

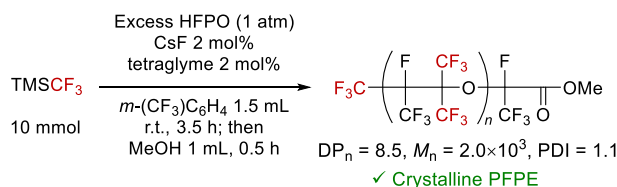
Synthesis of novel perfluoropolyethers using hexafluoropropylene oxide

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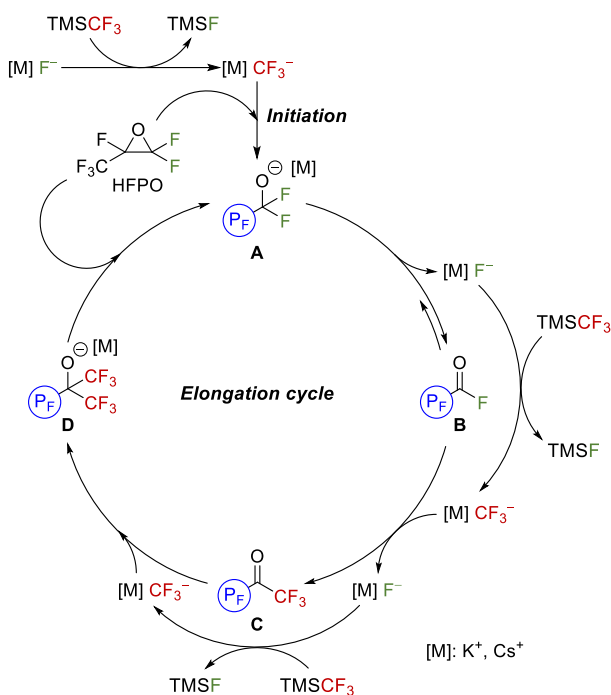
Organofluorine compounds have unique properties, and fluorinated polymers show significantly different physical properties from other polymers. Therefore, fluorinated polymers have received considerable attention in material chemistry.

In this study, the synthesis of a CF₃-rich perfluoropolyether (PFPE) has been achieved via the fluoride-catalyzed reaction of hexafluoropropylene oxide (HFPO) with (trifluoromethyl)trimethylsilane (TMSCF₃) (Scheme 1). Repetition of the sequence afforded a new PFPE as a solid, whose structure was confirmed using ¹⁹F NMR spectroscopy and GC-MS analysis. Thermal analysis and X-ray diffraction analysis revealed its crystalline character. To the best of our knowledge, this is the first example of crystalline PFPE. From contact angle measurements, the critical surface tension of this solid PFPE was determined to be 13.4 mN m⁻¹; this value demonstrated the higher water- and oil-repellency of the CF₃-rich PFPE compared to that of PTFE (18.5 mN m⁻¹).^[1]

A plausible reaction mechanism is shown in Scheme 2. Nucleophilic addition of a CF₃ anion to HFPO affords an acyl fluoride **B** via the ring-opening of HFPO followed by fluoride elimination. Further addition of CF₃ anions to the acyl fluoride **B** gives tertiary perfluoroalkoxide **D**, which attacks HFPO to regenerate an acyl fluoride.



Scheme 1. The synthesis of a CF₃-rich PFPE



Scheme 2. Proposed reaction mechanism

1) H. W. Fox, W. A. Zisman, *J. Colloid Sci.* **1950**, 6, 514–531.