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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polymerization of Perfluoro Epoxides

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To cite this Article Eleuterio, H. S.(1972) 'Polymerization of Perfluoro Epoxides', Journal of Macromolecular Science, Part A, 6: 6, 1027 – 1052

To link to this Article: DOI: 10.1080/10601327208056884

URL: <http://dx.doi.org/10.1080/10601327208056884>

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Polymerization of Perfluoro Epoxides

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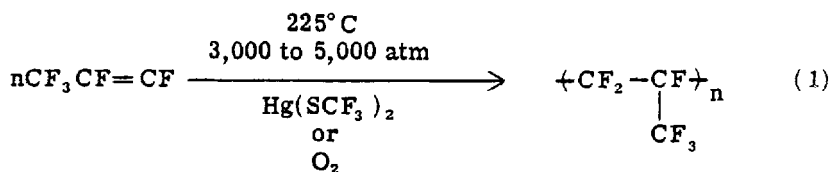
ABSTRACT

Epoxidation of perfluoroolefins to perfluoroepoxides has made a new class of monomers available. Perfluoroepoxides undergo facile ring-opening reactions with nucleophiles which under the proper reaction conditions can lead either to polyperfluoroethers or to other classes of fluorocarbons previously unavailable or available with great difficulty. The preparation of perfluoroepoxides is described.

The work which is described here originated during the middle 1950s in the Exploratory Section of the Polychemicals Department at the Du Pont Experimental Station. The main objective was to synthesize novel polymers containing only carbon and fluorine atoms in the backbone.

High-pressure studies of the homopolymerization and copolymerization of hexafluoropropylene and tetrafluoroethylene enabled us to prepare for the first time fluoropolymers containing 50-100 mole %

hexafluoropropylene (Eq. 1). Evaluation of the physical properties of these polymers filled sizable gaps in our knowledge of fluorocarbon polymers [1, 2].



To give some feel for how wide the knowledge gaps were, a polymer physicist made a prediction, that the physical properties of polyhexafluoropropylene (polyHFP) would be a rubber. Table 1 shows that

TABLE 1. Properties of Polyhexafluoropropylene

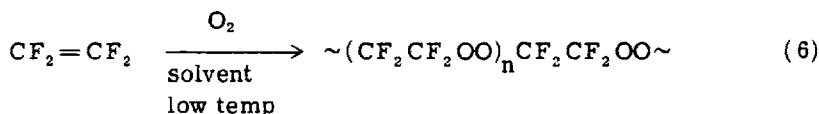
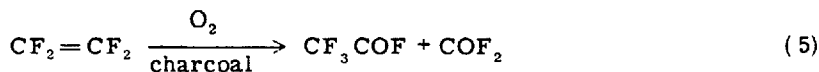
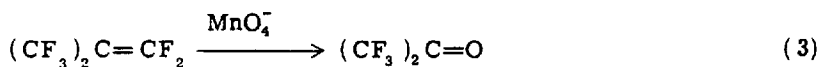
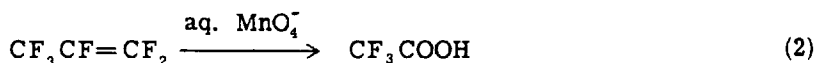
Density	2.08 g/cc
Softening range (°C)	225-250
Glass transition temperature (°C)	165
Solubility	Some fluorocarbon derivatives
Inherent viscosity (0.5% in FC-75)	0.2 to >1
Melt viscosity, 300°C	2×10^4 poises for sample $\eta_I = 0.4$
E for melt viscosity (kcal)	~50
Tensile strength/elongation	3,000-4,000 psi/3-4%
Flexural modulus (psi)	425,000
Izod impact strength (ft-lb/in. ³)	1.1
Electrical properties	
Dielectric constant	2.1
Dissipation factor	0.0001-0.0003 (10^2 to 10^6 Hz)
Volume resistivity (Ω -cm)	$>10^{17}$

polyHFP was in fact a very rigid polymer, with a flexural modulus of $>425,000$ psi [3]. The point, of course, is not how wrong the a priori predictions were; but serves to illustrate how vast the areas of ignorance were at the time.

When the exploratory phase of this work was completed, the search toward fluorocarbon polymers with a combination of physical properties useful over temperatures ranging from -60 to $+300^{\circ}\text{C}$ was redirected. The first efforts involved making low molecular weight polymers of tetrafluoroethylene for use as high-temperature fluids. This approach was aborted because the polymers were either too volatile or tended to crystallize at low temperatures.

It was speculated that perfluorinated polyethers might give the desired combination of physical properties without sacrificing chemical or thermal stability. Of several routes considered, polymerization of perfluoro epoxides to polyethers was the most attractive. In contrast to the voluminous literature describing hydrocarbon epoxides or the more limited literature describing partially fluorinated epoxides, references to completely perfluorinated epoxides were nonexistent. Efforts were started to explore novel preparative methods for perfluoro epoxides.

Over the years, all attempts to epoxidize perfluoro olefins gave carbonyl compounds. Some of these efforts are summarized in Eqs. (2)-(6) [4, 5].



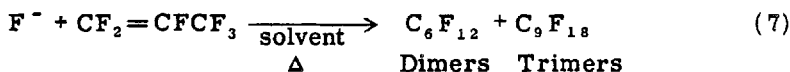
An excellent review of much of the early work can be found in the reference by Chambers [4].

Many of the early workers reported severe explosions in attempts to oxidize tetrafluoroethylene and chlorotrifluoroethylene.

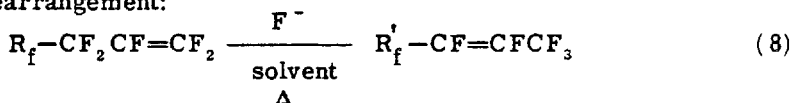
The initial experiments were carried out on hexafluoropropylene for two reasons, safety being of uppermost concern. The second reason for choosing hexafluoropropylene was its susceptibility to nucleophilic attack.

Fluoride ion catalysis in fluoro olefin systems, pioneered by Hanford in the 1940s [6], was discovered by Keith Bremer [7] and was put on a firm quantitative basis by W. T. Miller [8, 9]. Other workers have extended the reaction into a general preparative method (Eqs. 7-9) [10-12].

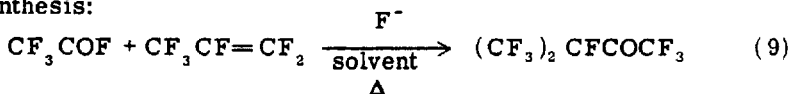
Oligomerization:



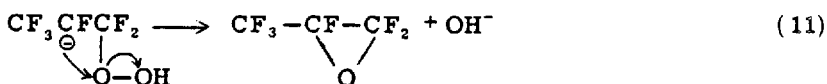
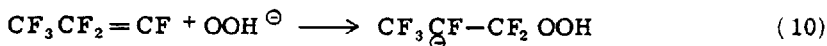
Rearrangement:



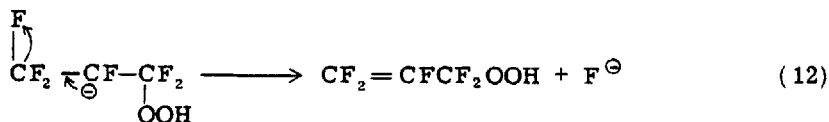
Synthesis:



It was speculated, as shown in Eqs. (10)-(12), that hydroperoxy anion (OOH^-) would be more nucleophilic than (OH^-) hydroxide ion, and it was guessed that it might be a strong enough nucleophile to add to hexafluoropropylene. Furthermore, it was hoped that hydroxide



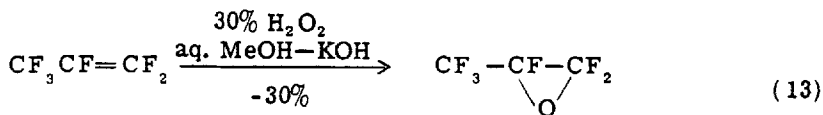
or



ion (OH^-) would be eliminated rather than fluoride ion (F^-). However, laboratory consensus favored preferential fluoride ion elimination, and it was further argued that even if hexafluoropropylene epoxide (HFPO) were formed, it would not survive the reaction conditions.

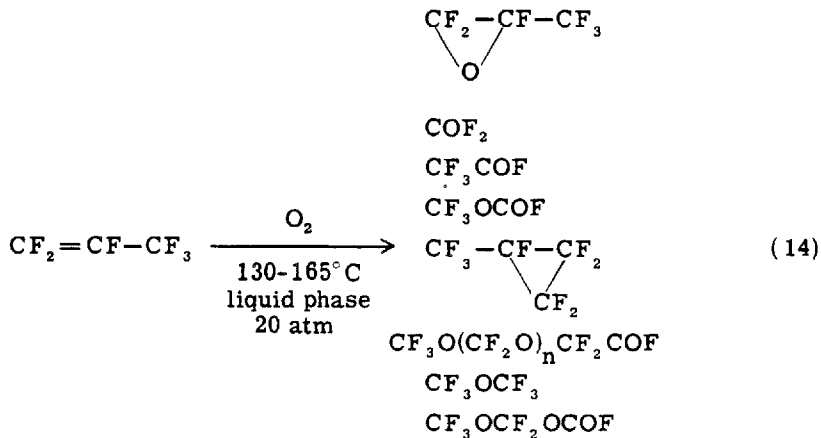
One possible route to HFPO was described in a British patent [13, 14], but there was skepticism that the reaction conditions described in the patent would give HFPO. In due course it was established that the product was perfluorotrimethylene ether and not HFPO.

After considerable experimentation, reaction conditions were worked out which permitted the synthesis of HFPO routinely in satisfactory yields and with complete safety (Eq. 13) [15]. A low reaction temperature and careful pH control (above 8) favors epoxide formation over side



reactions. The alkaline-hydrogen peroxide method of epoxidation is general for all perfluoro olefins except tetrafluoroethylene.

Continued and increased interest in HFPO-based polyethers prompted a search for a cheaper oxidant than hydrogen peroxide. Equation (14) shows the reaction conditions which permitted the preparation of sizable quantities of HFPO [16, 17]. The oxidation appears to be a radical chain reaction with trifluoromethyl radical as a primary chain carrier. Product distribution depends on the ratio of olefin to oxygen and the reaction temperature.



Other methods for preparing perfluoro epoxides are illustrated by a schematic sketch (Fig. 1) of the apparatus used for preparing tetrafluoroethylene oxide (TFEO) [18, 19].

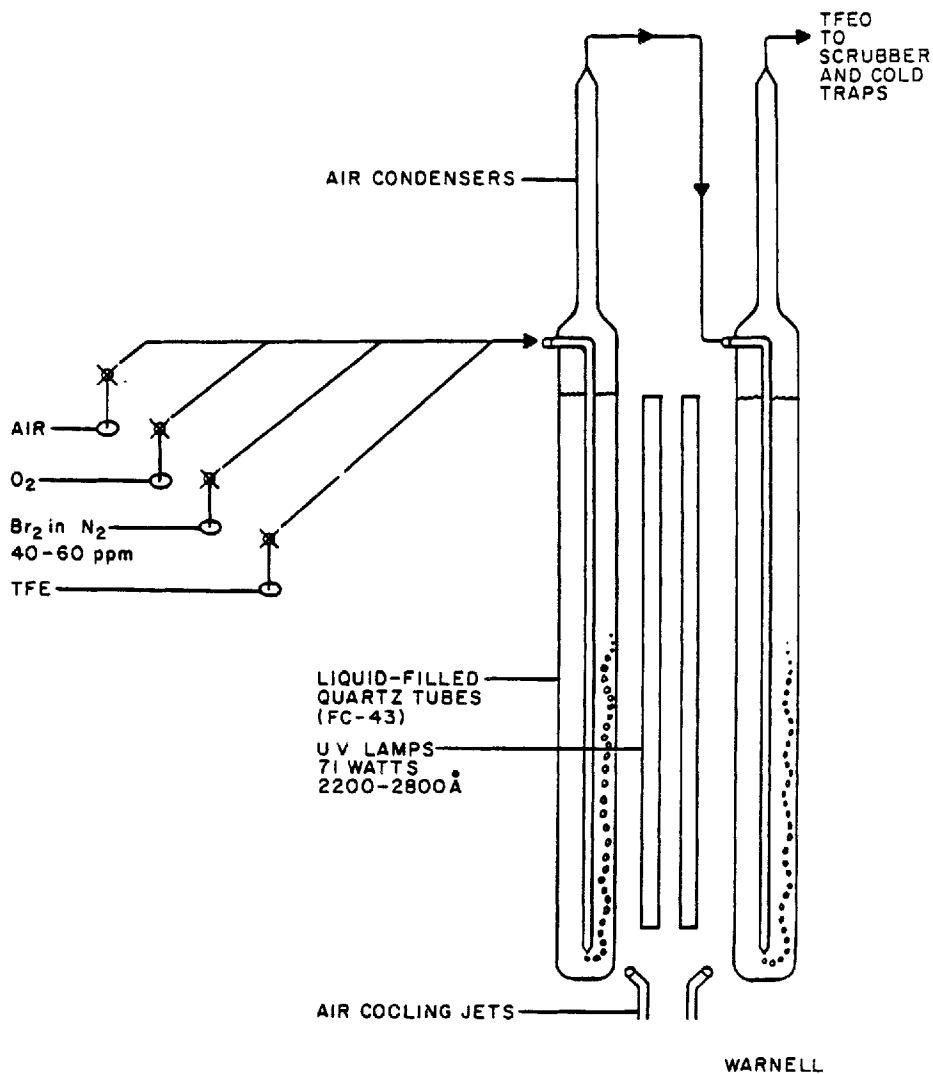


FIG. 1. Preparation of TFEO.

Considerable care is necessary in handling tetrafluoroethylene (TFE) and oxygen, for if the reactants are premixed the reaction can become explosively violent, but reactions were worked out to isolate TFEO in good yields [18, 19]. TFEO rearranges to trifluoroacetyl fluoride ($\text{CF}_3\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{F} \end{smallmatrix}$) at room temperature and should only be stored at temperatures below its boiling point (-65°C). Shortly after our work appeared in the patent literature [18-20], other workers published on various routes to the epoxides (Table 2) [21-38].

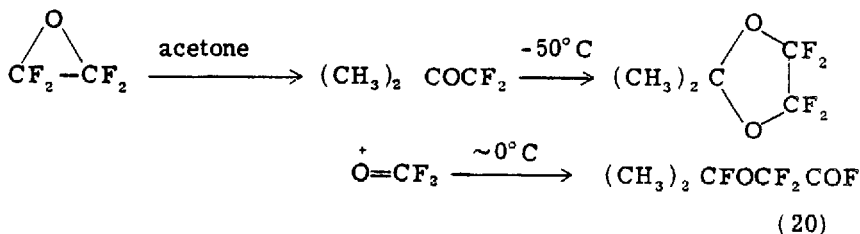
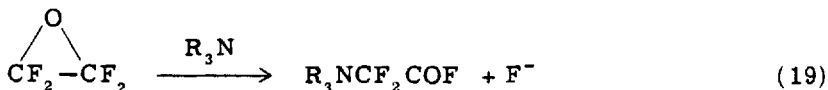
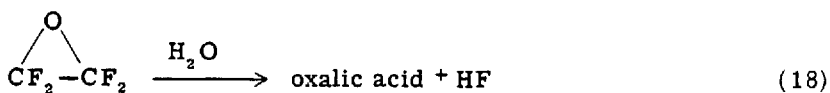
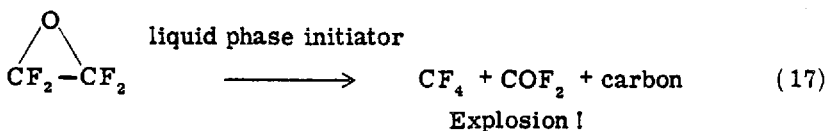
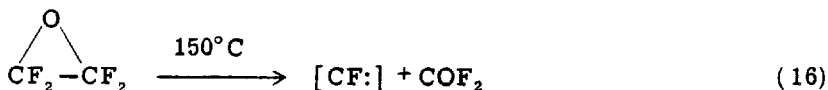
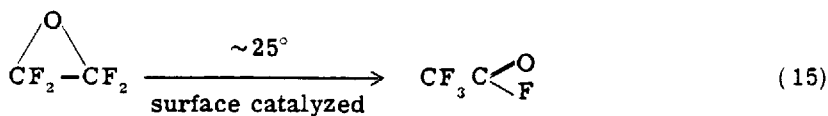
TABLE 2. Preparative Methods for Perfluoro Epoxides

Olefin/ O_2 /sensitizers	Sianesi
Photochemical	Mele
Halogen	Gozzo
Ozone	
Ionic reduction	
Olefin/ OF_2 /acceptors	Weinmayr
	Dale
Olefin/ HF/MnO_4^-	Knunyants
Ketone/carbenes	Sargeant
	Moore
	Mahler
	Knunyants
Ketone/ $\text{P}(\text{OEt})_3$	Knunyants
Pinacol/ P_2O_5	Knunyants
Dichloroepoxide/ Zn	Anderson

Of the approaches listed, particular mention should be made of the epoxidation in HF/MnO_4^- . This is, of course, epoxidation under electrophilic conditions as described by the Russian workers [31].

During the past 10 years, some two dozen structurally different perfluoro epoxides have been prepared. Except for tetrafluoroethylene epoxide, all the epoxides can be handled with the usual precautions accorded pure monomers.

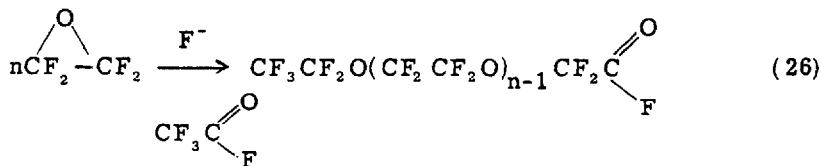
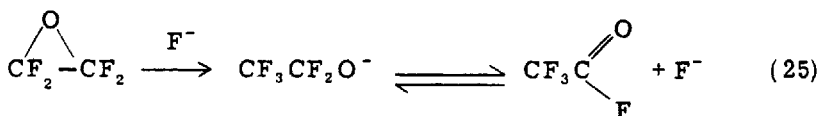
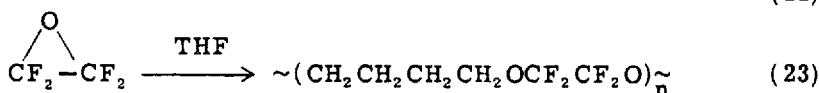
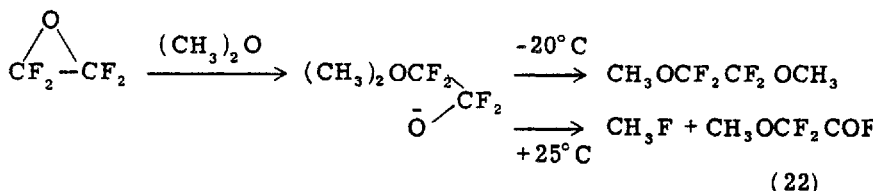
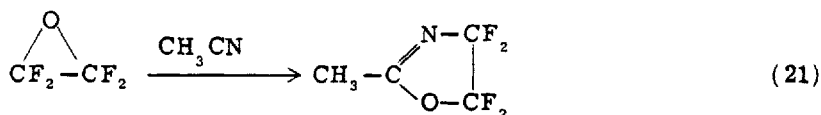
A number of the important reactions of TFEO are shown in Eqs. (15)-(20) [33-36]. TFEO undergoes a surface-catalyzed



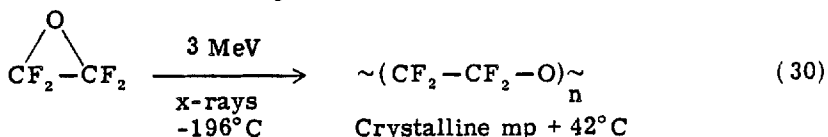
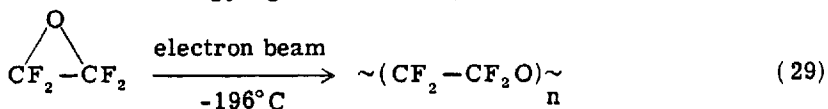
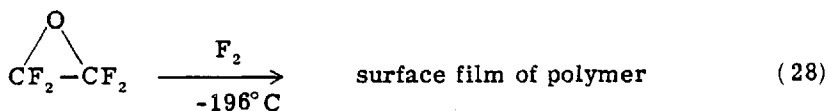
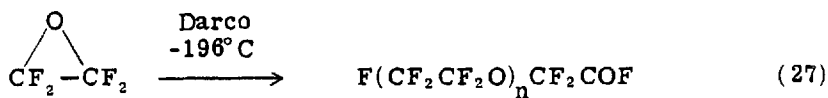
rearrangement at ambient temperatures to trifluoroacetyl fluoride. TFEO can be smoothly rearranged in the vapor phase to difluorocarbene and carbonyl fluoride. In the liquid phase, violent explosions may accompany fragmentation to carbon tetrafluoride, carbonyl fluoride, and carbon. Although TFEO is unreactive to water, it eventually is hydrolyzed. TFEO reacts with bases at -80°C to give isolatable adducts which rearrange to more stable products.

Acetone gives dioxolanes in better than 90% yield. Acetonitrile

gives oxazolines. The products obtained from dimethyl ether are temperature dependent. The reaction with fluoride ion gives equilibrium mixtures of alkoxides and acid fluorides which can further oligomerize to give polyether acid fluorides (Eqs. 21-26).



Polymerization of TFEO could be achieved Eqs. (27)-(30) [37-40] if chain termination by the reactions shown in Eqs. (15)-(26) is avoided. TFEO was condensed onto charcoal at -196°C ; vigorous polymerization took place on warming to -60°C with formation of solid white polymer. Attempts to prepare polymer with a degree of polymerization greater than 40 were not successful. Solid high molecular weight polymer was obtained by electron beam irradiation of the frozen monomer at -196°C .

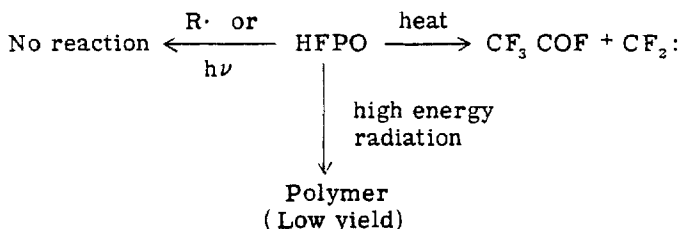


The use of 3 MeV x-rays at -196°C gave quantitative yields of polyTFEO. PolyTFEO has a crystalline melting point of $+42^\circ\text{C}$ and has excellent thermal and chemical stability. For example, in air, no weight loss was observed at $+440^\circ\text{C}$; at 550°C a 2% weight loss was observed in a nitrogen atmosphere. (TGA measurement heating rate, $15^\circ/\text{min}$.)

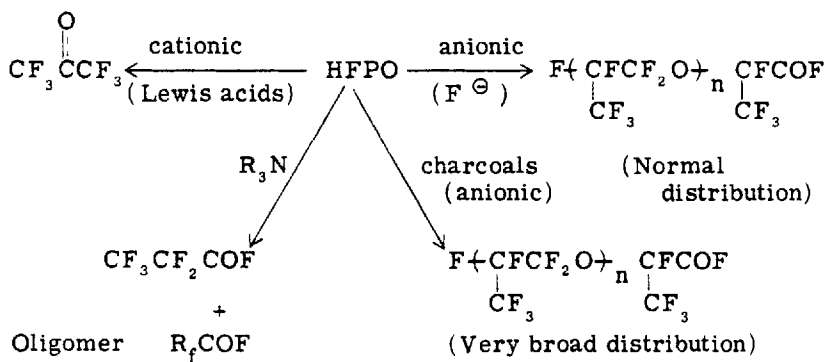
In marked contrast to TFEO, HFPO is thermally stable up to 150°C (Scheme 1) [41-47]. At 150°C , HFPO can be smoothly fragmented to difluorocarbene. This reaction has been used as a preparative method for generating difluorocarbene. HFPO is not affected by free radicals, and high-energy irradiation did not lead to high molecular weight polymer: the ionic reactions of HFPO have been those of greatest interest to us. HFPO can be rearranged to ketones with a variety of electrophiles. One reaction not listed in Scheme 1 with perfluoroisobutylene oxide and antimony pentafluoride in HF should be mentioned. Pavlik and Toren [42] of the 3M Company obtained perfluoro tertbutyl alcohol. The reaction of HFPO with nucleophiles will be discussed later in detail. The first successful attempts to polymerize HFPO were made using modified charcoals (Table 3) [48-51]. Charcoal catalysts gave polymers with a broad molecular weight distribution. After screening several hundred candidates, a polymerization scheme which includes low temperature, aprotic solvents, and fluoride ion evolved. Polymerization conditions are listed in Table 4 [52-54].

Fluoride ion preferentially attacks the substituted carbon atom, and the *n*-perfluoropropoxide ion reacts with more HFPO to give an equilibrium mixture of alkoxide and acid fluoride. Anionic polymerization of HFPO behaves like a "living polymer." The "living" nature of these polymerizations can be demonstrated by stopping monomer

Free Radical:



Ionic:



SCHEME 1. Potential polymerization systems.

TABLE 3. Anionic Systems

Charcoals: Source of small quantities of oligomers and polymers up to mol wt of 6000.

Indicated fluid characteristic and thermal stability of higher mol wt polymers.

F[⊖]: Used initially in bulk solvent systems (acetonitrile, glyme).

Source of oligomers up to octamer.

addition, sampling the polyether acid fluoride and determining its molecular weight, then allowing the polymer to remain dormant. Upon addition of more HFPO, the polymerization resumes as evidenced by monomer consumption. After an appropriate reaction time, resampling

of the polymerization mixture shows an increase in molecular weight. The process can be repeated at will until the polymer molecular weight exceeds the solubility limits of the particular solvent system.

One of the alternate fates for the perfluoro alkoxides is premature elimination of fluoride ion to acid fluoride. Redwood and Willis [50] first reported on the stability of perfluorinated alkoxides, and indeed fluoride ion elimination provides a pathway for chain transfer. Of all the catalysts employed, cesium and rubidium fluorides were found to be the preferred catalysts (Table 5).

TABLE 5. Typical F^{\ominus} -Glyme System for HFPO Polymerization

F^{\ominus} Source = CsF, low lattice energy and highly ionic nature.

Glyme = Tetraglyme $[CH_3O(CH_2CH_2O)_4CH_3]$.

Tetraglyme/CsF = 1/1 - indicates complexing of Cs^{\ominus} by polyether "horseshoe."

Temperature: Must be low to suppress: $R_fCF_2O^{\ominus} \longrightarrow R_fCOF + F^{\ominus}$,
resulting in chain transfer.

Between -30 to $-50^{\circ}C$ give reasonable propagation rates; mol wt up to 4000, DP = 24.

Condition: Strictly anhydrous!

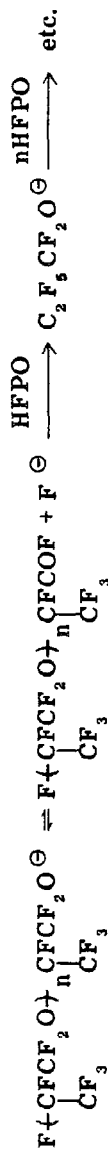
Cesium fluoride has the lowest lattice energy of the Group I metal fluorides. In order to suppress fluoride elimination, the preferred reaction temperature is below $-30^{\circ}C$. At this temperature tetraglyme (dimethyl ether of tetramethylene glycol) gave the best combination of desirable solvent characteristics. Polymer molecular weight build-up is largely influenced by chain transfer. Table 6 outlines the principal chain transfer steps.

Fluoride ion can also be transferred directly to another mole of monomer to give an acid fluoride and a new growing chain without the liberation of fluoride ion.

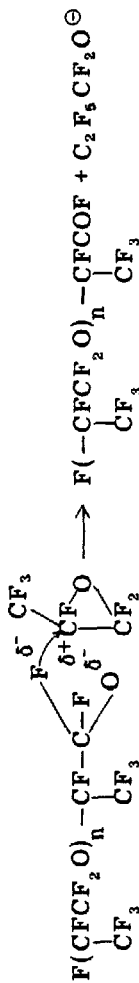
And yet a third possibility involves transfer between alkoxide and acid fluoride. One of the important factors which contributes to this last pathway is the availability of the monomer to the growing end of the chain. At these low temperatures the viscosity of the polymerization medium can restrict molecular weight build-up by mass transfer effects. An effective polymerization diluent was found to be

TABLE 6. Molecular Weight Build-up and Chain Transfer in HFPO Polymerization

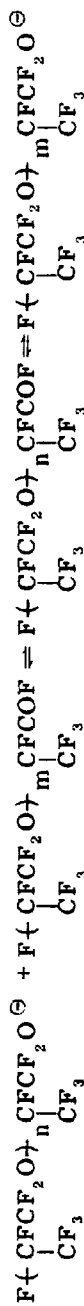
Transfer by F^\ominus loss from $R_fCF_2O^\ominus$:



Transfer of F^\ominus directly from $R_fCF_2O^\ominus$:



Transfer between $R_fCF_2O^\ominus$ and R'_fCOF :



Lower temperatures: Suppresses F^\ominus transfer to monomer.

When $m \gg n$ limits mol wt build-up with larger R'_fCOF by removing them, as a result of their low mobility, from equilibrium with smaller $R_fCF_2O^\ominus$.

TABLE 7. Use of HFP as Polymerization Diluent

Improved mixing and heat transfer
Higher mol wt (up to 12,000, DP = 72):
Preserves $R_fCOF-R'_fCF_2O^\ominus$ equilibrium
with larger RCOF.
Reduces F^\ominus transfer from $R_fCF_2O^\ominus$ to monomer.
Does not copolymerize.
HFP recovered as linear dimers and trimers: Can be used as diluents.

hexafluoropropylene (Table 7) [55-59]. Use of hexafluoropropylene permitted the preparation of polymer with a DP of at least 72 in excellent conversions. Interestingly enough, hexafluoropropylene does not copolymerize under these conditions. An interesting counterpart in the hydrocarbon series is the polymerization of acetaldehyde in isobutylene with BF_3 catalyst. In this case also, only polyacetaldehyde is formed, although without acetaldehyde the same reaction conditions gave high molecular weight polyisobutylene.

Equations (31)-(33) describe the essence of the $HFPO-F^\ominus-HFP$ system. Fluoride ion is scavenged by hexafluoropropylene, and the perfluoroalkyl anion can dimerize HFP to linear dimers and trimers. However, we have no evidence that HFP enters into the HFPO polymerization scheme by forming perfluoro esters with the alkoxide and acid fluoride intermediates. The reason for this lack of reactivity becomes apparent from an examination of molecular models which show that the epoxide ring can be approached more readily at the more substituted carbon atom, the carbon atom containing the fluorine atoms being virtually shut out from any attacking group. Therefore, ring opening in HFPO as well as in all the epoxides that have been studied thus far is influenced not only by the powerful electron-attracting inductive effect of the trifluoromethyl group, but also by steric requirements of the relatively large fluorine atoms.

Figure 2 depicts a plausible transition state for the propagation steps of the HFPO polymerization. The attack occurs from the backside of the carbon atom containing the trifluoromethyl and fluorine groups. Examination of molecular models shows that a perfluoro isopropyl anion cannot readily approach HFPO due to the steric bulk of the fluorine atoms.

Most of the problems that have been discussed thus far involve an understanding of ion pair equilibria. The quantitative understanding of these variables is, however, incomplete (Table 8) [60-63].

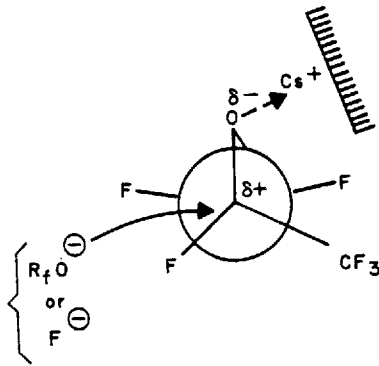
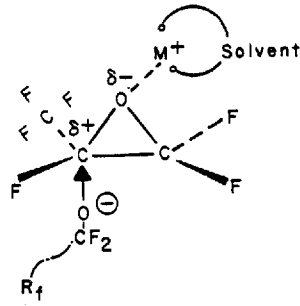


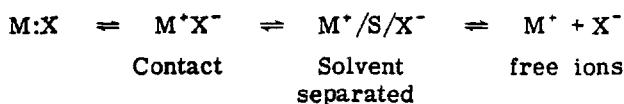
FIG. 2. A plausible transition state.

process is a continuous recycle process, the first time the polymerization is initiated a liquid catalyst solution, preferably containing a glyme solution of cesium alkoxide, is introduced from catalyst storage tank into reactor. A suitable balance of reaction variables is necessary in order to insure molecular weight control.

The rate of monomer addition and the ratio of monomer-catalyst-solvent, in combination with the degree of conversion, determines the final molecular weight. The viscosity of the polymerization medium can be continuously monitored by the judicious addition of solvent. PolyHFPO of number-average molecular weights of 5500 were prepared in market development quantities. The polymers in this molecular weight range are viscous fluids with acyl fluoride end groups. Since these polyethers were of particular interest as thermally stable fluids, it was necessary to convert the acyl fluoride

TABLE 8. Polymerization of Perfluoro Epoxides

Ion-Pair Equilibria:

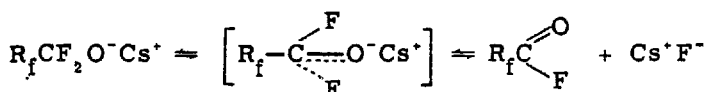


M = inorganic cation.

X = perfluoro alkoxide anion or fluoride ion.

Cs⁺: Large cation; low lattice energy; loose ion pairs; cation solvation depends on anion.

R_fO⁻: Primary or secondary alkoxides completely ionic species; tertiary alkoxides are covalent; primary or secondary alkoxides undergo alpha elimination; stability of alkoxides depends on cation, solvent, and temperature; solubility of R_fO⁻ depends on molecular weight of R_f groups.



end groups to nonreactive ends. Three stabilizing techniques that were evaluated are listed in Table 9.

The first two techniques, involving hydrogen and fluorine end capping, require that the desired molecular weight be achieved during the polymerization cycle. Irradiative coupling essentially doubles the molecular weight.

Table 10 briefly describes hydrogen end capping [65]. The advantage of the salt route is that it is a cleaner reaction giving rise to fewer by-products.

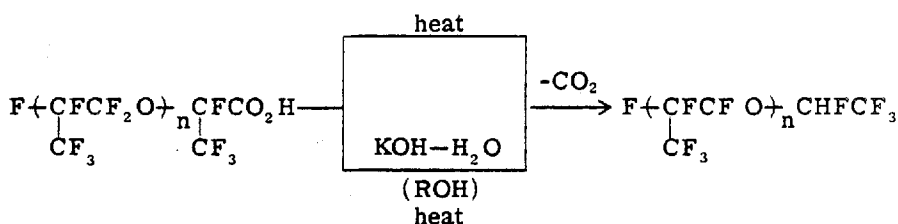
Equation (34) describes fluorination techniques for end capping [66, 67]. The top route presupposes the intermediacy of an oxyfluoro compound, the bottom route is presumed to go through a vinyl precursor.

Table 11 shows that irradiative coupling can lead to structural changes depending on the temperature [68, 69]. At temperatures lower than 100°C, carbonyl fluoride is obtained. At temperatures greater than 200°C, 80-90% of the polymer obtained has structure "B" and in addition to the coupled product trifluoroacetyl fluoride is isolated. Table 12 shows the effect of stabilizing techniques on thermal stability [70]. The

TABLE 9. Stabilizing Techniques

Purpose: To remove reactive (corrosive) acyl fluoride end group from $R_f\text{COF}$.	
Hydrogen endcapping: $R_f\text{COF} \longrightarrow R_f\text{-H}$	} Desired mol wt <u>must</u> have been attained during polymerization.
Fluorine endcapping: $R_f\text{COF} \longrightarrow R_f\text{-F}$	
Irradiative coupling: $2R_f\text{COF} \xrightarrow{h\nu} R_f\text{-}R_f$ Essentially doubles mol wt.	

TABLE 10. Hydrogen Endcapping



Thermal route: Higher temperatures.
Numerous by-products (free radical).

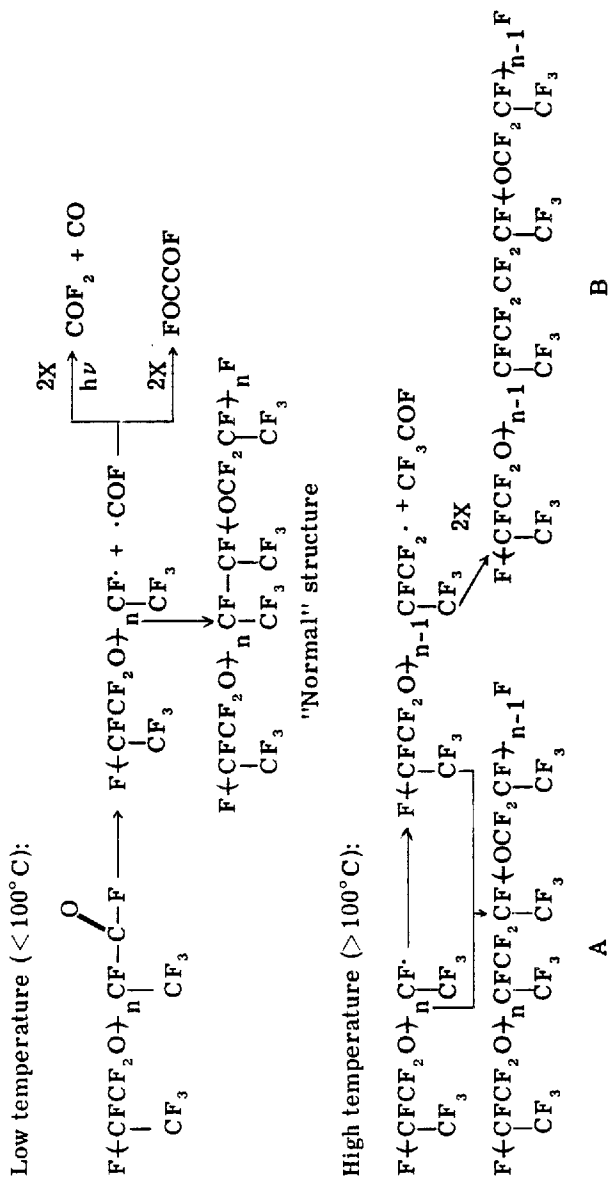
Salt route: Lower temperatures.
Single product type.

fluorine end-capped polymers have an incipient decomposition temperature above 410°C , the weakest bond in the structure is the in-chain carbon-carbon bond of the repeat unit.

Table 13 summarizes the chemical stability of HFPO polymers [71]. Perfluorinated polyethers fulfilled our original expectations of chemical and thermal stability. The Organic Chemicals Department of the Du Pont Company has made available a variety of these stabilized fluoropolymers in market development quantities under the Freon E and Krytox trademarks [72].

The discovery that perfluoro olefins could be epoxidized has made a new class of monomers available. Further reaction of these monomers has led not only to polyethers but also to other classes of fluorocarbons

TABLE 11. Irradiative Coupling Processes



Molecular weight decrease by "unzipping" insignificant.
 At 210°C, 80-90% "B."

TABLE 13. Chemical Stability of HFPO Polymers

Compatible reagents	
Material (test temperature)	Material (test temperature)
Liquid O ₂ (————)	Concd H ₂ SO ₄ (320°C)
N ₂ O ₄ (————)	P ₂ O ₅ (375°C)
Concd HNO ₃ (boiling)	BF ₃ (400°C)
Red fuming HNO ₃ (————)	
90% H ₂ O ₂ (————)	
	Molten NaOH (300°C)
Gaseous F ₂ (200°C)	(CH ₃) ₃ N (400°C)
Liquid ClF ₃ (boiling)	NaOCH ₃ (375°C)
CoF ₃ (200°C)	NH ₂ N(CH ₃) ₂ (————)
Steel (red heat)	
316 Stainless steel (red heat)	Metals ^a
Ti (red heat)	
Al (~650°C)	
Sodium fusion: Liberates F [⊖]	

^aIn absence of O₂.

previously unavailable or available only with great difficulty [73], for example, decarboxylation of the fluorocarbon ether dimer acids gives perfluorinated vinyl ethers in excellent yield [74]. Some of the chemistry of this area has been unraveled, but much remains to be done [75-83].

In 1968, Hoffman and Woodward commented on circumstances which led to the Woodward-Hoffman rules. Paraphrasing their remarks:

Chemistry remains an experimental science. Of necessity this work has been a marriage of poor theory with good experiment. Yet, in the hands of clever experimentalists these ideas were transformed into novel molecules with unusual properties.

Woodward's and Hoffman's remarks aptly apply to the work that is described in this paper.

ACKNOWLEDGMENTS

I would like to acknowledge the work of our clever experimentalists: F. Arbogast, P. Carlson, C. Fritz, F. Gresham, W. Gumprecht, J. Hill, R. Meschke, A. Milian, E. Moore, R. Putnam, P. Resnick, S. Selman, S. Temple, and J. Warnell. F. Gresham and R. Putnam were mainly responsible for guidance and encouragement.

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Accepted by editor September 10, 1971

Received for publication October 28, 1971