Recent Advances in Perfluoropolyalkylether (PFPAE) Chemistry

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In a collaborative study with DuPont' Performance Lubricants Business, we helped conclusively show that the perfluoro-*iso*-propyl end group is a common, but not predominate end group in their commercial family of PFPAEs or Krytox®. Samples of Krytox® with just perfluoro-*iso*-propyl end group as well as non-commercial samples of poly(hexfluoropropylene oxide) with just perfluoro-*n*-propyl and perfluoro-*n*-hexyl end groups were then isolated or prepared. All of the samples, including normal Krytox® with perfluoroethyl end groups, were then thermally stressed over an aluminum fluoride catalyst (a good estimate for tribological conditions on an aluminum surface), and the samples with C3 or larger end groups were unexpectedly found to displayed enhanced stability by as much as 25 to 40 ºC. The thermal stability of the PFPAE polymer chains with different end groups has also been studied by accelerating rate calorimetry (ARC) both in the presence and absence of molecular oxygen, and the results are consistent with those obtained from the aforementioned stressing experiments over AlF_3.

PFPAEs with primary perfluoroalkyl iodide end groups, $-CF_2I$, have also been prepared via a β-elimination of $CF_3C(O)F$ from corresponding PFPAEs ending with the secondary perfluoroalkyl iodide groups, $-CF(CF_3)I$. Both the primary and secondary perfluoroalkyl iodides are serving as useful substrates for preparing new PFPAE-based materials for work in fluorous media and fluorous biphase catalysis. New classes of linear (non-branched) PFPAEs have been prepared starting from diols and tetrafluoroethylene (TFE) and ending with solution-phase, direct fluorination. Most recently, we have developed the capability to obtain high-quality MALDI-TOF mass spectra on both non-functionalized and functionalized PFPAEs; whereas, the previous scientific literature would have led one to believe that the former would not be possible. These and related results will be presented.