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Communications to the Editor

Perfluoropolyether Synthesis in Liquid Carbon Dioxide by Hexafluoropropylene Photooxidation

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Dense carbon dioxide has been shown to be an excellent reaction medium for the synthesis of fluoropolymers traditionally synthesized in chlorofluorocarbon (CFC) media due to its inertness in free-radical polymerizations, its ability to dissolve highly fluorinated materials, its cost-effectiveness, and its numerous environmental advantages. Notable examples include the homogeneous free-radical polymerization of 1,1-dihydroperfluorooctyl acrylate[1] and the precipitation copolymerizations of fluoroolefins[2,3] in supercritical carbon dioxide. The polymerization of tetrafluoroethylene (TFE) and other fluoroolefins necessitates the utilization of inert solvents such as CFCs due to the propensity of fluorocarbon-based radicals to chain-transfer to hydrogen-containing solvents.[4] The recent ban on the utilization of CFCs has resulted in the development of alternative solvents such as hydrochlorofluorocarbons, hydrofluorocarbons, and perfluorocarbons. However, many of these solvents are not industrially attractive due to either insufficient long-term availability (as in the case of hydrochlorofluorocarbons), potential for chain transfer, high cost, or current lack of commercial availability. Thus, building upon our previous success in the polymerization of fluoroolefins in carbon dioxide, we have extended our studies to the photooxidation of fluoroolefins to synthesize perfluoropolyethers in liquid carbon dioxide.

Perfluoropolyethers are a class of fluoropolymers utilized primarily in high-performance lubricant applications such as for magnetic recording media and as heat transfer fluids. The fluoroolefin photooxidation method is one of the major industrial routes utilized for the commercial production of perfluoropolyethers.[5] In this process, a fluoroolefin is reacted with molecular oxygen at low temperature (typically −40 °C or lower) in the presence of ultraviolet light. Via a complex free-radical chain mechanism, a peroxidic perfluoropolyether is produced of which the structure is highly dependent upon the reaction conditions.[6] For example, a peroxidic polyether can be obtained from hexafluoropropylene (HFP) (Figure 1) that contains predominantly hexafluoropropylene oxide (C_3) units with decreasing amounts of difluoromethylene oxide (C_1) and fluoro(trifluoromethyl)methylene oxide (C_2) repeat units. Post-polymerization treatment of these raw products can yield nonperoxidic products with either neutral or functional end groups.

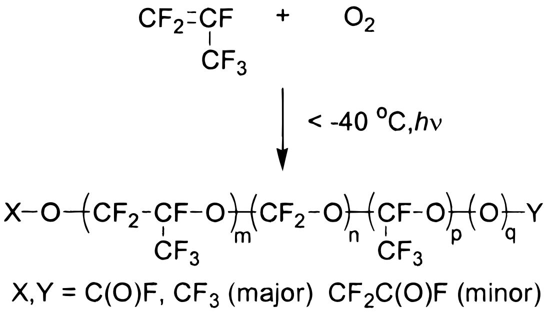

Figure 1. Peroxidic perfluoropolyether synthesis via HFP photooxidation.

In current commercial practice, the only fluoroolefins utilized in this process are hexafluoropropylene and tetrafluoroethylene.[5] The photooxidation of HFP is conducted in bulk monomer due to its inherently low reactivity. However, an inert diluent is required for TFE photooxidations in order to prevent fluoroolefin homopolymerization. Historically, dichlorodifluoromethane has been the preferred solvent, but the use of other low boiling perfluoroalkanes has been recently described.[7,8] Though CFCs have traditionally been hailed as being highly inert, chain transfer to CFCs is known to occur in fluoroolefin photooxidation reactions.[9]

In this study, HFP photooxidation reactions were conducted with varying HFP concentrations (8.8−3.7 M) in carbon dioxide. Parallel reactions were conducted in bulk HFP and perfluorocyclobutane (PCB) for comparison. The photooxidation reactions were conducted in a previously described high-pressure reactor[10] modified for use at low temperature and UV irradiation. The reactions were irradiated under an oxygen head pressure of ca. 2 bar for 15 h at −40 °C. All reactions were homogeneous throughout the irradiation period and produced water-white liquids with isolated yields ranging from 16 to 48%.[11] Product analysis by ^{19}F NMR provided information on the polymer composition, number-average molecular weight (M_n), and peroxide content.[12,13]

The mechanism of the low-temperature (<−40 °C) liquid-phase photooxidation of HFP has been well studied, resulting in the development of a kinetic model describing the relative importance of the elementary reactions occurring during the process.[6,14] The polymerization begins after a short induction period where minute quantities of HFP are converted to CF_3COF and peroxides. Photolysis of these compounds generates radical species and initiates the photooxidation process. Some of the important elementary reactions in the mechanism that contribute to chain propagation and termination are illustrated in eqs 1−9.

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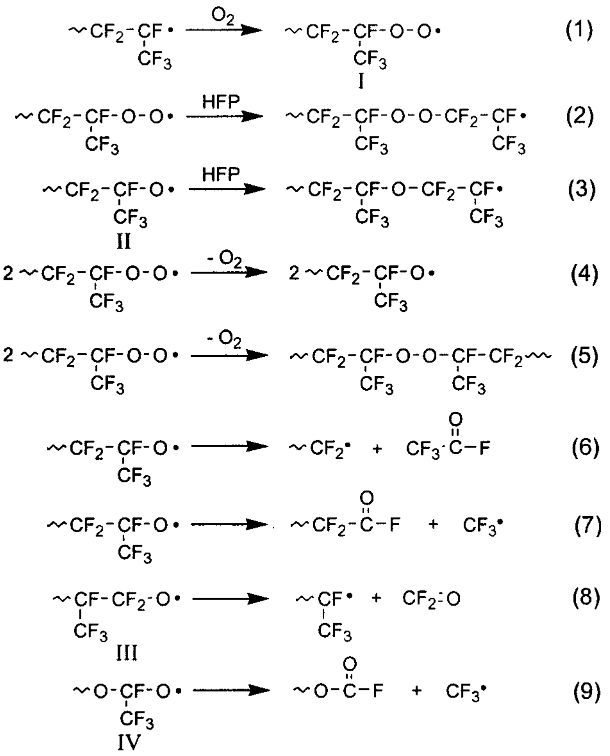

$$\sim CF_2-\underset{CF_3}{CF}\cdot \xrightarrow{O_2} \sim CF_2-\underset{\underset{\text{I}}{CF_3}}{CF}-O-O\cdot \quad (1)$$

$$\sim CF_2-\underset{CF_3}{CF}-O-O\cdot \xrightarrow{HFP} \sim CF_2-\underset{CF_3}{CF}-O-O-CF_2-\underset{CF_3}{CF}\cdot \quad (2)$$

$$\sim CF_2-\underset{\underset{\text{II}}{CF_3}}{CF}-O\cdot \xrightarrow{HFP} \sim CF_2-\underset{CF_3}{CF}-O-CF_2-\underset{CF_3}{CF}\cdot \quad (3)$$

$$2 \sim CF_2-\underset{CF_3}{CF}-O-O\cdot \xrightarrow{-O_2} 2 \sim CF_2-\underset{CF_3}{CF}-O\cdot \quad (4)$$

$$2 \sim CF_2-\underset{CF_3}{CF}-O-O\cdot \xrightarrow{-O_2} \sim CF_2-\underset{CF_3}{CF}-O-O-\underset{CF_3}{CF}-CF_2\sim \quad (5)$$

$$\sim CF_2-\underset{CF_3}{CF}-O\cdot \longrightarrow \sim CF_2\cdot + CF_3-\overset{O}{\overset{\|}{C}}-F \quad (6)$$

$$\sim CF_2-\underset{CF_3}{CF}-O\cdot \longrightarrow \sim CF_2-\overset{O}{\overset{\|}{C}}-F + CF_3\cdot \quad (7)$$

$$\sim \underset{\underset{\text{III}}{CF_3}}{CF}-CF_2-O\cdot \longrightarrow \sim \underset{CF_3}{CF}\cdot + CF_2=O \quad (8)$$

$$\sim O-\underset{\underset{\text{IV}}{CF_3}}{CF}-O\cdot \longrightarrow \sim O-\overset{O}{\overset{\|}{C}}-F + CF_3\cdot \quad (9)$$

Fluorocarbon radicals react at diffusion-controlled rates with oxygen to produce peroxy radicals (**I**) (eq 1). Through a nonterminal disproportionation reaction (eq 4), these peroxy radicals are transformed to perfluoroalkoxy radicals (**II**). Subsequent addition of **II** to HFP (eq 3) yields an ether linkage in the polymer chain and a new fluorocarbon radical to repeat the propagation cycle. This propagation cycle is significantly faster than addition of **I** to HFP (eq 2), thus leading to an overall low peroxide content (1–3 wt %) in the polyethers under appropriate irradiation conditions. The major bimolecular termination reaction in the polymerization is that of peroxy radicals (eq 5); however, this reaction only contributes to a small amount of the overall peroxide content.

The mechanism of the bulk photooxidation of HFP becomes more complex at temperatures above −50 °C, where β-scission reactions of **II** (eq 6) become competitive with propagation (eq 3) and become more important with increasing temperature.[6] Expulsion of trifluoroacetyl fluoride and generation of a difluoromethylene radical chain end (eq 6) results in an increased C_1 content while expulsion of a trifluoromethyl radical (eq 7) results in chain termination and reinitiation (chain transfer). The C_2 content is typically low compared to the C_1 content due to the highly competitive β-scission reactions of **IV**,[15] which results in chain transfer (eq 9). Thus, in the bulk photooxidation of HFP, temperature is the primary factor controlling molecular weight and polymer composition.

At constant temperature, however, HFP concentration governs the polymer composition and molecular weight. This dependence is observed in the HFP photooxidations conducted at varying [HFP] in liquid CO_2 and PCB. A concomitant decrease in C_3 content (Figure 2) and M_n (Figure 3) is observed with decreasing HFP concentration. Decreasing the [HFP] allows the unimolecular β-scission reactions to become increasingly competitive with addition of **II** to HFP. The C_3 content and M_n's of the polyethers synthesized in liquid CO_2 were comparable to those made in PCB at relatively high concentration, with only slight deviation at the lowest concentrations employed. Thus, dilution of HFP with a solvent has the greatest impact on the polymer structure and not whether the solvent is CO_2 or PCB.

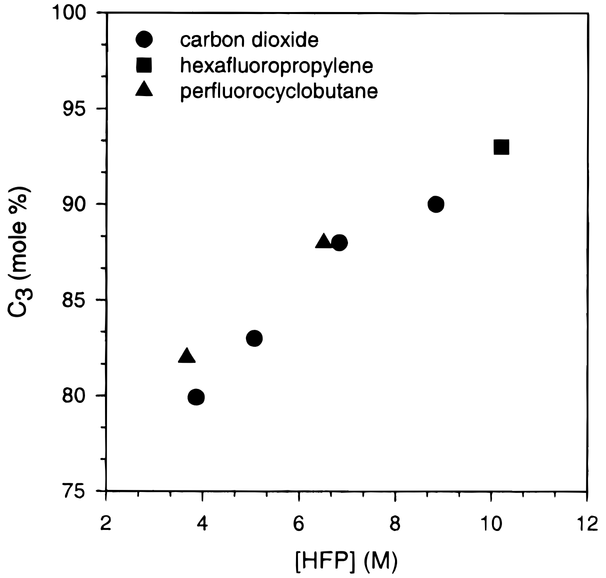

Figure 2. Hexafluoropropylene oxide repeat unit (C_3) content as a function of HFP concentration in (●) carbon dioxide, (■) bulk HFP, and (▲) PCB at −40 °C.

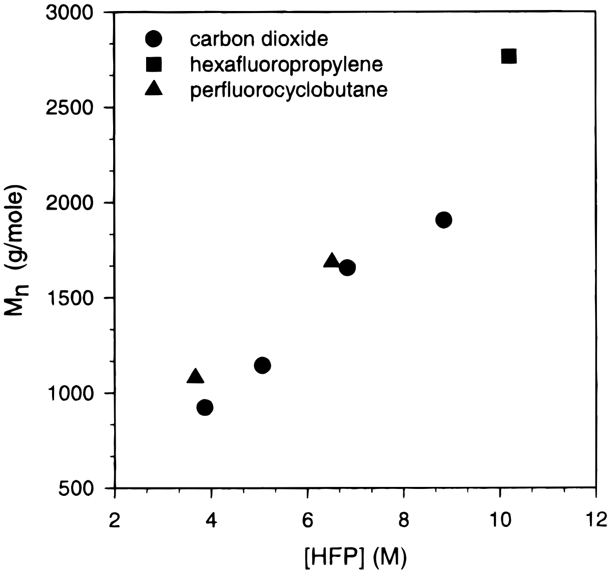

Figure 3. Perfluoropolyether molecular weight (M_n) as a function of HFP concentration in (●) carbon dioxide, (■) bulk HFP, and (▲) PCB at −40 °C.

The influence of [HFP] on the peroxide content of the polyethers follows a similar trend to composition and molecular weight. The primary pathway of peroxide incorporation is HFP addition to peroxy radicals while peroxide depletion occurs through photolysis to generate alkoxy radicals.[6] This correlation of peroxide content with [HFP] is observed in Table 1 where the peroxide content decreases with decreasing [HFP]. This trend is observed for the polyethers synthesized in both PCB and liquid CO_2. However, the polyether synthesized at the lowest concentration in CO_2 (entry 4) has a peroxide content about 3 times less than the one synthesized in PCB (entry 5) at the same concentration.

Table 1. Peroxide Content in the Perfluoropolyethers Synthesized under Varied HFP Concentration in HFP, CO_2, and PCB

entry	[HFP] (M)	solvent	peroxide content (wt %)	volume HFP (vol %)
1	10.2	HFP	1.8	100
2	6.8	CO_2	1.1	67
3	6.5	PCB	1.2	64
4	3.9	CO_2	0.29	38
5	3.7	PCB	0.85	36

An explanation for this difference in peroxide content can be derived from solvent viscosity effects. Liquid CO_2 has a viscosity of 0.20 cP at −40 °C,[16,17] which is much less than that of PCB (1.1 cP)[18] and most common fluorocarbon solvents[18] at similar conditions. The lower viscosity of CO_2 may be increasing the effective quantum yield for peroxide photolysis by favoring diffusive separation of the geminate perfluoroalkoxy radicals over recombination in the solvent cage.[19] This influence would be expected to be most dramatic in the reactions at the lowest [HFP] (entries 4 and 5), where the solvent has the major influence on the viscosity of the reaction medium. Since HFP is the major component in the reactions conducted at the higher [HFP] (entries 2 and 3), the difference in viscosity between the reactions conducted in CO_2 and PCB is much less, thereby resulting in a smaller difference in the respective peroxide levels. Analogous viscosity effects for other free-radical reactions conducted in dense carbon dioxide have been shown through increased free-radical initiator efficiencies[20] and decomposition rates.[21,22]

No systematic studies of solvent effects on the photooxidation of HFP or TFE have been previously reported in the literature, particularly with regard to solvent viscosity and solvent quality. HFP photooxidation is particularly difficult to study in these aspects due to the overall mechanistic complexity of the reaction and the strong dependence of molecular weight and polymer composition on [HFP]. Further investigations into the influence of solvent, particularly liquid carbon dioxide, on the mechanism of the photooxidative synthesis of perfluoropolyethers is currently being undertaken with tetrafluoroethylene photooxidations.

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Supporting Information Available: Description of the high-pressure reactor setup, experimental details including reaction yields and average reaction pressures, and a representative ^{19}F NMR spectrum of a peroxidic perfluoropolyether spectrum with assignments. This material is available free of charge via the Internet at http://pubs.acs.org.

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