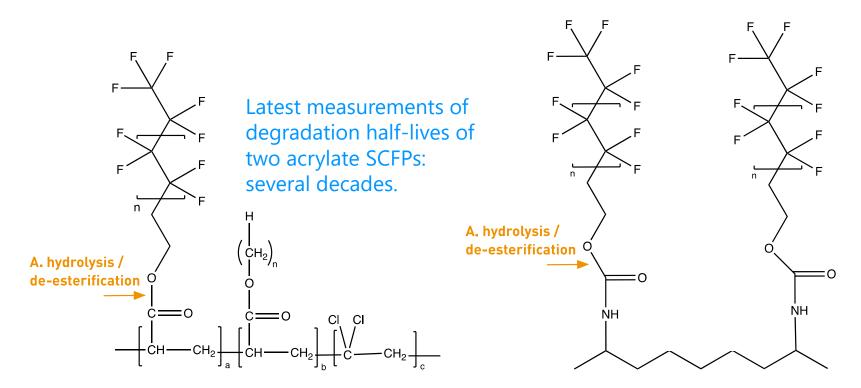
→ No mass balance studies of the fate and distribution of these non-polymeric PFASs during application of commercial SCFPs are identified.

# Degradation of Acrylate and Urethane SCFPs



Latest measurements of degradation half-lives of two acrylate SCFPs: several decades.

A. hydrolysis / de-esterification

an example of fluorotelomer acrylate polymers

conceptual chemical composition of a fluorotelomer urethane polymer

# Acrylate and Urethane SCFPs: Releases

- Significant amounts of SCFPs and other PFASs have been and are released along the life cycle of SCFPs

  - During the application of commercial formulations and the processing of treated materials into articles

    → 3M, 1999: 10–25% loss, in the case of fibre, textile and leather

  - During the use and disposal of treated articles

- Target urethane SCFP compositions measured in lake sediment, soil samples, sludge from WWTPs and landfill leachates.

→ **They act as long-term sources of perfluoroalkyl acids in the environment.**

# Life Cycle of Oxetane SCFPs



**C. an example of PACF-based** oxetane** SCFPs
CASRN 449177-99-5

# Life Cycle of Oxetane SCFPs

- **Production:** little is known in the public domain ...

- **Uses:** Primarily as wetting, flow and leveling agents in coatings, electronic applications, floor finish, and inks; as reactive intermediates for solvent-based coatings, adhesives, electronics and lubricants

- **Presence of other PFASs:** little is known, but at least unreacted raw materials and intermediates + reaction by-products (cyclic oligomers)

- **Degradability:** No studies identified and hard to predict ...



C. an example of PACF-based** oxetane SCFPs
CASRN 449177-99-5

vs. Lower average molecular weight (ca. 1500 Dalton in some cases)
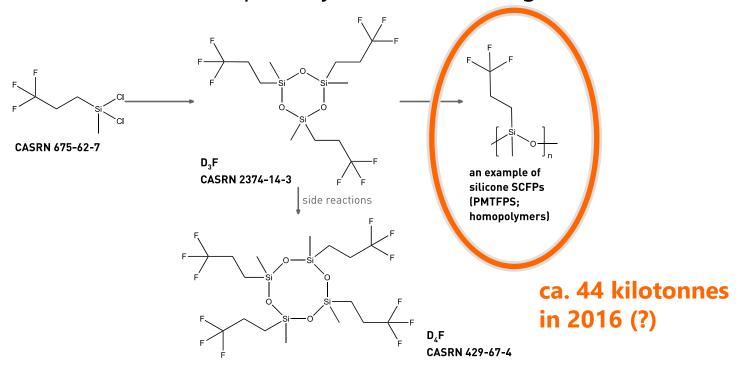
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- **Degradability:** No studies identified and hard to predict ...

- **Environmental releases:** No studies identified, but likely occurring

# Life Cycle of Silicone SCFPs

■ **Production:** limited data are publicly available, but significant



CASRN 675-62-7

D$_3$F
CASRN 2374-14-3

side reactions

an example of silicone SCFPs (PMTFPS; homopolymers)

D$_4$F
CASRN 429-67-4

**ca. 44 kilotonnes in 2016 (?)**

# Life Cycle of Silicone SCFPs

- **Production:** limited data are publicly available, but significant

- **Uses: surface protection** (e.g., nylon-cotton fabrics, leather, stone, glass, ceramics, concrete structures, metals, wood); **medical applications** (e.g., tubing, treatment of eye diseases; PDMS implants); **personal care products** (e.g., cosmetic foundations, hand lotions); **antifoams** (e.g., in the petroleum industry, in diesel fuels); **lubricants** (e.g., for pumps and compressors in harsh chemical service); **rubber applications** (e.g., o-rings for fuel lines)

- **Presence of other PFASs:** little is known, but at least unreacted raw materials and intermediates + reaction by-products (cyclic oligomers)

# Life Cycle of Silicone SCFPs

- **Degradability:** poor thermal stability and tend to degrade when exposed to high temperature (e.g., in the case of PMTFPS, over 200 ℃, with cyclic siloxanes such as $D_3F$ and $D_4F$ as the primary products); photodegradability; oxidation via TOP assay

- **Environmental releases:**

  - Elevated levels of $D_3F$ and $D_4F$ detected in surface water, sediments, landfill leachates, WWTP effluents, sludge

  - No measurements of other ones identified

# Life Cycle of Ethoxylate SCFPs

**D. an example of PASF-based ethoxylate SCFPs**
CASRN 68298-79-3

# Life Cycle of Ethoxylate SCFPs

- **Production:** little is known in the public domain, but likely significant …

- **Uses:** surfactants/surface treatment in industrial processing, commercial applications and consumer uses

    - e.g., caulks, paints, coatings, adhesives, ink, oil and gas drilling, soap and cleaning products, automotive care products, lubricants, food packaging, fire-fighting foam agents, anti-fog sprays and cloth

- **Presence of other PFASs:** little is known, but at least unreacted raw materials and intermediates (up to 4%)

- **Degradability:** biodegradable (though possibly rather slow)

- **Environmental releases:** detected in the leachates of a disposal facility

# Take-Home Messages

- A wide range of SCFPs have been produced and used in many different applications, with at least some at high volumes (up to 10'000s tonnes/year).

- Many non-polymeric PFASs may be present in SCFPs, sometimes at % levels.

- During the life cycle of SCFPs and related products, substantial amounts of SCFPs and associated non-polymeric PFASs may have been released.

- Degradtion of SCFPs to form non-polymeric PFASs, including PFCAs and/or PFSAs, in the environmental and biota can be well expected.

- **Many SCFPs are acting as long-term significant sources to the global burden of non-polymeric PFASs.**

- **Concerted action is needed to address SCFPs, while filling data gaps!**

# Acknowledgements

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

Series on Risk Management No. 73

OECD

# Thank You for Your Attention!

## Your feedback is most welcome!
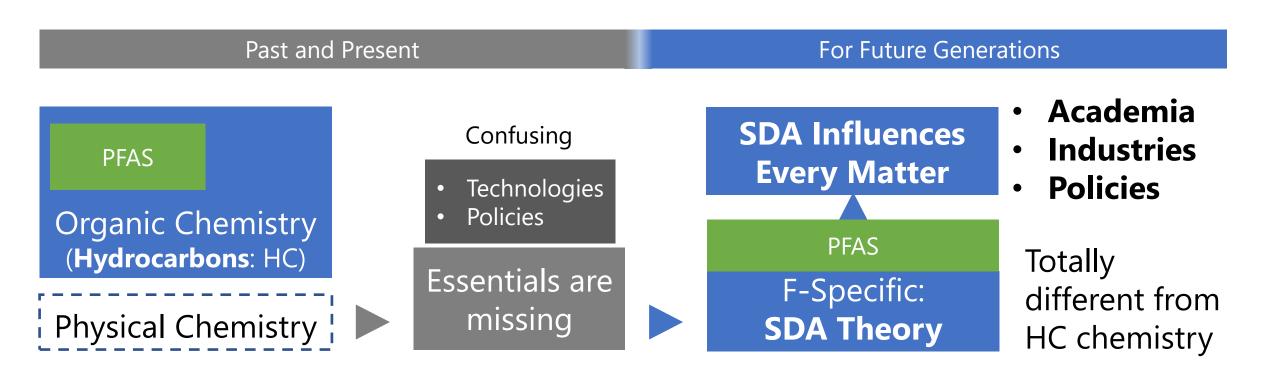
# **SDA Theory** | F-Specific Essential Basis for PFAS

## Takeshi Hasegawa

ICR, Kyoto University, Japan

- **Talk for:** OECD Webinar for "Advances in Understanding PFAS"

- **Date and Time:** 13:25 ~ 13:45 (GMT+1) on Tuesday, December 6, 2022

# **SDA** for Current Problems of PFAS

| Past and Present | For Future Generations |
|---|---|

**PFAS**

**Organic Chemistry**
(**Hydrocarbons**: HC)

Physical Chemistry

▶

Confusing

- Technologies
- Policies

Essentials are missing

▶

**SDA Influences Every Matter**

PFAS

F-Specific:
**SDA Theory**

- **Academia**
- **Industries**
- **Policies**

Totally different from HC chemistry

# PFAS-Specific Properties | "Hydrocarbon chemistry" does not work at all

| Molecular interaction | Fluorous | Vib Spectroscopy | Optical property |
|---|---|---|---|
| **High mp** Strong interactions | **w/o repellency** Why low surf energy? | Very **strong IR** absorption | Low **permittivity** |
| **Weak adhesion** between surfaces | **C8** Critical length | νCF: Raman is lower than IR **by 400 cm$^{-1}$** | |
| **Adhesive** between stretched tapes | **Insoluble** in non-F solvents | νCF: **Higher shift** on R$_f$ length | |
| | **Molecular water adsorbs** on stretched tape | **Surface-mode active** on thin films | |



Alkyl (R)  →  **Perfluoroalkyl (R$_f$)**
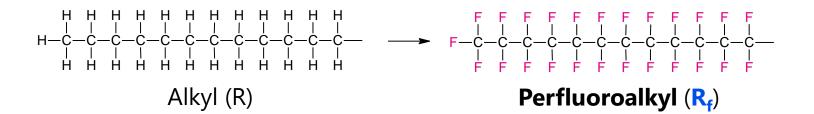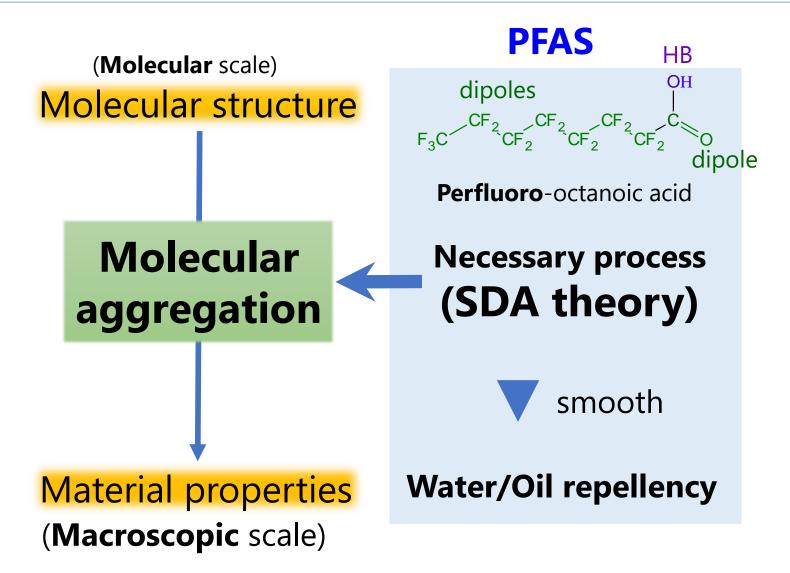
**SDA** | Theorizing Molecular Aggregation of PFAS

# Molecular interactive forces | Origin of molecular assemblies

1. Ionic interaction (~250 kJ mol$^{-1}$)

2. Hydrogen bonding (~25 kJ mol$^{-1}$)

- J. N. Israelachvili in *Intermolecular and Surface Forces, 2nd Ed.*, Academic Press, London, **1991**, pp. 83–136.
- P. Atkins, J. de Paula in *Physical Chemistry, 8th Ed.*, Oxford University Press, Oxford, **2006**, pp. 629–651.

3. **van der Waals forces** (~2 kJ mol$^{-1}$)

F. London *Trans. Faraday Soc.* **33**, 8 (1937).

**HC**

i) Dispersion effect

$$\bar{U}_{\text{dispersion}} = -\frac{3}{4R^6} h\nu_0 \alpha^2$$

Molecular polarizability: **$\alpha$ is small** for F

ii) Induction effect

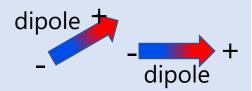$$\bar{U}_{\text{induction}} = -\frac{2}{R^6} \mu^2 \alpha$$

**PFAS**

iii) Orientation effect

$$\bar{U}_{\text{orientation}} = -\frac{1}{3R^6} \frac{\mu^4}{k_B T} \left(1 + 3\cos^2\theta\right)$$

Dipole moment: **$\mu$ is large** for F

dipole

dipole

T. Hasegawa *Chem. Phys. Lett.* **626**, 64 (2015).

**F: weak dispersion effect**, but large orientation effect

| gas | gas | liquid | solid |
|---|---|---|---|
| $F_2$ | $Cl_2$ | $Br_2$ | $I_2$ |

amb. temp.

**b.p**: −188.11 °C    -34.04 °C    58.8 °C    184.3 °C

**m.p.**: −219.67 °C    −101.5 °C    -7.2 °C    113.7 °C

amb. temp.

## Halogen molecules:

- Dumbbell-shaped **homonuclear diatomic** molecule: **No dipole** → Dispersion
- Molecular **polarizability , $\alpha$,** depends on **flexibility of electron cloud**
- **Flexibility is larger** for **a larger atom**
- **$\alpha$ is larger on going down in periodic table**

$$\bar{U}_{\text{dispersion}} = -\frac{3}{4R^6} h\nu_0 \alpha^2$$

7

# **Dipole**- vs **Dispersion**-effects

F. London *Trans. Faraday. Soc.* **33**, 8 (1937).

$$\bar{U} = -\frac{1}{R^6}\left(\frac{2}{3}\frac{\mu_I^2\mu_{II}^2}{kT} + \mu_I^2\alpha_{II} + \mu_{II}^2\alpha_I + \frac{3h}{2}\alpha_I\alpha_{II}\frac{\nu_I\nu_{II}}{\nu_I + \nu_{II}}\right)$$

TABLE III.—THE THREE CONSTITUENTS OF THE VAN DER WAALS' FORCES.

| | $\mu \cdot 10^{18}$. Minkin | $\alpha \cdot 10^{24}$. Miller | $h\nu_0$ (Volts). NIST | **Keesom** — Orientation Effect $\frac{2}{3}\frac{\mu^4}{k293°} \cdot 10^{60}$ [erg cm.⁶]. (6.96%) | **Debye** — Induction Effect $2\mu^2\alpha \cdot 10^{60}$ [erg cm.⁶]. (3.44%) | **London** — Dispersion Effect $\frac{3}{4}\alpha^2 h\nu_0 \cdot 10^{60}$ [erg cm.⁶]. (**89.6%**) |
|---|---|---|---|---|---|---|
| **C-H** | 0.40 | 0.652 | 10.64 | 0.422 | 0.209 | 5.43 |
| CO . | 0·12 | 1·99 | 14·3 | 0·0034 | 0·057 | 67·5 |
| HI . | 0·38 | 5·4 | 12 | 0·35 | 1·68 | 382 |
| HBr . | 0·78 | 3·58 | 13·3 | 6·2 | 4·05 | 176 |
| HCl . | 1·03 | 2·63 | 13·7 | 18·6 | 5·4 | 105 |
| NH₃ | 1·5 | 2·21 | 16 | 84 | 10 | 93 |
| H₂O . | 1·84 | 1·48 | 18 | 190 | 10 | 47 |
| **C-F** | 1.39 | 0.555 | 9.11 | 61.5 (**91.8%**) | 2.14 (3.20%) | 3.37 (5.03%) |

at 293 K

**Dipole-driven** ▲
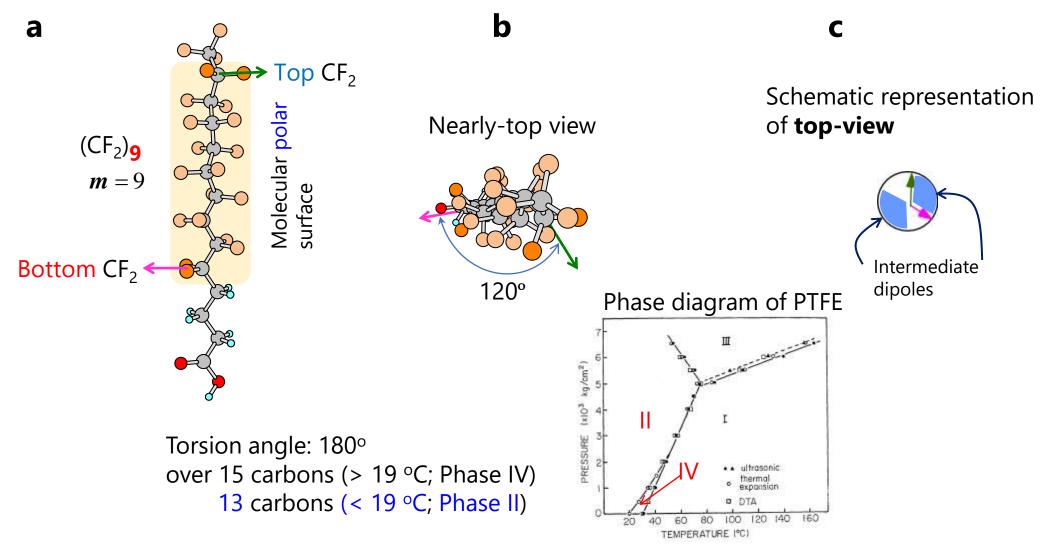
Polarizability contribution

*Chem. Phys. Lett.* **626**, 64 (2015).

Experimental fact: **Strong IR absorption**

# Dipoles-Interaction and a **helical structure**

**a**



Top CF$_2$

(CF$_2$)$_9$

$m = 9$

Molecular polar surface

Bottom CF$_2$

Torsion angle: 180°
over 15 carbons (> 19 °C; Phase IV)
13 carbons (< 19 °C; Phase II)

**b**

Nearly-top view



120°

Phase diagram of PTFE



S. Hirakawa and T. Takemura
*Jpn. J. Appl. Phys.* **8**, 635 (1969).

**c**

Schematic representation of **top-view**
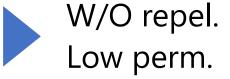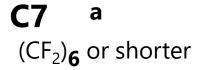


Intermediate dipoles

# Stratified Dipole-Arrays (**SDA**) Theory

**On macroscopic scale, μ <u>looks</u> small** ▶ **Ori**. effect: **weak**

Molecular polarizability, **α**, **is intrinsically small** ▶ **Disp**. effect: **weak**

▶ W/O repel. Low perm.

$$P = \sum \vec{\mu}_j \approx 0 \quad \text{(Macroscopic)}$$
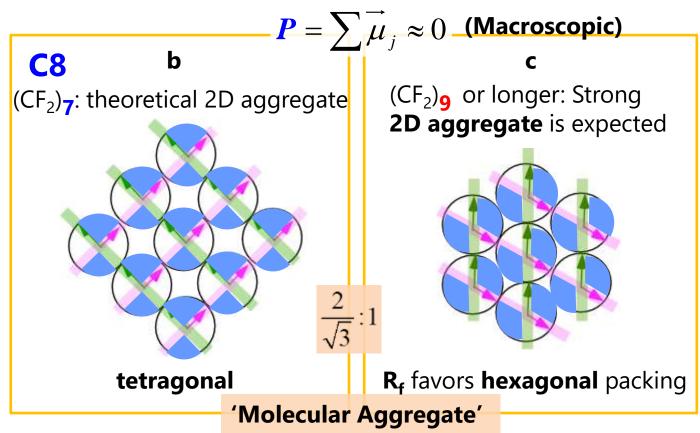
$$\varepsilon_0 \varepsilon_r E = \varepsilon_0 E + P$$

permittivity

**C7** a

$(CF_2)_6$ or shorter

Not aggregate
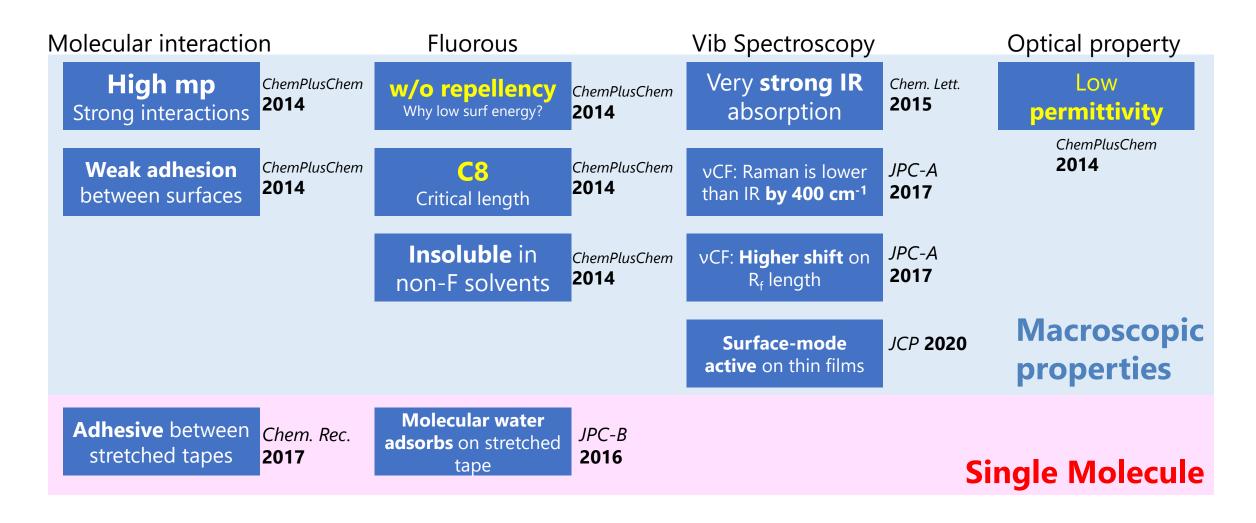
'Molecular dipoles' are faced to outside

**'Single Molecular'**

Deep valley of material properties

**C8** b

$(CF_2)_7$: theoretical 2D aggregate



**tetragonal**

$\dfrac{2}{\sqrt{3}} : 1$

c

$(CF_2)_9$ or longer: Strong **2D aggregate** is expected



$R_f$ favors **hexagonal** packing

**'Molecular Aggregate'**

T. Hasegawa et al. *ChemPlusChem* **79**, 1421 (2014).
T. Hasegawa *Chem. Rec.* **10**, 903 (2017).

# SDA comprehensively explains various PFAS-specific properties

**Molecular interaction**

**Fluorous**

**Vib Spectroscopy**

**Optical property**

| | | | |
|---|---|---|---|
| **High mp** Strong interactions — *ChemPlusChem* **2014** | **w/o repellency** Why low surf energy? — *ChemPlusChem* **2014** | Very **strong IR** absorption — *Chem. Lett.* **2015** | Low **permittivity** — *ChemPlusChem* **2014** |
| **Weak adhesion** between surfaces — *ChemPlusChem* **2014** | **C8** Critical length — *ChemPlusChem* **2014** | $\nu$CF: Raman is lower than IR **by 400 cm$^{-1}$** — *JPC-A* **2017** | |
| | **Insoluble** in non-F solvents — *ChemPlusChem* **2014** | $\nu$CF: **Higher shift** on R$_f$ length — *JPC-A* **2017** | |
| | | **Surface-mode active** on thin films — *JCP* **2020** | **Macroscopic properties** |

| | |
|---|---|
| **Adhesive** between stretched tapes — *Chem. Rec.* **2017** | **Molecular water adsorbs** on stretched tape — *JPC-B* **2016** |

**Single Molecule**

**Key**: **Single** and **Macro must** strictly be discriminated

# Model compounds examining the SDA theory



$m = 3$

$m = 5$
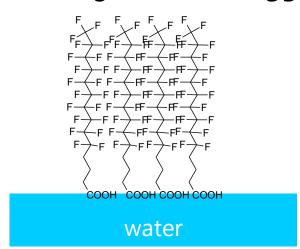
Both ends would interact with water surface

water

**Boundary length**

$m = 7$

$m = 9$
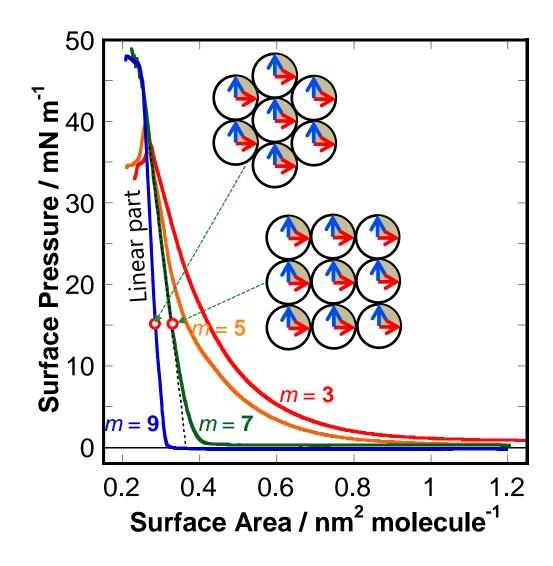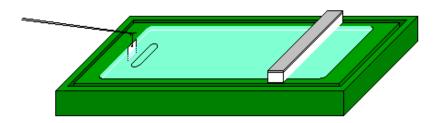
Expected to generate **2D-aggregate**
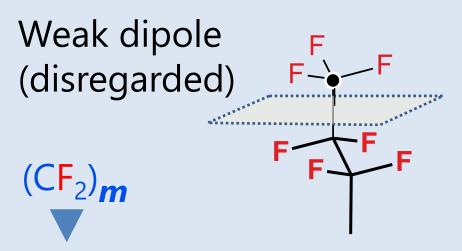
COOH   COOH COOH COOH

water

12

- Monolayers of $m$ = **9** and **7** are intrinsically different from those of $m$ = **5** and **3**.

- The surface area of the lowest limit of the linear parts of $m$ = **9** and **7** show a beautiful quantitative correlation.

$$0.286 \times \frac{2}{\sqrt{3}} = 0.330$$

hexagonal $\qquad$ tetragonal

# Note: Definition of **m** in SDA disregards terminal $CF_3$

Weak dipole
(disregarded)



$(CF_2)_m$

▼

- **$m \geq 7$ ($n \geq 8$): Self-aggregation**
- $m \leq 6$ ($n \leq 7$): Single dipolar character

**Definition in SDA framework**

Conventional: **C8** or **$n = 8$**

$m = $ **7** PFOS   $F_3C$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$SO_3H$

BAFs = 3,548 (fish)

$m = $ **6** PFOA   $F_3C$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—$CF_2$—COOH

BAFs = 144 (fish)

*Environ. Toxicol. Chem.* **2021**, *40*, 1530.

**PFAS:** Molecular **aggregation** is driven by $(CF_2)_m$
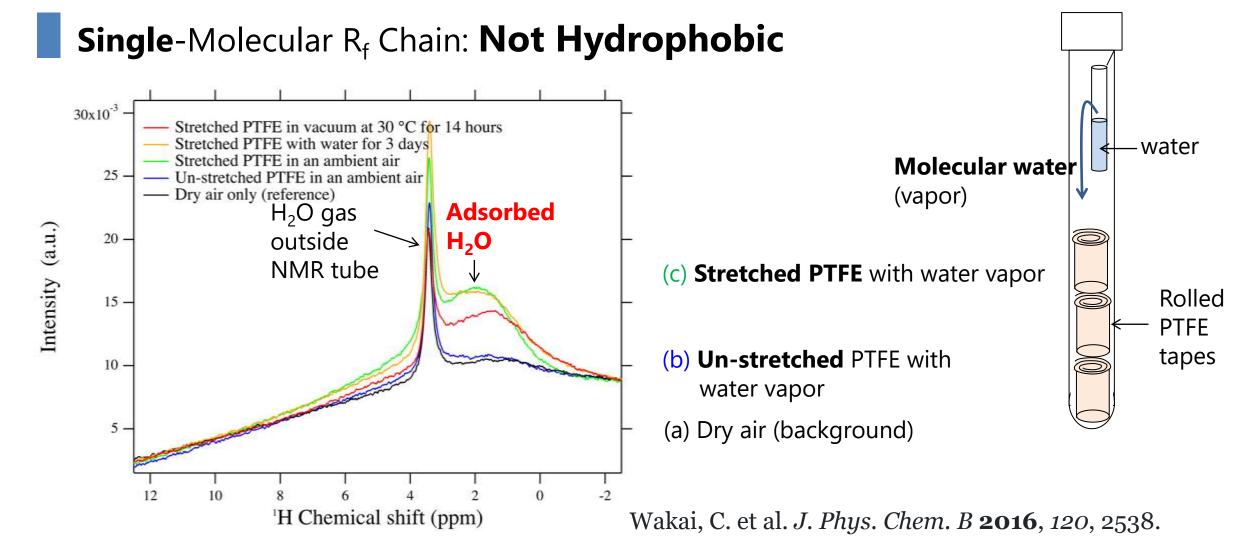
# Stretched PTFE tape | **Single-Molecular Character Appears**



Stretch ▶

(a) SDA aggregation          (b) **Disaggregated** by stretch

Using water **droplet**: No change (**macroscopic**)

| PTFE tape | Contact Angle ($P \approx 0$) |
|-----------|-------------------------------|
| As is | ~123°±3° |
| Stretched | ~124°±6° |

# **Single**-Molecular $R_f$ Chain: **Not Hydrophobic**



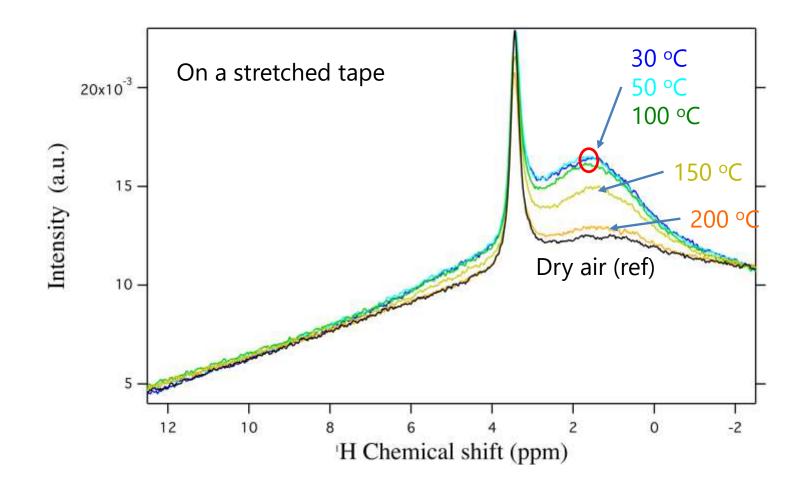Wakai, C. et al. *J. Phys. Chem. B* **2016**, *120*, 2538.

## **As predicted by SDA theory:**

**Molecular water *adsorbs* on stretched PTFE by single-molecular character**

# $^1$H NMR spectra of water desorption **on heating**



On a stretched tape

30 °C
50 °C
100 °C
150 °C
200 °C

Dry air (ref)

**Single R$_f$ Chain is NOT hydrophobic**

# Hydrophilic / Hydrophobic → **Careful Reconsideration using SDA is Needed**

**Conventional** Concept

| C–F | **Hydrophobic** |
|-----|-----------------|
| C–H | Hydrophobic |
| O–H | Hydrophilic |

Corrected by SDA

| C–F | **Orientation Effect** (Dipole-Dipole) |
|-----|----------------------------------------|
| C-H | Dispersion Effect |
| O-H | Hydrogen-Bonding |

First Criteria of PFAS

*Bulk | $m \geq 7$ ($n \geq 8$)*
**Self-aggregation**: Bio-debris source
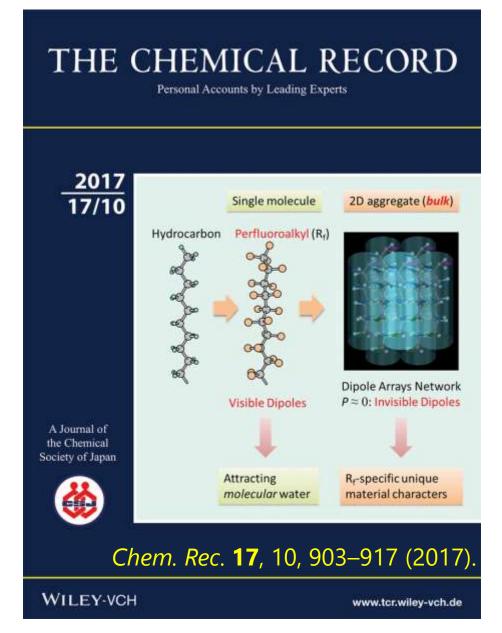
*Singular | $m \leq 6$ ($n \leq 7$)*
**Protein interaction**: Transportation into cells

## **New Concept on SDA**

| **C–F**, C=O, C–O etc. | **Orientation Effect** (Dipole-Dipole) |
|------------------------|-----------------------------------------|
| C–H | Dispersion Effect |
| O–H | Hydrogen-Bonding |

# SDA theory is being rapidly accepted by chemistry community



THE CHEMICAL RECORD
Personal Accounts by Leading Experts

2017 17/10

Single molecule | 2D aggregate (*bulk*)

Hydrocarbon | Perfluoroalkyl (Rf)

Visible Dipoles | Dipole Arrays Network $P \approx 0$: Invisible Dipoles

Attracting *molecular* water | Rf-specific unique material characters

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*Chem. Rec.* **17**, 10, 903–917 (2017).

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1. **Dipole-dipole** interaction governs the aggregation of $R_f$ groups

Binary → Ternary

Aq. : H-bonding
Oil : Dispersion
**Rf**: D-D interaction

2. An $R_f$ group has **a helical skeleton**

"**spontaneous**" tight "**2D aggregation**"

***P* ≈ 0** in a **macroscopic** scale
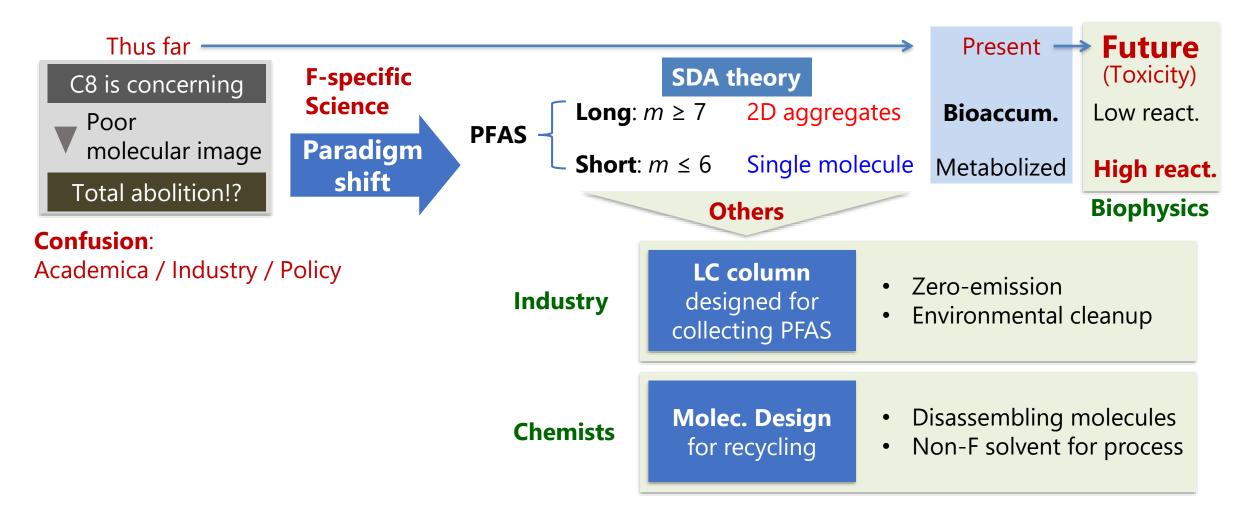
- Low surface energy: **Fluorous**
- Low permittivity
- High m.p. (+ entropy)
- Low Solubility

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