

Biodegradability of Telomer-Based Polymeric Products

1. Goal

The goal of the biodegradability study is to examine end-use telomer-based polymeric products for potential transformation to PFOA in sludge if the product enters a domestic sewage treatment plant. The study will be designed to meet LOI commitments to EPA.

2. Assumptions

- a. PFOA may be present as an impurity at low levels in telomer-based polymeric products.
- b. Large molecular weight polymers are non-polar and insoluble in water and are not expected to be available to microorganisms or undergo transformation.
- c. Impurities in the polymeric product may be a possible source for PFOA formation
- d. Analyses
 - i. PFOA - The degradation compound which will be monitored.
 - ii. F⁻ - Could be analyzed but the correlation between F⁻ formation and PFOA formation has not been well-defined.
 - iii. CO₂ and O₂ - Although mineralization to CO₂ is not a major issue to EPA, levels of DOC (dissolved organic carbon) will be measured to assess initial test compound levels and monitor degradation of a reference chemical.
- e. If PFOA is formed by incubation of telomer-based polymeric products with sludge, the mechanism involved in PFOA will not be defined.

3. Inherent biodegradability protocol considerations

- a. Guideline Selection
 - i. Selected guideline— Modified OECD 302 B: Zahn-Wellens/EMPA Test Guideline using activated sludge as a carbon source will optimize biodegradation
 - ii. Disregarded alternative guidelines
 - 1. OECD 301D to test "ready" biodegradability with a limited carbon source may be too stringent and minimize biodegradation under typical sewage treatment conditions
 - 2. OECD 302A involves daily addition of settled sewage feed with long time exposure of the test chemical. This "test does not simulate those conditions experienced in a sewage treatment plant" and favors selection of microorganisms capable of degrading the test compound.
 - 3. OECD 302C assessing biochemical oxygen demand depends upon the test chemicals as sole organic carbon

source and is best for test chemicals with water solubility >100 ppm

4. OECD 302D involves test chemical incubation with a mixed population of microorganisms that are pre-exposed to the test chemical. This test may artificially induce biodegradation through microbial pre-exposure.
- b. Test compounds - The same 12 acrylate and urethane products tested in the product and article aging studies will be selected as they represent 85% of the telomer-based products that TRP members manufacture and sell.
- c. Reference compound - Ethylene glycol, diethylene glycol or lauryl sulfonate will be used to verify sludge functional capability. Biodegradation must reach at least 70% DOC or COD within 14 days.
- d. Guideline testing levels –
Test substance - DOC of 50 to 400 mg/L
Sludge - 0.2 – 1.0 g dry matter/L
Ratio sludge/test substance DOC – 2.5:1 to 4:1

Polymer products are 20% aqueous dispersions
Incubate 500 mg formulated polymeric product ~1000 mg sludge in 1 L mineral medium
- e. Sampling intervals -3 hr (0 time), 7, 14, 21, and 28 days

4. Analytical Method Development for PFOA in Sludge

- a. Estimated PFOA in product is 1 ppm
- b. At 200 µg/L fortification of adapted bacterial culture from sludge, spike recoveries were 69-81% (DuPont EMSE Report No. 15-03, Accelerated Biodegradation of 8-2 telomer B alcohol). Additional results are shown below.

Sample	Treatment	µg/L PFOA	Peak Area
Blank	Methanol Solvent		126
Matrix Control	Bacterial culture – 8-2 Alcohol		143
Spiked Control	30 µg/L PFOA in bacterial culture		997
Abiotic Control	8-2 Alcohol + Killed bacterial culture (Day 28)	ND	144
Treated	8-2 Alcohol + bacterial culture (Day 28)	9.6	828

- c. Method development for PFOA in sludge will be initiated after analysis of PFOA in product and articles is resolved.

d. Sample calculations

If initial PFOA is 1 ppm in polymeric products, sludge treated with 500 mg polymeric product/L, would contain:

$$PFOA \text{ in sludge} = \mu g \text{ PFOA} / g \text{ product} \times 500 mg \text{ product} / L = 0.5 \mu g \text{ PFOA} / L$$

e. Target LOQ for PFOA will be ?? ppb

f. Starting method for PFOA in sludge

0.34 mL 6 N H₂SO₄ and 30 mL chilled MBTE are added to sample bottles containing 20 mL test medium. The bottles are shaken at room temperature for approximately 2 hr. After settling, the MTBE phase is transferred to polypropylene centrifuge tubes. The MBTE phase is centrifuged. A 20 mL aliquot is transferred to a glass scintillation vial and 6 mL is removed and dried in a GC vial under nitrogen and is redissolved in 1.5 mL methanol.

5. Outcome

Initial levels of PFOA will be compared to levels after incubation with sludge to provide information on whether telomer-based polymeric products may transform or break down to PFOA if the products enter domestic sewage treatment plants. This screening study will provide an initial picture of exposure caused by biotic processes on telomer-based polymeric products released from plants into the environment. The study is not designed to determine where PFOA originates.

6. Initiation of additional testing

If a significant amount (> ? ppm) of PFOA is generated, the source for its formation may be explored by fractionating representative polymeric products by size exclusion and testing the separate fractions or testing impurities.