

RADIOLYSIS OF SELECTED PERFLUOROPOLYETHERS [P-15]

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UV/VIS absorption spectra of e-beam irradiated, pure and doped polyperfluorinated ethers (PFPEs) were recorded in glassy samples at 77 K and during their thermal annealing. Pulse radiolysis method was used to study transient species in liquid PFPEs irradiated at temperatures above glass transition. Perfluoropolyethers are the family of medium-low molecular weight liquids composed of carbon, fluorine and oxygen atoms. They can be homopolymers or copolymers, linear or branched macromolecules build of mer units: - (OCF₂)_m -, - (OCF₂CF₂)_n -, - (OCF₂CF₂CF₂)_p -, and - (OCF(CF₃)CF₂)_q - capped with CF₃ group. Novel functionalized perfluoropolyethers have backbone terminated with polar groups - CH₂OH, -CF₂H. PFPEs used were commercial products known under trade names: Fomblin, Galden, Krytox, Demnum. These polyethers exhibit high thermal stability also in the presence of chemical and oxidizing reagents but show only moderate radiation resistance. Irradiation of liquid PFPs results in chain scission, $G_{\text{scission}} = 0,3 - 1,8$ and formation of few volatile products (mainly COF₂ and CF₄) with G_{gas} ranged from 1 to 7. Both yields depend on the chemical structure of polymers. In the general mechanism of radiolysis¹ separate paths involving reaction of excited states, ionic and radical reactions were proposed. Contribution of each path has still to be determined and proved. Present investigations were aimed on identification of primary observable transients. Because of very high IP ~ 13,5 eV, PFPEs should effectively donor positive charge, if hole transfer process can compete with dissociation of primary radical cations. Electrons are not stabilized in the matrices at low temperatures. No evidence was also found for their solvation in irradiated mono- or di-OH terminated ethers. Most likely electrons are scavenged by fluorine atoms as proposed in¹. Formation of new absorption bands in PFPEs irradiated as viscous liquids and low temperature glasses in the presence of electron scavengers (C₆F₆, C₆F₅Br, perfluoronaphthalene) was observed. This indicates that electrons can react with additives even in such specific, fluorine rich bulk PFPEs. The only information on the rate of electron scavenging was obtained by pulse radiolysis using -CF₂H terminated Galden-H dissolved in simple alcohols. Rate constants k_s for this reaction were found similar and equal to: $1.5 \cdot 10^8$, $1.2 \cdot 10^8$, $1.2 \cdot 10^8$ dm³/mol·s for MeOH, EtOH and 2-PrOH respectively. Present investigations lead to conclusion that main absorption bands in irradiated PFPEs probably represent neutral radicals.

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[1] A. Faucitano, A. Buttafava, S. Karolczak, P.A. Guarda, G. Marchionni, *Journal of Fluorine Chemistry* **2004**, 125, 221-241