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The Free-Radical Chemistry of Fluoroketones. II. Reaction with Unsaturated Compounds

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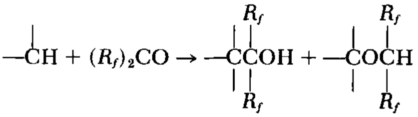
Summary

Free radicals induce two principal types of interaction between fluoroketones and olefins, both of which lead to polymeric products. Copolymerization of the fluoroketone through its carbonyl group leads to polyethers. Hydrogen abstraction, presumed to be largely intramolecular, also occurs to give highly branched polymers with fluoroalcohol groups at terminal positions on the branches.

Polyfluoroketones react with most olefins and dienes to form adducts. With dienes, dihydropyrans result (*1*) while photoaddition to fluoroolefins yields oxetanes (*2*). Oxetane formation also occurs with vinyl ethers, but the ring opens spontaneously to give acyclic unsaturated fluoroalcohols (*3*). Olefins having α-methyl groups add thermally to form unsaturated alcohols (*4*). In the first paper of this series (*5*), polyfluoroketones were shown to react via a free-radical-chain mechanism with saturated organic substrates, the products being formed by the net insertion of a fluoroketone into a C—H bond:



$$-\overset{|}{C}H + (R_f)_2CO \rightarrow -\overset{|}{\underset{|}{C}}\overset{R_f}{\underset{R_f}{C}}OH + -\overset{|}{\underset{|}{C}}O\overset{R_f}{\underset{R_f}{C}}H$$

In this investigation the free-radical sensitivity of fluoroketones was shown to permit their interaction with simple olefins to form mainly polymeric products.

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[*] Contribution No. 1255.

EXPERIMENTAL

Reaction of Ethylene and Hexafluoroacetone

The reaction was run in a stainless-steel tube with 40 ml of benzene, 0.5 g of di-*t*-butyl peroxide, and 15.5 g of hexafluoroacetone. The mixture was subjected to 500 atm of ethylene pressure at 135°C over a period of 6 hr, during which a total pressure drop of 332 atm was observed. The product, a mobile liquid (48 g), was distilled. A fraction, b.p. 155–173°C/0.3 mm, 4.0 g, was found to contain 52.61% F, corresponding to 76.5% combined hexafluoroacetone, corresponding to a ratio of 1 mole of hexafluoroacetone to 1.35 moles of ethylene.

The residue from the distillation, 4.2 g, contained 53.72% fluorine or a mole ratio of 1 hexafluoroacetone to 1.6 ethylene.

In another experiment, when a greater amount of ethylene was used, a solid polymer resulted.

A mixture of 100 ml of benzene, 1 g of di-*t*-butyl peroxide, and 17 g of hexafluoroacetone was heated at 135°C with ethylene at 500 atm until a pressure drop of 105 atm was observed. There resulted a benzene-insoluble fraction of polymer weighing 12 g. A sample was dissolved in hot benzene. After filtering the hot solution, the solid was reprecipitated by cooling. The polymer was found to contain 7.84% fluorine, which corresponds to 11.4% of combined hexafluoroacetone. Its inherent viscosity as a 0.5% solution in α-chloronaphthalene at 135°C was 0.48. This corresponds to $[(CH_2CH_2)_{46}CH_3COCF_3]_{25}$. This polymer showed no appreciable decomposition until it reached 400°C, where it lost 1.5% of its weight when heated at a rate of 3°C/min. Even up to 470°C it lost only 8.7% of its weight. When the polymer was boiled with 5% sodium hydroxide for 5 hr, the material gained 4.7%, owing to the absorption of sodium ion by the acidic hexafluoroisopropyl alcohol groups.

Polymerization of Ethylene with Hexafluoroacetone in a Protonated Medium

A Hastelloy bomb which had been thoroughly cleaned and conditioned by treating with hexafluoroacetone hydrate was charged with 50 g of $CF_3COCF_3 \cdot 1.6H_2O$ and 0.15 g of a 75% solution of *t*-butyl peroxypivalate. The mixture was heated at 55°C under a pressure of 600 atm of ethylene until a pressure drop of 125 atm occurred. When dried, the white polymer weighed 11.5 g and was easily pressed into a transparent film. After extracting with petroleum ether for 2 days in a Soxhlet extractor, the polymer was found to have the following analysis:

F, 15.17%, which corresponds to 22.1% combined hexafluoroacetone; inherent viscosity as 0.1% solution in tetralin at 125°C, 0.90.

When the reaction was carried out at 60–80°C using benzoyl peroxide as a catalyst, a tacky polymer resulted that dissolved in warm petroleum ether. On cooling, 4.5 g of polymer precipitated.

Analysis: F, 27.12%, inherent viscosity, 0.32

Evaporation of the petroleum ether gave 8.5 g of polymer

Analysis: F, 26.76%, inherent viscosity, 0.27

Reaction of Hexafluoroacetone and Linear Polyethylene

A mixture of 200 ml of dry benzene, 35 g of hexafluoroacetone, 0.2 g of di-*t*-butyl peroxide, and 20 g of linear polyethylene was heated at 135°C for 8 hr in a stainless-steel shaker tube. The dried polymer weighed 33 g. A sample was further purified by dissolving in hot benzene, in which the polymer is extremely soluble, filtering while hot, cooling to reprecipitate the polymer, and filtering. The polymer contained 30.67% F and had the properties given in Table 1.

TABLE 1

Physical Changes in Polyethylene Grafted with Hexafluoroacetone

Property	Value for original linear polyethylene	Value after grafted with hexafluoroacetone
Appearance	Hard, rigid, hazy	Soft, flexible, clear
Density, g/ml	0.95	1.21
Tensile impact strength, kg-cm/mil	1.5	2.3
Tensile strength, psi	3,000	3,100
Modulus, psi	150,000	39,000
Elongation, %	900	385
Dyeable	No	Yes
Adhesion	Fair	Good
Stick temp., °C	133	126

Terpolymerization of Sulfur Dioxide, Butene-2, and Hexafluoroacetone

A mixture consisting of 28 g (0.5 mole) of butene-2, 41 g (0.6 mole) of sulfur dioxide, 33 g (0.2 mole) of hexafluoroacetone, and 1 ml of saturated solution of silver nitrate in ethyl alcohol was placed in a silver-lined tube and kept at 34–38°C for 16 hr. After washing with water and drying, there resulted 45 g of a white solid polymer which contained 2.11% fluorine.

Reaction of Hexafluoroacetone and Vinyl Acetate

A three-necked 500-ml flask, fitted with magnetic stirrer, condenser, thermometer, and gas inlet tube, was charged with 200 ml of benzene, 86 g (1 mole) of purified vinyl acetate, and 0.2 g of $[(CH_3)_2C(CN)N{=}]_2$. A slow stream of N_2 was bubbled through the solution as it was heated to 60°C, then the nitrogen was replaced with hexafluoroacetone gas at a rate of 2 ml/min. At the end of 3½ hr, the reaction mixture was cooled and the solvent was removed by vacuum evaporation. The polymer was extracted with hexane and dried at 100°C/0.2 mm (20 g).

Analysis: Found 9.04% F, equivalent to 13% of combined hexafluoroacetone

When hexafluoroacetone (0.2 mole) and vinyl acetate (0.5 mole) were sealed in a Pyrex polymer tube with the same catalyst (0.2 g) at 60°C for 5 hr, the resulting polymer (inherent viscosity 0.3) had 29.05% F, equivalent to 42.5% combined hexafluoroacetone.

Copolymerization of Hexafluoroacetone and Vinyl Fluoride

A chemically resistant pressure vessel was charged with 12.8 g (0.4 mole) of methanol, 0.23 g of 75% *t*-butyl peroxypivalate, and 67 g (0.4 mole) of hexafluoroacetone. The mixture was shaken and pressured at 45°C to 400 psi with vinyl fluoride equivalent to 54 g of the monomer. As indicated by pressure drop, the reaction occurred at 50–55°C over a period of 4.5 hr. The polymer was dried under vacuum at 60°C and weighed 42 g. From the dry ice/acetone trap used during the drying, 70 g of the methanol/hexafluoroacetone complex was recovered.

Analysis: Found, F, 43.05; inherent viscosity as a 0.24% solution in dimethylformamide at 130°C, 1.00

The polymer gave a 12% solution in hot dimethylformamide from which a colorless sparkling clear film was cast. The film was oriented 10 diameters in an oil bath at 120°C.

Copolymerization of Hexafluoroacetone and Tetrafluoroethylene

The polymerization system consisted of 87 g (0.525 mole) of hexafluoroacetone, 4.7 g (0.26 mole) of water, 5.3 g (0.053 mole) of tetrafluoroethylene, and 0.2 g of benzoyl peroxide. The mixture was heated at 60, 70, 80 and 90°C, each for 3 hr in a 240-ml Hastelloy C reactor. There resulted 3 g of white polymer that was extracted with hot toluene for 2 days. An infrared absorption spectrum as KBr pellet had bands at 10.3 μ and 10.45 μ in addition to those found for tetrafluoroethylene.

Further proof that a copolymer had been formed was uncovered in its X-ray powder pattern. The pattern indicated the product to be like polytetrafluoroethylene, with a lattice disorder along the chain direction. Interchain distance is approximately 3.5% greater than in polytetrafluoroethylene.* Pendant CF_3 groups resulting from the inclusion of hexafluoroacetone into the polymer chain would account for this distortion.

Preparation of High Molecular Weight Tetrafluoroethylene/Hexafluoroacetone Copolymer

A reactor free of all organic materials was charged with a solution of 0.06 g of $(NH_4)_2S_2O_8$ in 7.5 g (0.42 mole) of water. After cooling in an ice/water bath and evacuating, the reactor was charged slowly with 140 g (0.8 mole) of hexafluoroacetone and 12 g of tetrafluoroethylene. Polymerization occurred at 75°C. When the pressure dropped below 200 psi, 5 g more of the olefin was pressured in until 30 g was so added over a period of 6.5 hr. The product was washed with water and acetone and dried at 150°C/0.2 mm; weight, 39 g. Films were pressed at 375°C/800 psi to colorless, slightly hazy, tough, orientable films.

Photolytic Reaction of Hexafluoroacetone and Propylene

Propylene (8.4 g, 0.2 mole) and hexafluoroacetone (33.2 g, 0.2 mole) were irradiated 7 days. The liquid product (7.25 g) was distilled to yield a fraction (b.p. 74–95°C, 5.0 g) containing three prod-

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* We are indebted to Dr. J. F. Whitney of our laboratories for the X-ray data.

ucts. These materials were isolated by preparative G.L.C. One product was the previously identified 1,1,1-trifluoro-2-trifluoromethyl-2-hydroxy-4-pentene. The two additional products have been identified as 2,2-bis-trifluoromethyl-4-methyloxetane (V, major) and 2,2-bistrifluoromethyl-3-methyloxetane (VI, minor) on the basis of their proton and fluorine NMR spectra, their infrared spectra, and their analyses. The infrared spectrum of both materials shows no carbonyl absorption and only weak absorption at 2.9 μ attributed to hydroxylic impurities. The proton NMR spectrum of V (neat) has a six-line multiplet centered at 5.33τ, a broadened seven-line multiplet centered at 7.55τ, and a doublet centered at 8.90τ in the ratio 1:2:3 and attributed to the methinyl, methylene, and methyl hydrogens, respectively. The fluorine NMR spectrum (neat) shows two broadened, skewed quartets. The proton NMR spectrum of VI (mixed with the alkenol) shows an eight-line multiplet centered at 5.63τ, a multiplet centered at 6.65τ, and a doublet further split to quartets ($j = 1.3$ cps) centered at 8.97τ in the ratio 2:1:3 and attributed to the methylene, methinyl, and methyl hydrogens, respectively. The fluorine spectrum shows two quartets (separated by 340 cps) with the lower field quartet slightly broadened (instrument resolution was limited to about 2 cps).

Thus one isomer has a methyl group split into a doublet by its adjacent hydrogen and further split into a quartet by a trifluoromethyl group. The assignment of this splitting to the 1,2 rather than 1,3 isomer lies in the fact that in one isomer the methylene hydrogens are at lowest field, and in the other the methine hydrogen is at lowest field. Since an oxygen atom next to a C—H bond unshields the proton and the resonance occurs at a lower field than usual, it follows that V is the 1,3 isomer and VI is the 1,2 isomer. Further, the postulated mechanism (7) requires that the oxetane product be the isomer resulting from oxygen coupling to the most stable radical formed from the olefin.

Analysis: Calcd. for $C_6H_6F_6O$: C, 34.62; H, 2.91; F, 54.78
Found for V: C, 34.39; H, 3.08; F, 55.05
Found for VI: C, 34.55; H, 3.18; F, 55.08

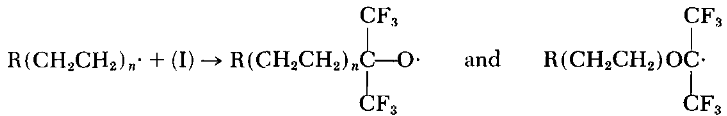
RESULTS AND DISCUSSION

Our results demonstrate the occurrence of several of the reactions possible in a free-radical system composed of, for example, ethylene and hexafluoroacetone. These reactions lead to products with complicated structures, the exact nature of which depends on the starting olefin. In the case of ethylene, free-radical polymerization occurs with the normal initiation (1) and propagation (2) steps.

(1) $R\cdot + CH_2{=}CH_2 \rightarrow R{-}CH_2CH_2\cdot$

(2) $RCH_2CH_2\cdot + (n-1)CH_2{=}CH_2 \rightarrow R(CH_2CH_2)_n\cdot$

Hexafluoroacetone (I) can react by radical attack at the oxygen or at the carbon of the carbonyl system in the manner known for other alkyl radicals (5):

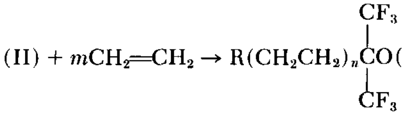


(3) $$R(CH_2CH_2)_n\cdot + (I) \rightarrow R(CH_2CH_2)_n\overset{CF_3}{\underset{CF_3}{C}}{-}O\cdot \quad \text{and} \quad R(CH_2CH_2)O\overset{CF_3}{\underset{CF_3}{C}}\cdot$$

(II) (III)

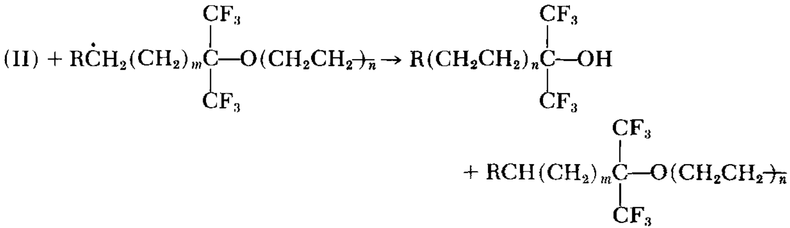
The chain might continue to propagate from either (II) or (III).

According to Walling (6), the *t*-butoxy radical should be electrophilic. The hexafluoroisopropoxy radical end group of (II) would be even more electrophilic in view of the electron-attracting nature of the six adjacent fluorine atoms. Hence (II) should react with the electron-rich ethylene but not with the electron-poor hexafluoroacetone:



(4) $$(II) + mCH_2{=}CH_2 \rightarrow R(CH_2CH_2)_n\overset{CF_3}{\underset{CF_3}{C}}O(CH_2CH_2)_m\cdot$$

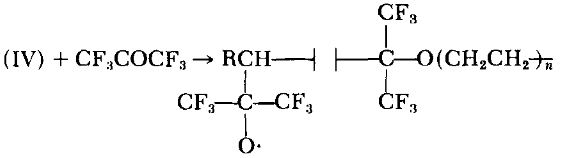
The tendency of the fluoroketone to react with olefins is not limited to simple copolymerization, since chain branching and chain transfer can occur by hydrogen abstraction, either intra- or intermolecularly:



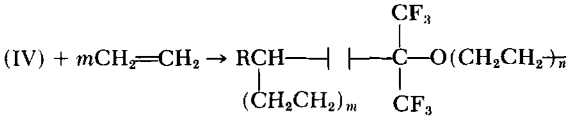
(5) $$(II) + R\dot{C}H_2(CH_2)_m\overset{CF_3}{\underset{CF_3}{C}}{-}O(CH_2CH_2)_{\overline{n}} \rightarrow R(CH_2CH_2)_n\overset{CF_3}{\underset{CF_3}{C}}{-}OH + RCH(CH_2)_m\overset{CF_3}{\underset{CF_3}{C}}{-}O(CH_2CH_2)_{\overline{n}}$$

(IV)

Intermediates such as (IV) react with more (I) [reaction (6)] or with ethylene [reaction (7)] to form a branch growing from the new radical site. Reactions (5) and (7) occur repeatedly.



(6) $$(\mathrm{IV}) + \mathrm{CF_3COCF_3} \rightarrow \underset{\substack{| \\ \mathrm{CF_3{-}C{-}CF_3} \\ | \\ \mathrm{O\cdot}}}{\mathrm{RCH}}{-}\!\!\dashv\ \vdash\!\!{-}\underset{\substack{| \\ \mathrm{CF_3}}}{\overset{\substack{\mathrm{CF_3} \\ |}}{\mathrm{C}}}{-}\mathrm{O(CH_2CH_2)}_n$$

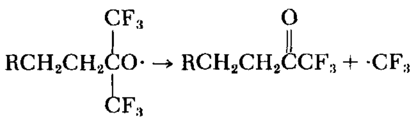


(7) $$(\mathrm{IV}) + m\mathrm{CH_2{=}CH_2} \rightarrow \underset{\substack{| \\ \mathrm{(CH_2CH_2)}_m}}{\mathrm{RCH}}{-}\!\!\dashv\ \vdash\!\!{-}\underset{\substack{| \\ \mathrm{CF_3}}}{\overset{\substack{\mathrm{CF_3} \\ |}}{\mathrm{C}}}{-}\mathrm{O(CH_2CH_2)}_n$$

creating in each polymer molecule chains terminated with mainly hexafluoroisopropyl alcohol groups.

The reaction of hexafluoroacetone and ethylene is easy to effect. For example, at 135°C and 500 atm of ethylene pressure with benzene as a solvent and *t*-butyl peroxide as radical source, low molecular weight oils and waxes containing as much as 53% fluorine are formed. The important features of their infrared spectra are the strong C—F bands (8–9 μ), OH group (unassociated, 2.78 μ; associated, 2.90), and a medium-intensity carbonyl band (5.83 μ), probably adjacent to a fluorocarbon group. The intensity of the hydroxyl band corresponds approximately to that of a C_{10} alcohol; for the carbonyl, that of a C_{20} ketone.

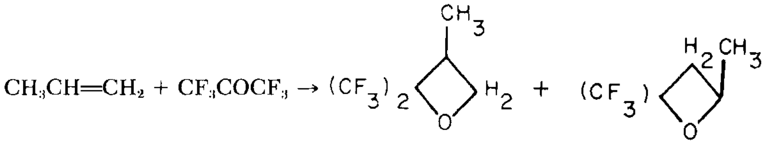
The results demonstrate that addition of the growing chain to the ketone is accompanied mainly by chain transfer [reaction (5)] and branching [reaction (6)]. An eighth reaction is proposed to account for the presence of the carbonyl group:



(8) $$\mathrm{RCH_2CH_2}\underset{\substack{| \\ \mathrm{CF_3}}}{\overset{\substack{\mathrm{CF_3} \\ |}}{\mathrm{C}}}\mathrm{O\cdot} \rightarrow \mathrm{RCH_2CH_2}\overset{\substack{\mathrm{O} \\ \|}}{\mathrm{C}}\mathrm{CF_3} + \cdot\mathrm{CF_3}$$

This reaction was also found with saturated substrates (5).

Another free-radical-induced reaction was found in photolysis experiments, where hexafluoroacetone and propylene undergo cyclization to oxetanes [(V) and (VI)] as well as yielding the linear addition product (VII):



(V) (VI)

$$+ CH_2{=}CHCH_2C(CF_3)_2OH$$
(VII)

The frequency with which reactions (3) and/or (6) occur is decreased by lowering the concentration of the fluoroketone. This can in principle be accomplished by carefully metering (I) into the pressure vessel during the polymerization, but the concentration of (I) is more easily controlled by the addition of water to the system.

Hexafluoroacetone forms addition complexes with water and other compounds (7). Although the hydrate is stable, it exhibits some carbonyl absorption at 5.65 μ in its infrared spectrum at room temperature. Hence the reaction must be reversible:

$$\underset{(I)}{(CF_3)_2CO} + H_2O \rightleftharpoons \underset{(VIII)}{(CF_3)_2C(OH)_2}$$

Since heat is liberated during the formation of (VIII), the reaction should be reversed at higher temperatures, hence increasing the concentration of (I). The concentration can also be controlled by the amount of water or other protonated liquid present. Experiments were carried out using a large excess of hexafluoroacetone hydrates or alcoholates so that the relatively small amount of hexafluoroacetone reacting would not seriously affect concentration. The effectiveness of this system can be judged by examining the data in Table 2.

The first three experiments are striking evidence that the presence of water does limit the fluoroketone available for polymerization yet some ketone is available even when as much as 24 moles of water to 1 mole of the ketone is present. The fourth and fifth examples show the same effect when methanol is used in place of water.

Experimental evidence suggests that the products from the free-radical polymerization of ethylene in the presence of hexafluoro-

TABLE 2

Polymerization of Hexafluoroacetone with Ethylene (500 atm)

*n*ROH Complexed with 1 mole HFA	Polymerization temp., °C	Polymer composition	
		% F	Inherent viscosity
None	135[a]	53	Grease and wax
$6.5H_2O$	135	4.75	0.85
$24H_2O$	135	2.47	
$1CH_3OH$	55[b]	28.71	
$1.5CH_3OH$	55	3.02	
$1.6H_2O$	80[c]	15.17	0.90
$1.6H_2O$		27.21	0.32

[a] *t*-Butyl peroxide initiator.
[b] *t*-Butyl peroxypivalate initiator.
[c] Benzoyl peroxide initiator.

acetone have the structures resulting from a combination of reactions (1), (2), (3), (5), (6), (7), and (8). The molecular weight and fluorine content of one product prepared by using the hydrate technique matched closely those of a polyethylene grafted with hexafluoroacetone using a free-radical initiator. The outstanding property of the copolymer was its solubility in cold benzene, whereas the grafted material was completely insoluble. Highly branched structures are in general more soluble than straight-chain isomers, substantiating the branched structure predicted by the proposed reactions.

Spectroscopic differences between grafted and copolymerized products also support this conclusion. The infrared absorption bands at 6.82 μ and 7.33 μ due to the $—CH_2—$ and CH groups, respectively, give some indication of polymer chain branching. In the copolymer, the 6.82-μ (CH_2) band is more intense than the 7.33-μ (CH) band, whereas in the grafted product the relative intensities of these bands are reversed. In grafting, every fluoroketone entering the polymer creates a tertiary hydrogen group. Hence not all the fluoroketone in the copolymer is as pendant hexafluoroisopropyl groups, but rather some are in the chain [reaction (4)] and as terminal fluoroalcohols [reaction (5)]. The infrared spectra of polyethylenes grafted with hexafluoroacetone have sharper bands than do those of the copolymers. The sharpness of bands is related to the orderliness of structure and the copolymer is pictured as a complicated mixture of highly branched polymer chains, whereas the grafted material has an orderly backbone with fluoroketone units attached randomly.*

All polymers prepared with ethylene and various fluoroketones had a carbonyl band at about 5.8 μ as well as the associated and unassociated hydroxyl bands. In contrast, vinyl fluoride and hexafluoroacetone copolymers containing as much as 28% combined ketone had no significant carbonyl group according to infrared analysis, but they did possess an unassociated hydroxyl group, as made evident by a single sharp intense band at 2.82 μ. The associated hydroxyl in the ethylene copolymers could be due to interaction between carbonyl groups and not simply between hydroxyl groups. That this is so was indicated by preparing a homogeneous mixture of vinyl fluoride/10% hexafluoroacetone copolymer and polymethyl methacrylate and measuring its infrared absorption spectrum. The sharp 2.82-μ band shifted to 3.0 μ and became broad. This effect also supports assignment of the 5.8-μ band to carbonyl absorption.

The reaction of fluoroketones with unsaturates was tried with several typical monomers, and it was found that the electronic character of substituents present in the olefin was important in determining the extent of fluoroketone participation in the reaction. In general, monomers containing electron-donating groups gave polymers that were easily formed and were rich in fluorine. For example, simply bubbling hexafluoroacetone through a vinyl acetate polymerization gave a product containing 13% combined ketone. When the substituent was electron-attracting, such as a cyano or a carbomethoxy group, the degree of participation of the fluoroketone in free-radical polymerization was small but real. Although it is apparent that hexafluoroacetone shows preferences for the monomers with which it polymerizes, it was not possible to measure reactivity ratios with any monomer, because methods have not yet been devised to determine the amounts of fluoroketone in the chain and pendant on the chain (Table 3).

One of the more interesting polymers studied was that from vinyl fluoride. Poly(vinyl fluoride) is intractable, presumably because of its high crystallinity. However, even with so little combined hexa-

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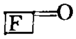
* We are indebted to Professor R. C. Lord for help in interpreting the infrared data.

TABLE 3

Copolymerization of Fluorocarbonyl Compounds with Unsaturates

Monomer	Fluoroketone	Catalyst system[a]	Product
Ethylene	HFA	Peroxides/55–185	Oils to solids
Ethylene	$ClCF_2COCF_2Cl$	t-Bu_2O_2/135	Grease 25.24% F
Ethylene		t-Bu_2O_2/135	Solid 7.02% F
Ethylene	$CF_3CF_2CF_2CHO$	t-Bu_2O_2/135	Soft solid 30.23% F
Ethylene	CF_3CHO	$(CH_3)_3CCO_3C(CH_3)_3$/55	Solid 8.31% F
Vinyl acetate	HFA	AZO[b]/60	Solid up to 40.37% F
Vinyl fluoride	HFA	$(CH_3)_3CO_3C(CH_3)_3$/55	Up to 25% HFA
Vinyl acetate	$(CF_3CF_2CF_2)CO$	AZO/60	18.01% F
Vinyl acetate	$H(CF_2)_4COC_2F_4H$	AZO/60	30.91% F

[a] Initiator temp., °C.

[b] Bisisobutyroazonitrile.

fluoroacetone that it could not be detected by infrared or fluorine analysis, the high molecular weight polymer isolated was quite soluble in dimethylformamide, dimethylsulfoxide, and dimethylacetamide at 120°C. An explanation of the extreme effectiveness of the hexafluoroacetone in moderating the polymer crystallinity lies in the fact that it not only can enter the polymer chain in two different fashions [Eq. (3) structures (II) and (III)] but also can graft onto the polymer chain.

Finally, the copolymerization of hexafluoroacetone and tetrafluoroethylene was studied. Here, reaction (5) would be impossible

TABLE 4

Copolymers of Hexafluoroacetone (HFA) and Tetrafluoroethylene (TFE)

Property	TFE/HFA copolymer	Poly TFE
T_g heating	−10°C	14°C
T_g cooling	8°C	19°C
T_m	312°C	327°C
TGA (5% wt. loss)	540°C	560°C
Melt flow (at 350°C)	0.5–1 g/10 min	No flow

and straight-chain copolymer structures should result. The structure of the resulting product was substantiated by infrared and X-ray analyses. The X-ray data were the most impressive because they indicated that the interchain distance of the copolymer was greater than in polytetrafluoroethylene. This is caused by the CF_3 groups from the combined HFA protruding and inhibiting close packing of the smaller diameter core of $—CF_2CF_2—$ groups in the polymer chain. The polymer had weak bands in the infrared at 9.77 μ and 10.30 μ, where polytetrafluoroethylene does not absorb.

Properties of the copolymer were different from high molecular weight polytetrafluoroethylene, the most noteworthy being its flow when melted. Comparable properties are given in Table 4.

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Zusammenfassung

Freie Radikale induzieren zwei Arten von Reaktionen zwischen Fluorketonen und Olefinen, die beide zu polymeren Produkten führen. Kopolymerisation der Fluorketone mittels ihrer Carbonylgruppe führt zu Polyäthern. Wasserstoffabstraktion, wahrscheinlich hauptsächlich intramolekular verlaufend, ergibt ebenfalls hochverzweigte Polymere mit Fluoralkoholgruppen als Endgruppen der Verzweigungen.

Résumé

Les radicaux libres provoquent deux types principaux d'interaction entre les fluorocétones et les oléfines qui fournissent des produits polymerisés. La copolymérisation de la fluorocétone par son groupe carbonyle produira des polyéthers. L'abstraction d'hydrogène qu'on assume être largement intamoleculaire, prend aussi place et donne des polymères très ramifiés, avec des groupes fluoroalcooliques aux positions terminales des chaines.

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