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Characterization and biodegradation of two technical mixtures of side-chain fluorinated acryl copolymers

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Introduction

- PFAA sources to the environment: direct & indirect.
- Biodegradation of side-chain fluorinated acryl copolymers (fluorotelomer alcohols (FTOH) based), leaching of residual perfluoroalkylacids (PFAA) and biodegradation of residual monomers/oligomers as sources of PFAA?
- Large uncertainty of the indirect sources for fluorotelomer based products 6-160 t (Prevedouros, 2006) vs. amount of produced FTOH based side-chain fluorinated copolymer (4000 to 5200 t/year for 1995-2004)
- Both side-chain fluorinated acryl copolymers are used for coating of food paper and board packaging

- **Aim of the study: Characterize two fluorinated acryl copolymers and their PFAA precursor potential**

Figure 1: 10% polymer solutions before centrifugation

Materials & Methods

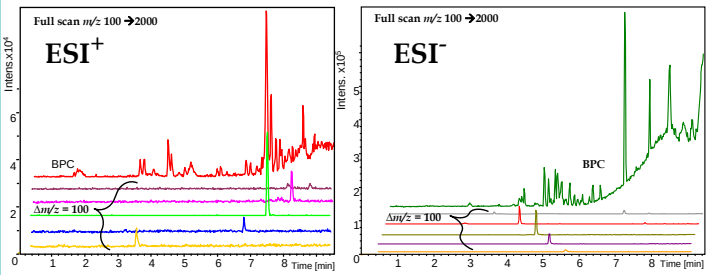
- Two technical mixtures of side-chain fluorinated acryl copolymers were obtained:
  Copolymer 1: cationic, solvated in methanol
  Copolymer 2: non-ionic, solvated in water
- 10% solutions ultracentrifuged:3 kDa mass cutoff analyzed
- Biodegradation experiments at 100 mg/L
  Innoculum: wastewater treatment plant effluent
- Instrumentation:
  - UHPLC-ESI$^-$-QqQ (Waters Quatro Ultima)
  - UHPLC-ESI$^{+/-}$-QTOF (Bruker, MicroTOF)
  - ^{19}F-NMR (500 MHz Varian Unity Inova)

Figure 2: Biodegradation setup

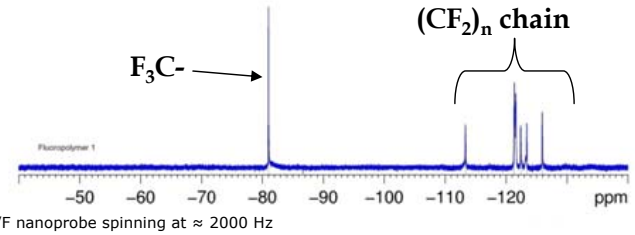
Results & Discussion

Side-chain fluorinated acryl copolymer 1

- Large amount of residuals FTOH and PFAA present in fluoropolymer mixture. FTOH: C6 (2%), C8 (45%), C10 (40%) and C12 (13%).
- UHPLC-ESI+ microQTOF scan shows homologues series separated by $\Delta m/z$=100 (CF_2CF_2), probably from fluorotelomer acrylates (FTAc)



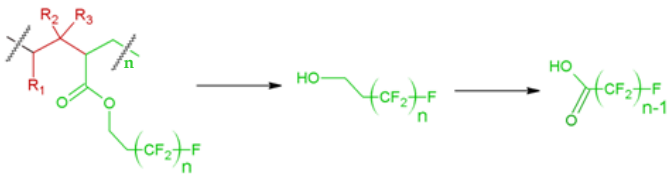
- ^{19}F-NMR spectrum:



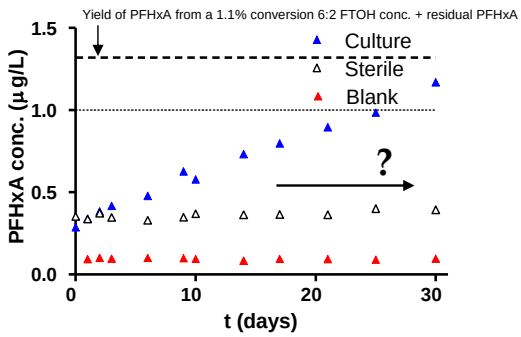
H/F nanoprobe spinning at ≈ 2000 Hz

Side-chain fluorinated acryl copolymer 2

- 1‰ of residual FTOH and minor amounts of PFAA present in fluoropolymer mixture: FTOH: C6 (90%), C8 (5%) and C10 (5%).
- Degradation of a fluorinated acryl copolymer



- First results on biodegradation experiment of residual 6:2 FTOH or C6 based side-chain fluorinated acryl copolymer technical mixture



Conclusions

- FTOH and PFAA residuals were present in both mixtures.
- Homologues series of "unknown" fluorinated compounds were found in fluorinated copolymer 1 by accurate MS (LC-QTOF MS)
- Perfluorinated side chains were observed in copolymer 1 by ^{19}F NMR
- Side-chain fluorinated acryl copolymer 2 had broad peaks in the ^{19}F NMR spectrum, possibly due to micellization.
- Degradation of FTOH residuals or side-chain fluorinated acryl copolymers are sources of PFAA in food packaging and in the environment
- More knowledge on production volumes of side chain fluoropolymers and individual brands is required for a thorough assessment of the precursor potential of side-chain fluorinated acryl copolymers

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