ANNUAL INTERIM REPORT

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National Aeronautics and Space Administration
Contract NSR-10-005-047

SYNTHESIS OF ELASTOMERS FOR USE WITH LIQUID FLUORINE

Henry C. Brown
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Submitted by
Department of Chemical Engineering
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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

PAGE

TABLE OF CONTENTS (Cont'd)

I. INTRODUCTION

The objective of this research is the synthesis of elastomeric polymers that will be resistant to the strong oxidizing effect of fluorine, oxygen difluoride, nitrogen tetroxide and similar agents. In addition,the desired material should be flexible at cryogenic temperatures.

During the present contract period the work on this project has been devoted principally in two areas: (a) to find suitable initiators for homo or copolymerization of hexafluorobutyne-2 under milder conditions; (b) synthesis of perfluoro mono- and diisocyantes from the corresponding hydroxamic acids, their purification and attempted synthesis of new monomers of general type $R_FCF=N-C\equiv N$ ($R_F=F,CF_3$, C_2F_5, etc.) from the monoisocyantes.

Previously it was known that hexafluorobutyne-2 could be homopolymerized in high yields to an insoluble, infusible polymer only under the influence of high dose rate γ-radiation at or above room temperature. The present work indicates that chlorine radicals, generated by ultraviolet radiation from chlorine, 2,3-dichlorohexafluorobutene, dichlorohexafluorocyclopentene or carbon tetrachloride can initiate polymerization and that the process is rapid and efficient. Acid fluorides of varying molecular weight, generated by keeping hexafluoropropylene epoxide in contact with finely divided activated carbon, under ultraviolet radiation are capable of initiating homopolymerization of hexafluorobutyne, the polymerization being quick and efficient. Hexafluoropropylene epoxide or hexafluoroacetone have a marked influence on homopolymerization of hexafluorobutyne-2 under γ-radiation, but under ultraviolet radiation, the effect is not pronounced.

Attempted copolymerization of hexafluorobutyne-2 with trifluoronitrosomethane in the presence of the above initiating agents failed. This indicates that trifluoronitrosomethane behaves as an inhibitor in such systems, as does trifluoromethyl iodide.

Attempts have been made to determine the limiting conditions for initiation of polymerization of hexafluorobutyne-2 in presence of 2,3-dichloro-1,1,1-4,4,4-hexafluoro-2-butene (initiator). From our experiments, it seems probably that hexafluorobutyne-2 is most susceptible to the attack of chlorine radicals. Photolysis of the dichloro-compound under a medium intensity ultraviolet lamp at or above room temperature has, to date, been found to be the most effective method of initiation for polymerization of hexafluorobutyne-2.

Attempted copolymerizations of hexafluorobutyne-2 with a number of possible comonomers have produced several types of polymers under different reaction conditions. The dichloro-compound has been used as initiator in most of the reactions. The rates of polymerization and yields in the presence of comonomers have almost always been found to be lower than those for homopolymerization of hexafluorobutyne-2.

Attempted copolymerization of perfluoronitrile and tetrafluoroethylene under ionic conditions has not been successful to date.

In accordance with the proposed scheme of synthesis, (Ref: NSR-10-005-047, Annual Interim Report, Sept. 1967), three isocyanates ($R_FN{=}C{=}0$ $F_F$being CF_3, C_2F_5 and C_3F_7) have been prepared through the corresponding hydroxamic acid route and the isocyanates have been thoroughly purified. However, reactions of the isocyanates with ammonia, the next step in the proposed synthesis, have resulted in the formation of a number of products; separation of the products in pure form has not yet been possible except for the C_3F_7NCO and ammonia reaction products, where one of the products has been isolated in pure form. We have also prepared perfluoroglutaro hydroxamic acid for synthesis of the corresponding diisocyanate.

Attempts have also been made to polymerize perfluorobutadiene with sulfur tetrafluoride in presence of cesium fluoride catalyst. To date, a high boiling liquid and some water insoluble solid have been found to be only products; neither has been properly characterized to date.

II DISCUSSION

A. Homopolymerization of Hexafluorobutyne-2

1. By Co^{60} γ-radiation

As regards polymerization capability, hexafluorobutyne may be considered to be a fairly inert monomer. Previously it was reported a sufficiently pure monomer could be almost completely polymerized only by many hours of Co^{60} γ-irradiation of high dose rate (10,000-25,000 r/min). Co^{60} γ-irradiation of lower dose rates (~2000 r/min) even for 85 hrs polymerized it only to the extent of 14%. Ultraviolet irradiation (100 or 550 W lamp, high pressure) seemed to have little or no effect at all on hexafluorobutyne-2 in a Vycor or Pyrex vessel, polymerization proceeding only to the extent of 4-10% for many hours of irradiation. A pure hexafluorobutyne-2 sample is characterized by its infrared peaks at 4.0-4.2μ, 4.65-4.85μ, 5.08μ and 6.3μ and no other peaks in the higher energy region; it has a very strong characteristic peak at 11.05μ.

2. By agents generating chlorine radicals

The impurities present in the crude hexafluorobutyne-2 have been found to have a profound influence on its polymerization capability. A crude monomer having an extra infrared peak at 5.8μ was found to undergo quick polymerization to the extent of 40-50% under ultraviolet radiation in a Vycor or Pyrex vessel;

the remaining gas did not show the 5.8μ peak. The polymer was a mixture of polyhexafluorobutyne-2 (as obtained by γ-irradiation) and some tetrahydrofuran-soluble gum showing an infrared peak at 5.8μ. The gas chromatographic analysis of such a crude monomer showed the presence of at least four higher boiling components (in trace amount) besides hexafluorobutyne-2. Attempts were made to collect these higher boiling impurities in sufficient amount, so that they could be analyzed and their initiating capability could be tested.

A supply of about 50 ml. of the residual material from the preparation of a large quantity of hexafluorobutyne was obtained and examined. This material showed the following infrared absorption maxima:

5.8μ(sharp), 5.95μ(hump), 6.2μ(sharp), 6.95μ(sharp), 7.45μ,
7.7μ, 7.85μ, 8.3-8.6μ(broad), 10.35μ, 10.75μ,

From previous examination, it was apparent that the impurity acting as initiator had infrared peaks somewhere between 5.6-6.2μ; peaks such as 5.95μ or 6.2μ were perhaps not detected in the crude monomer due to their presence in trace amounts. Hexafluorobutyne-2 could be polymerized to an extent of 60-65% in the presence of this material (Expt X-a) and some THF soluble gum was also obtained. Infrared spectra of the residual gas showed complete absence of the 5.8μ peak, while all other peaks were present. Gas chromatographic analysis of this material showed the presence of at least five major componants, one having a much higher retention time than the other four.

Fractional distillation of this residual liquid was attempted and three major functions were collected -

a. Fraction (low boiling) collected in dry ice cooled trap

b. Fraction having boiling point 32.5°-34°C.

c. Fraction having boiling point 67-69°C

Other characterizations were as follows:

Fraction (a) Mol. wt. of the first fraction volatizing in the vacuum system, 162

I.R. peaks: 5.8μ (strong), 7.45-8.9μ (C-F), 10.8μ (strong), 11.05μ (small)

This fraction was assumed to be mainly CF_3-CH=CH-CF_3 with a little CF_3-C≡C-CF_3. The complete fraction, however, showed the presence of a 5.95μ peak also and average mol. wt. was 168. A peak for C-H (3.4μ) stretching was surprisingly absent.

Fraction (b) Mol. wt. 176-178

I.R. peaks: 5.95μ (strong), 5.8μ (present), 6.95μ (very strong), 7.3-9μ (C-F), 10.3μ, 11.5μ, etc.

It was assumed to be a mixture of CF_3-CH=CH-CF_3 (small) and mainly $CF_3CH=CClCF_3$ (I.R. peak at 5.95μ). Complete separation of these two components may be difficult due to their close boiling point.

Fraction (c) Mol. wt. 235 (average)

I.R. peaks: 6.2μ (very sharp), 7.5-8.8μ (C-F), 10.6-10.9μ (broad), 11.8μ.

This was assumed to be mainly $CF_3-CCl=CCl-CF_3$. None of the fractions were chromatographically pure. Fraction (c) showed two almost equal peaks in its major fraction and may be a mixture of cis and trans isomers.

On examining the initiating capability of each of the fractions, only fraction (c) was found to have this capability under ultraviolet radiation (THF soluble gum) but could not initiate it by itself. The high initiating efficiency of fraction (c) also indicates that limited polymerization of pure hexafluorobutyne-2 under ultraviolet or low dose rate γ-radiation might be due to the presence of trace amount of the dichloro compound as an impurity in the monomer.

Fraction (c) was passed through the "Autoprep" chromatograph for isolation of the major fraction (about 80% of the input) and about 1 ml of the chromatographically pure material was thus collected and the following analysis results were obtained.

Infrared peaks: 6.2µ(very strong)

(only peak below 7µ)

Elemental analysis:	Reported	[Calculated for $CF_3CCl=CCl-CF_3$]
%F	49.02	48.95
%Cl	30.72	30.44
%C	20.33	20.60
%H	0	0

Comparison of these results with those reported by Henne et al [J.A.C.S.,67 (1906)1945] indicate it to be a cis-trans mixture of $CF_3-CCl=CCl-CF_3$. It could polymerize $CF_3-C\equiv C-CF_3$ to an extent of about 50% within 30 minutes under ultra violet radiation, its concentration in the system being only 5%. (Expt X-8).

Synthesis of this dichloro compound was carried out by limited dehalogenation of 2,2,3,3-tetrachlorohexafluorobutene by zinc in refluxing dioxane medium. Using about 1:1 molar ratio of zinc and tetrachloro compound and allowing the least possible time for refluxing, about 40% of the theoretical quantity of dichloro compound was obtained as a pure fraction (mixture of cis and trans), as indicated by b.p. (68-69°C),infrared spectra, mol. wt. (230-235)etc.

The polymer obtained by initiation with this dichloro compound appeared to be the same previously prepared polyhexafluorobutyne-2 (as obtained by γ-radiation) and very little of the dichloro compound was consumed in the process. The obvious mechanism appeared to be generation of chlorine radicals by photolysis of the dichloro compound.

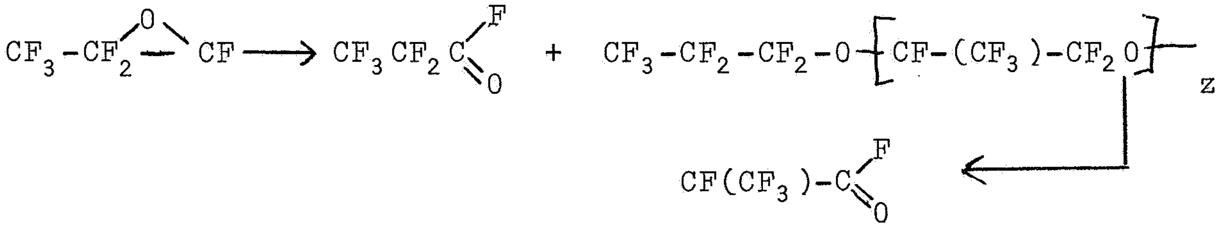
The rate of photolysis of the cis and trans components might be different but no attempts have yet been made to determine this. Other supporting evidences in favor of initiation by chlorine radical come from the runs with chlorine gas (Expt X-17), carbon tetrachloride (Expt X-15) or hexafluorobutyne-2 under ultraviolet radiation. Perfluorobutene-2 (CF_3-CF=CF-CF_3) could not initiate the polymerization under identical conditions, probably due to the greater C-F bond strength. The polymers produced in all experiments resembled that of polyhexafluorobutyne-2 (white powder) in infrared spectra and thermal resistance (shows no apparent change on heating up to 300°C). The radical nature of initiation in all these cases (including Co^{60} γ-radiation) was also presumed from the fact that initiation never did occur in the presence of trifluoronitrosomethane of trifluoromethyl iodide. Failure of both $CF_3CCl=CClCF_3$ and $CF_3CF=CFCF_3$ to undergo polymerization may perhaps be attributed to their structure (symmetry and stability).

3. By hexafluoropropylene epoxide or hexafluoro acetone

Hexafluoropropylene epoxide and hexafluorobutyne-2, when exposed to low dose rate Co^{60} γ-radiation for a long time under high pressure, lead to almost complete polymerization of of hexafluorobutyne-2 as indicated by absence of HFB-2 in the infrared spectra of residual gas. It appeared from a material balance that little or no epoxide was polymerized; polymer resembled that of polyhexafluorobutyne-2 in infrared spectra (Exp. A-127). Similar results were obtained using hexafluoroacetone. The initiating efficiency of the epoxide was also tested under ultraviolet radiation but this resulted in only about 15% polymerization of perfluorobutyne-2 (Expt X-f). The exact mechanism of initiation is not known; it is assumed that it is of free radical nature from the fact that no such initiation occurs in presence of trifluoronitrosomethane (Expt X-h).

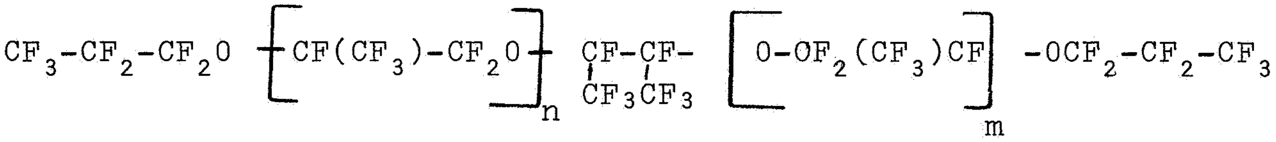
4. By acid fluorides derived from hexafluoropropylene epoxide

Hexafluoropropylene epoxide, when kept in contact with Darco activated carbon, undergoes isomerization and the products are acid fluorides of varying molecular weight with ether linkages in the chain (DuPont, U.S.P.3,214,478).



(z being 0, 1,2...etc.)

The monomeric and dimeric forms in the product are volatile enough to be transferred in a vacuum system while higher isomers are high boiling (oil, wax, etc.) These acid fluorides, when exposed to ultraviolet radiation, for a long time, show a disappearance of the carbonyl group and a corresponding increase in molecular weight by coupling



$$\mathrm{CF_3{-}CF_2{-}CF_2O\left[CF(CF_3){-}CF_2O\right]_n\ \underset{CF_3}{CF}{-}\underset{CF_3}{CF}{-}\ \left[O{-}OF_2(CF_3)CF\right]_m\ {-}OCF_2{-}CF_2{-}CF_3}$$

If this process proceeds through a free radical mechanism (exact mechanism is not known), then free radicals with ether linkages would be generated from all the acid fluorides except the monomeric one. If these radicals can be introduced in a polymeric chain as end-groups (through initiation or terminations) interesting properties may develop; perfluoroolefin epoxide polyethers formed by coupling of two radicals might be difficult to remove from such a system, however, and hydrolysis of any unchanged absorbed acid fluoride to acid is another possibility.

The above mentioned acid fluorides were prepared in the laboratory and conversion was almost complete. The products showed only one infrared peak at 5.25μ in the high energy region and there was no trace of the epoxide left. The monomeric and dimeric acid fluorides (as determined by mol. wt. determination and gas chromatography) were removed in the vacuum system at room temperature. Both of them were found to be quite efficient in initiating polymerization of hexafluorobutyne-2 under ultraviolet radiation, even when present in very small concentrations (less than 10%) (Expt X-1,12) and the percentage polymerization was generally more than 80%. The polymer (white powder) was found to be typically polyhexafluorobutyne-2 with a little adsorbed acid fluoride (infrared peak at 5.35μ). The higher molecular weight acid fluorides have not yet been tested for their initiating efficiency.

5. By Chlorodifluoroacetonitrile ($ClCF_2CN$)

Chlorodifluoronitrile gas, when mixed with hexafluorobutyne-2 in the ratio of 1:1 or 1:5 and irradiated under ultraviolet lamp (140W) in a quartz vessel at room temperature, could bring about homopolymerization of HFB-2 to certain extent, but the nitrile itself was recovered almost fully and no copolymer was formed. The initiation probably occurred by generation of chlorine radicals in the system during u.v. radiation of the nitrile (Expt 42, Table I).

6. Conclusion

From above-mentioned results, it seems that as the monomer $CF_3-C\equiv C-CF_3$ is quite inert, the radical derived from it is perhaps very reactive. Once it is formed, it perhaps goes all the way forming highly branched or cross-linked polymer, irrespective of nature and concentration of other initiating radicals present in the system, and thus the same type of product is formed under different initiating conditions. That all the above mentioned initiators fail to initiate polymerization of hexafluorobutyne-2 in presence of CF_3NO or (CF_3I) may perhaps be explained in terms of the stable free radical characteristics of CF_3NO, resulting in immediate scavenging of any initiating radicals generated in the system. The absence of any peak in higher energy region of the infrared spectra is another feature of polyhexafluorobutyne-2. It is difficult to rule out the possibility of presence of C=C bonds in the polymer, since it is doubtful whether such a bond will be detectable by infrared analysis. Such a bond in tetrafluoroethylene is difficult to detect by infrared, even a high pressure (100 mm) probably due to symmetry in structure; however, the presence of such a bond in a copolymer of C_2F_4 and $CF_3-C\equiv C-CF_3$ may show up in the spectra.

B. Some Studies on the Initiation Mechanism of 2,3-Dichloro-1,1,1,4,4,4-hexafluoro-2-butene.

1. Ultraviolet absorption spectra of 2:3 dichloro-1,1,1,4,4,4-hexafluoro-2-butene (initiator).

The ultraviolet absorption spectra of the gaseous dichloro compound indicates that it begins to absorb rather sharply at about 260 mμ respectively. The extinction coefficient could not be calculated as the sample was taken in arbitrary concentration in air. but the two absorption maxima were perhaps for the two isomers (cis, trans) present. Above 260 mμ, there is practically no absorption and this is the reason why the dichloro compound failed to initiate polymerization of hexafluorobutyne-2 in a Pyrex vessel under ultraviolet radiation (Expt X-0,Table I). It is apparent that in order to photolyze the dichloro compound (for chlorine radical generation), the ultraviolet radiation must come through either a quartz or a Vycor wall.

2. Effect of ultraviolet radiation intensity on photolysis of 2,3,-dichloro-1,1,1-4,4,4-hexafluoro-2-butene.

The dichloro compound, on exposure to ultraviolet radiation in the gas or gas-liquid phase, undergoes photolysis; the rate of photolysis varies directly with the radiation intensity (Expts X-M, N, P & 38, Table II). Radiation of the gaseous compound in the absence of another monomer in a quartz or Vycor vessel has been found to form colored, higher boiling reaction products (collected as liquid), part of which was volatile under vacuum (colorless) and rest was mostly soluble in tetrahydrofuran. The primary photolysis step is evidently the dissociation of the C-Cl bond with corresponding generation of chlorine radicals. In the presence of a suitable substrate, such as hexafluorobutyne-2, these radicals perhaps are mainly utilized for initiation of polymerization, thereby forming very little tetrahydrofuran-soluble product. In the absence of such substrate, the primary radicals may undergo a series of secondary reactions (including recombination) forming starting material, chlorine, hexafluorobutyne-2, or other higher molecular weight chlorinated products.

The intensity of ultraviolet radiation has been found to have some influence on rate of photolysis (measured in terms of amount of starting material present after radiation). Irradiation of gaseous compound from a 550 watt lamp placed in a water-cooled immersion quartz well in a Pyrex reaction vessel (most intense radiation condition so far applied) led to very quick photolysis and the residual gas showed complete absence of starting material within 3 hours (Expt. X-M). The colored liquid product formed, which could not be transferred under vacuum, was found to be completely soluble in tetrahydrofuran and showed a broad infrared band between 5.5-6.15μ. This quick rate of photolysis might be responsible for the low yield (and probably low molecular weight) of products formed during copolymerization reactions carried out under similar initiation conditions (Expt. X-22, Table V). Irradiation of the dichlorocompound in the gas or gas-liquid phase from ultraviolet lamps of intensities of 550 W, 140 W, and 30 W respectively, placed at a distance of about 4-6 inches from the reaction vessels (made of quartz or Vycor), resulted always in partial photolysis even after long hours (15-20 hrs) of irradiation, the extent being greater with the highest intensity lamp. The residual gas, volatile under vacuum always showed the presence of starting material (infrared peak at 6.2μ) and some other higher molecular weight reaction products having infrared peaks in the 5.8-6.1μ region. Presence of a little chlorine gas in the mixture is also a possibility. The remaining colored liquid product was soluble in tetrahydrofuran and showed a broad infrared band in 5.5-6.1μ region (Expts. X-N, P, 38).

As regards polymerization of hexafluorobutyne-2 in the presence of the dichloro compound as an initiator, (8-16 mole%), the process has been found to be most rapid with low yield (50% yield in 30 minutes) by irradiation from a 550 watt lamp (Expt. X-8, Table I);the process was slowest and almost complete in the case of irradiation from a 30 watt lamp (97% yield in 18 hours). With a 100 watt lamp extent of polymerization was about 75%. (Expt. X-C, Table I). From all considerations, a 100 or 140 watt lamp, either ordinary or immersion type, seems best suited for the purpose.

3. Effect of temperature on the dichloro-compound initiated process.

The homo- or copolymerization of hexafluorobutyne-2 in the presence of the dichloro compound as an initiator always proceeds in gas phase; the appearance of white clouds indicates initiation. In one experiment (Expt. X-22, 35, Tables V & I) the reactants were cooled to Dry-Ice temperature while being irradiated by a 550 watt lamp through quartz well. Some polymerization was observed at the warner part of the reactor but none at the cold part. Profuse polymerization started on all parts of the vessel only when the reactants were heated to about 10°C (Expt. X-22, Table V). It seems that either photolysis of the dichloro compound takes place only in the gas phase or the activation energy of the polymerization reaction is not low enough for it to be carried out at low temperature.

4. Attempted initiation by the dichloro-compound in the presence of Co^{60} γ-radiation.

Attempted copolymerization of hexafluorobutyne-2 in the presence of tetrafluoroethylene (Expt X-QI,Table V) and tetrafluoroethylene and hexafluorobutadiene (Expt. X-QII Table V) using the dichlorocompound as an initiator in the presence of Co^{60} γ-radiation (about 2000 r/minute) failed to give encouraging results. Even after 6 days of irradiation, there was only partial polymerization in X-QI and little or no polymerization in X-QII. Similar experiments carried out under ultraviolet radiation produced about 50% polymerization within a few hours (Expt X-32, Table V). Partial polymerization in X-QI might be due to the radiation itself while little or no polymerization in X-QII might be due to mutual inhibition of the radicals generated by radiation from the three monomers.

C. Effectiveness of Chlorine Gas as an Initiator in the presence of Ultraviolet Radiation.

Homopolymerization of hexafluorobutyne-2 can be effectively initiated by ultraviolet irradiation of chlorine gas, present in the system to an extent of about 10% (Expt X-17, Table III),about 75% of the monomer is rather quickly polymerized in the process, the product being typical polyhexafluorobutyne-2. Some dichlorocompound, $CF_3CCl{=}CClCF_3$ has been detected in the residual gas. Tetrafluoroethylene can also be polymerized to some extent under similar conditions, but it should be mentioned that tetrafluoroethylene can be polymerized almost completely by ultraviolet radiation alone. Analysis of the residual gas indicates the presence of reaction products of C_2F_4 and chlorine gas (Expt X-21, Table III).

Chlorine gas is not an efficient initiator in copolymerizing a 1:1 molar mixture of hexafluorobutyne-2 and tetrafluoroethylene. While large amount of chlorine gas (about 30-35% of monomer mixture) could induce about 30% polymerization (Expt X-19, Table III), there was almost no polymerization with 3% chlorine gas (Expt X-20, Table III). The inefficiency may perhaps be attributed towards a rather fast reaction of chlorine with the monomers (particularly C_2F_4) and a rather slow copolymerization rate (probably due to mutual inhibition). It may be concluded that chlorine gas is a quite efficient initiator for homopolymerization of hexafluorobutyne-2 (its reaction product with the monomer being a quite effective initiator for the system); however, for initiation of copolymerization of hexafluorobutyne-2 and tetrafluoroethylene, it is rather inefficient.

D. Initiator Selectivity of Hexafluorobutyne-2.

Though hexafluorobutyne-2 is susceptible to free radical initiation of polymerization, it shows some selectivity towards initiating radicals. To date (a) Co^{60} γ-radiation of high dose rate; (b) chlorine radicals generated by ultraviolet radiation of suitable agents and (c) radicals generated by ultraviolet radiation of acid fluorides derived from hexafluoropropylene epoxide (Table I) have been found to be effective initiators. Conventional free radical initiators such as persulfate, benzoyl peroxide, etc. failed to initiate such polymerization .

Di-tert.-butylperoxide in the gas phase at about 130°C for 65 hours, conditions which polymerized hexafluorobutadiene, (Polymer Preprints 9 (1), 697 (1968)) did not initiate polymerization (Expt X-39, Table I). Trifluoromethyl iodide under ultraviolet irradiation in a quartz vessel not only failed to initiate such polymerization but also inhibited the initiation in presence of the dichloro compound; perhaps the iodine radical generated by photolysis acted as an inhibitor (Expt. X-40, Table IV). The results were similar to those obtained with trifluoronitrosomethane (CF_3NO) where, most probably the NO radical was an effective inhibitor.

All attempts to copolymerize CF_3NO and $CF_3-C\equiv C-CF_3$ to date failed. All the initiating systems described in (A) have been tried, but with no success (Expt X-c,h,16, Table IV). Perfluorobutyne-2 was recovered unchanged after each experiment and CF_3NO was slowly converted to dimers, etc. during ultraviolet or γ-radiation. Only on one occasion, a laboratory-made perfluorobutyne-2 sample was found to react with CF_3NO with about 70-80% conversion, the product being very viscous, colored liquid with strong smell. The monomer on analysis was found to have average mol. wt. of 94 and by G.C. analysis, at least five components were found to be present, one being perfluorobutyne-2. From infrared analysis, it appeared that the butyne-2 did not react and the product was due to reaction of CF_3NO with some other components which have not been characterized.

E. Attempted Copolymerization of Hexafluorobutyne-2.

1. With tetrafluoroethylene:

Attempts have been made to copolymerize hexafluorobutyne-2 and tetrafluoroethylene in the presence of four types of initiators: (a) Co^{60} γ-radiation and (b) ultraviolet radiation of chlorine gas, 2,3-dichloro-1,1,1-4,4,4-hexafluoro-2-butene or acid fluorides derived from hexafluoropropylene epoxide. For (a) the product was always a white powder, (Annual Interim Report, 1967) but in the case of (b), the product was a white sticky solid to semisolid mass depending on the conditions of the experiment (Expt. X-2-5, 11, 14, 19,20, 22, 23, 24, 36, Tables III, V and VI). It may be mentioned that homopolymerization of either hexafluorobutyne-2 or tetrafluoroethylene under identical conditions produce only white powder-like polymer (Expts X-1,8 (Table I); 17,21 (Table III) and 37 (Table V)) and that tetrafluoroethylene undergoes almost complete polymerization under ultraviolet radiation for many hours in a quartz flask. Thus, even if copolymerization does take place, the product may contain some homopolymer of tetrafluoroethylene. In all the copolymerization attempts so far made, the subsequent analysis indicated consumption of both the monomers during polymerization, but the product might be a mixture of homopolymers of the two monomers or might contain some copolymer also.

Attempted copolymerization under γ-radiation (both low and high dose rate) resulted in white powdered polymer, which appeared to undergo some type of surface softening in between 200-300°C in a melting point tube. Infrared spectra when compared with that of polyhexafluorobutyne-2 (obtained by γ-radiation) showed a noticeable hump at 5.7-6.1μ region (C=C) and the sample could be molded to an almost transparent disc (100-200°C above 4200 lbs./#2 press) which was brittle. The lack of strength of molded material might be due to presence of homopolymers in the mixture (Annual Interim Report, 1967, Expt 17 & 18, Table II).

Attempted polymerization under ultraviolet radiation in presence of photolytic agents such as $CF_3-CCl=CCl-CF_3$, or monomeric and/or dimeric acid fluorides from hexafluoropropylene epoxide (transferable in vacuum system at room temperature) did produce some interesting polymers. The nature of the products ranged from white sticky powders to waxy or semisolid masses; all of them turned to a molten mass of some fluidity from about 200°C, when heated in a m.p. tube and stirred with a fine wire. Further heating didn't bring about any further noticeable change except in case of one sample initiated with acid fluoride (Expt X-4) which turned to almost liquid at about 200°C. The extent of polymerization in all these cases ranged from 70-90%, based on fluoro-olefins used and polymerization was rapid with quick initiation at room temperature. Polytetrafluoroethylene or polyhexafluorobutyne-2, prepared under similar conditions did not show any change up to 300°C, while being heated in m.p.

tubes with stirring by a fine wire and these polymers did not show any noticeable peak or hump at the 5.6-1.1μ region of the infrared spectra. It may therefore be assumed that at least some amount of copolymerization had taken place. Attempted molding of two samples at above 4200 lbs/#2 press and 100-200°C temperature did result in flowing of the material out of the mold and exact conditions of molding have not yet been determined.

The infrared spectra of copolymer samples initiated with 2:3 dichloro hexfluorobutene showed a small, broad hump in the 5.6-6.2μ region in most of the cases and the residual gas consisted of all the three components (Expts X-3, 5, 22, etc , Table V).

The infrared absorption at 5.6-6.2μ was not due to the presence of initiator as it was present even after subjecing the sample to high temperature heating (≈ 200°C and/or vacuum.)

In case of acid fluoride induced initiation (Expts X-2,4,11,14; Table VI) the polymer showed infrared absorption peaks at 5.35μ, 5.6μ and a hump ranging from 5.6-6.2μ. The acid fluoride used as initiator had only one sharp infrared peak at 5.25μ in this region, but these acid fluorides are succeptible to hydrolysis; they fume in air and higher boiling acid fluorides, when kept in air, slowly and gradually turned to acids as shown by gradual disappearance of the 5.25μ peak and appearance of a new peak at 5.6μ. The acid, however, has no initiating power. The infrared peaks at 5.35μ and 5.6μ in the copolymer might be explained in terms of adsorption of relatively higher boiling fractions of acid fluoride in a tacky polymer matrix (it could not be removed, however, in vacuum system) and the subsequent hydrolysis. Complete removal of these adsorbed materials was not possible by repeated washing with acetone or tetrahydrofuran or even by heating up to 200°C. A small part of the product was found to be soluble in tetrahydrofuran giving a gum, having almost the same spectra as that of the original product. The residual gas was found to consist of all the three initial components. The melting behavior of these polymers may perhaps be due to the presence of ether linkages at the end or due to presence of some perfluoro-olefin epoxide polyethers (produced in the system as by-products by ultraviolet radiation of acid fluorides) as plasticizers. The problem of adsorption and hydrolysis of acid fluoride is not prominent in case of homopolymerization of hexafluorobutyne-2 or tetrafluoroethylene, as the polymer produced is a loose white powder. However, it is believed that on right selection of experimental conditions, useful copolymers may be produced with these initiators. Further work is in progress.

In regards to solubility, the copolyers had three distinct components. The first, (a), was a small amount of viscous liquid or semisolid mass soluble in tetrahydrofuran. It has been considered as either a photolysis product of the dichloro-compound (Sec. B-2) or its copolymer with tetrafluoroethylene and in some cases, it was about 50-80% by weight of the dichloro compound used. It showed prominent infrared peaks in the 5.6-6.1μ region. The second, major portion of the residual mass, (b), (up to 80%) was soluble in hexafluorobenzene (C_6F_6). The soluble part was a sticky solid to semisolid and showed infrared peaks in the 5.6-6.2μ region in most of the cases by much less prominent than that in (a). This portion (b) might be the copolymer but the infrared peak is not completely definitive as the tetrahydrofuran might not have extracted all the soluble portion (a) from the sticky product. Molecular weight determination of one of such fractions from Expt.36, Table V, in a vapor phase osmometer (VPO) using hexafluorobenzene (C_6F_6) as solvent, gave a molecular weight of only 1250 (approx), which also might be in error due to same reasons. The remainder of the product was a solid mass, insoluble in both tetrahydrofuran and hexafluorobenzene and having no infrared peak at 5.6-6.1μ region. This might be polyhexafluorobutyne-2. The polytetrafluoroethylene, initiated by the dichloro compound, also had these three components but the hexafluorobenzene soluble portion showed only a small peak in the 5.8μ region. (Expt X-37). Polyhexafluorobutyne-2, initiated by the dichloro compound, had only a negligible amount of soluble in tetrahydrofuran and hexafluorobenzene (Expt X-8). The solubility of other two products in hexafluorobenzene might be due to the presence of chlorine atoms in the chain.

2. With chlorotrifluoroethylene

Attempts have been made to copolymerize hexafluorobutyne-2 and chlorotrifluoethylene in different molar ratios, using the ultraviolet-irradiated dichloro compound as the initiator. With increasing molar ratios of chlorotrifluoroethylene, the product changed from a white solid to a very viscous semisolid and increasing amount of the product became soluble in tetrahydrofuran; the soluble portion was a light-colored semisolid for the lowest concentration of chlorotrifluoroethylene used and a viscous yellow liquid for the highest concentration used, (Expt. X-26, 28, 34; Table V). The tetrahydrofuran insoluble part was white (occasionally sticky) solid and both parts showed prominent infrared bands between 5.6-6.1μ. The rate of polymerization was quite slow and conversion was low. There was no initiation in the absence of the dichloro compound (Expt. X-28a, Table V). The residual gas always contained all three starting materials. On treating the product with hexafluorobenzene a major portion went into solution; separation gave a semisolid mass having infrared peaks at 5.6-6.1 (Expt. X-28); the hexafluorobenzene- insoluble part (wax-like solid) did not show absorption in this region. It is difficult at present to say which part is the copolymer of hexafluorobutyne-2 and chlorotrifluoroethylene; analysis will be obtained.

3. With hexafluorobutadiene

Attempted homopolymerization of hexafluorobutadiene in the presence of the dichloro compound under ultraviolet radiation (Expt. X-29, Table V) produced a very small amount of colored gum having strong infrared peaks at 5.55μ and 7.2μ and a hump at 5.7μ, (as reported for polyperfluorobutadiene, Polymer Preprint 9(1), 703(1968). The attempted copolymerization of hexafluorobutadiene with hexafluorobutyne-2 and terpolymerization with hexafluorobutyne-2 and tetrafluoroethylene under similar initiation condition produced a white solid and a viscouse semisolid, respectively. Both the products were partially soluble in tetrahydrofuran, allowing separation of a colored gum for the copolymer and a colored viscous liquid for the terpolymer. The insoluble portion was a white powder for the copolymer and sticky white solid for the terpolymer. All the components showed infrared bands in the 5.6-6.1μ region, with peaks at 5.6μ and 5.1μ and at 7.2μ. Both the rate and the yield were low (Expt. X-30, 32, Table V). The white powder did show some amount of surface melting above 250°C.

4. With perfluoroheptene-1

Attempted copolymerization in the presence of the dichloro-compound under ultraviolet radiation produced a white solid product having a small tetrahydrofuran-soluble portion (Expt. X-31, Table V). The infrared spectra of the white solid resembled that of polyhexafluorobutyne-2 and it showed almost no change on heating up to 300°C. The tetrahydrofuran soluble part (colored, visions semisolid) did show infrared peaks in 5.5-6.3μ region.

5. With hexafluoroacetone

Attempted copolymerization in presence of the dichloro compound produced a white powder (Expt. X-33, Table V) yield being about 40% of the monomers used. The product had a little tetrahydrofuran soluble fraction (viscous, colored semisolid) and residual white powder showed a peak at 6.1μ. At least a part of the polymer softened at a temperature above 250°C in an m.p. tube.

F. Attempted copolymerization of perfluorobutynitrile and tetrafluoroethylene.

Attempts were made to copolymerize the two monomers in the presence of cesium fluoride, n-butyl lithium and tributylantimony oxide. In all cases, monomers were taken in a pressure tube fitted with Teflon gasket, metal top and valve. Monomers were dried by passing through "Drierite".

1. Cesium fluoride, 0.5g, was dried under vacuum at about 220° for 2 hours in a pressure tube of 75 ml. capacity.Per-

fluorobutyronitrile, 3.26g, and tetrafluoroethylene, 1.80g, were condensed in the tube and kept in Dry-Ice for 65 hours. No apparent reaction took place; the reactor was warmed and let stand at room temperature. The gas mixture showed no change in pressure. Hexafluoroacetone, 1.86g, was injected in as a termonomer. Again keeping it in dry ice or room temperature did not show any apparent change. The tube was then heated in an oven to 109°C; no change was observed. The tube exploded at a higher temperature.

2. n-Butyl lithium (2m solution in hexane), 0.5 ml, was placed in a 75 ml pressure tube under nitrogen atmosphere. Perfluorobutyronitrile, 2.63g, and tetrafluoroethylene, 1.32g, were condensed in the tube. The tube was kept in Dry-Ice. Some white fumes were visible and the mixture turned dark; it was then warmed to room temperature and kept there for a few hours. The gaseous mixture was transferred in a vacuum system and condensed in a tube fitted with inlet and outlet tubes and a magnetic stirrer. The residue in the pressure tube was a dark colored gum.

n-Butyl lithium solution, 0.5 ml, was injected through a rubber septium in the condensed gas mixture with stirring. Again while fume was observed and some dark colored gum was formed. After washing out residual gas, total weight of gum was found to be 0.6-0.7 gm. The infrared spectrum of the gum showed peaks at 2.7μ, 2.95μ, 3.1μ, 3.35μ (strong), 5.95μ , 6.25μ, and 6.4μ, and average mol. wt. by VPO (in THF solution) was found to be about 600 (compared with benzophenone). A similar type of product was obtained by reacting this nitrile and n-butyllithium only and as such, it may be assumed that C_2F_4 did not react. Some type of trimerization of nitrile (not triazine) is a possibility.

3. Tributylantimony, 0.5 ml, when kept in contact with pure oxygen in a pressure tube at room temperature, ignited spontaneously, forming the white oxide. The products were evacuated under vacuum for a long time and C_3F_7CN (2.6g and C_2F_4(1.20g) were condensed in the tube. Some light colored, high boiling liquid formed in the tube as it was kept first at low temperature and then at room temperature. Mol. wt. of residual gas was 108 and almost all of C_2F_4 used was recovered. The somewhat viscous liquid (along with solid oxide) left has not been analyzed.

G. Attempted Polymerization of Perfluorobutadiene with Sulfur Tetrafluoride.

Sulfur tetrafluoride (SF_4)and trifluoromethyl sulfur trifluoride (CF_3SF_3) have been reported to form tetracoordinate sulfur (IV) fluorides on addition - to perfluoroalkanes in the presence of cesium fluoride as catalyst at about 150°C. Ref: R. M. Rosenberg & E. L. Muetterties, Inorg. Chem., 1, 756 (1968) The role of the cesium fluoride is ascribed to perfluoro carbanion formation and subsequent neucleophilic attack of SF_4. Ref: J. Amer. Chem. Soc., 82, 3091 (1960) . It therefore seemed possible that a perfluoroalkyldiene, such as perfluorobutadiene, might undergo polymerization under similar conditions.

$$CF_2{=}CF{-}CF{=}CF_2 \quad + \quad SF_4 \xrightarrow{C_sF} \left[CF_2{-}CF_2{-}CF_2{-}CF_2{-}SF_2 \right]_n$$

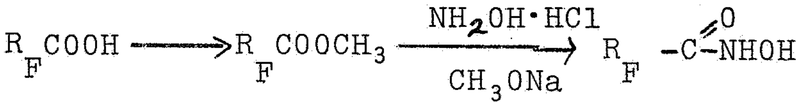
The grouping $-CF_2-SF_2-CF_2-$ has already been reported to be stable to hydrolysis, and if fluorinated, would probably be converted to even more stable hexavalent sulfur compound.

In the first attempted reaction, (Expt. A-262), the three components were taken in a pressure tube of 100 ml capacity ($CF_2{=}CF{-}CF{=}CF_2$: 1.30 g; SF_4 : 1.04 g; C_sF; dried by heating under vacuum; 1 g) and kept there under pressure (4-6 atmosphere) at elevated temperature ($\approx$130°C) for 3 days. The product was a higher boiling colorless liquid. The boiling point of the liquid product by micro capillary method was found to be 146-148°C. The infrared spectra of the liquid product showed only weak absorption at 6.0µ and no other peak at higher energy region, but it showed strong absorption in C-F region and several other sharp peaks at lower energy region. The product has not yet been characterized. The residual gas was mostly SF_4, as determined by molecular weight determination and spectra.

H. Synthesis of Perfluoroalkylisocyanates and Their Reaction with Ammonia.

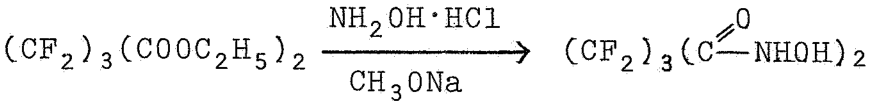
1. Perfluoroalkyl hydroxamic acids.

Four hydroxamic acids have been prepared from the corresponding esters; the method of synthesis can be schematically shown as:



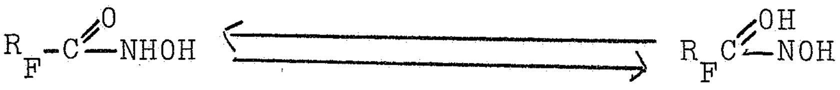
1

$(R_F = CF_3,\ C_2F_5$ and $C_3F_7)$



2

The hydroxamic acids can exist in two isomeric forms:

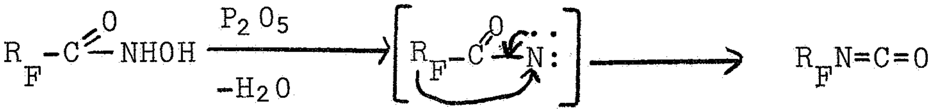


1a 1b

The infrared spectra of these compounds indicate that Structure 1a is predominant; however, the absence of a sharp melting point seems to indicate that both the forms might be present. The softening of the compound before melting might also be due to gradual breaking of hydrogen bonds with rise of temperature.

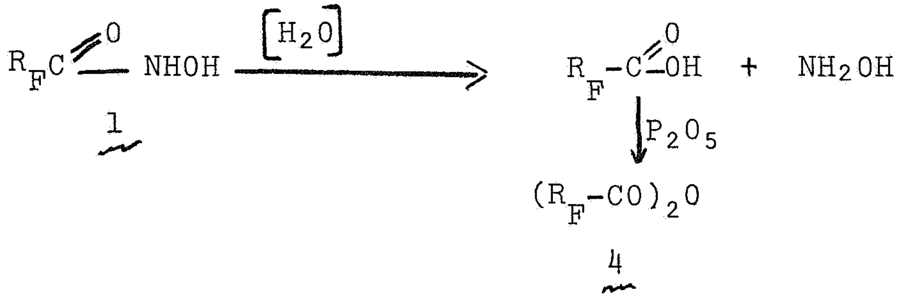
2. Perfluoroalkylisocyanates

By heating the perfluoroalkylhydroxamic acids with phosphorous pentoxide, a dehydration and subsequent rearrangement of the Loessen type occurred and perfluoroalkyl isocyanates were formed:



1 3

Analysis of the reaction products showed that production of the isocyanate was not the only reaction taking place. Some carbon dioxide was always found in the crude product, but this possibly might have come from the atmosphere. The higher boiling fractions, having strong infrared peaks at 5.3μ and 5.5-5.6μ have been characterized as anhydrides of corresponding perfluoro carboxylic acids. This can possibly be explained in terms of hydrolysis of some hydroxamic acid.



$$\underset{1}{R_FC(=O)NHOH} \xrightarrow{[H_2O]} R_F\text{-}C(=O)OH + NH_2OH \xrightarrow{P_2O_5} \underset{4}{(R_F\text{-}CO)_2O}$$

The infrared spectra of the product collected during attempted synthesis of $(CF_3)_7(NCO)_2$ did indicate the presence of some isocyanate (infrared peaks at 4.2-4.3μ and 6.75-6.9μ) with other materials. Further characterization was not possible as only a small quantity of sample was available.

3. Characterization of isocyanate-ammonia addition products.

Of the three addition products with three isocyanates, the addition product of CF_3NCO was quite different from the other two in solubility, melting characteristics, and infrared spectra. The formation of ammonium salts during the reaction (indicated by liberation of NH_3 from aqueous solution on addition of NaOH) and detection of fluoride ion in the water soluble portion of the C_3F_7NCO and NH_3 reaction product indicate possible liberation of HF from the primary reaction product and its subsequent reaction with NH_3.

$$\underset{\mathbf{5}}{C_3F_7NHCONH_2} \xrightarrow{-HF} \underset{\mathbf{6}}{CF_3CF_2CF{=}N{-}CONH_2} + HF$$

On reaction of NH_3 with **5**, a large number of reaction products can be formulated and the reaction may proceed as long as there is a kinetic pathway for liberation of HF. On analysis of the three reaction products, it appears that each of them is a mixture of components and probably each of them contains some amount of NH_4F. Further characterization is being tried.

III EXPERIMENTAL

A. Attempted Homo-, Co-, or Terpolymerization Experiments of Hexafluorobutyne-2.

All of the ultraviolet irradiated polymerization experiments have been carried out either in quartz or Vycor vessels, attached to the vacuum system through glass joints or in Pyrex reaction vessels having a water-cooled quartz well for insertion of the ultraviolet lamp. Ultraviolet lamps of intensities of 550 W, 140 W and 30 W have been used, lamps being placed at 3-6 inches from the surface of the reaction vessel for outside exposure. After the experiment, the vessel was degassed under vacuum, the residual gas was analyzed (mol. wt., infrared spectra, etc.) and the product was taken out for examination.

For Co^{60} γ-radiation initiation, the components were sealed in thick-walled Pyrex tubes and exposed (Expt. X-QI & II). For examining the initiation capabilility of di-tert-butyle peroxide, the components were placed in a pressure tube fitted with metal valve and heated. (Expt. X-39).

For attempted low temperature polymerization of hexafluorobutyne-2, a specially designed reaction vessel made of Pyrex, was used. The vessel had the water-cooled quartz well for insertion of ultraviolet lamp and a Dry-Ice-cooled side tube fitted through a standard taper joint for keeping the ingredients in liquid condition. The liquid received direct radiation from the lamp (Expt. X-35).

For taking the ultraviolet spectra of the dichloro-compound, a drop of it was placed in the quartz cell and reference was air. It was opened for dilution with air to obtain a suitable concentration in the gas phase.

B. Synthesis of Perfluoroalkylisocyanates and Their Reaction with Ammonia.

1. Preparation of perfluoroalkyl hydroxamic acids:

Hydroxamic acids, $R_F\overset{O}{\overset{/\!/}{C}}-NHOH$, R_F being CF_3, C_2F_5 or C_3F_7, were all prepared by mixing the corresponding methyl esters (R_FCOOH_3), hydroxylamine hydrochloride and sodium methoxide in equimolar proportions in dry methanol; yield of crude products was 80-90%. Purification was carried out by sublimation under vacuum at temperatures ranging from 40-60°C. The sublimates were hygroscopic and most probably all of them started decomposing above their melting points.

None of the perfluoroalkyl hydroxamic acids gave sharp melting points; each began to soften before the melting point was reached, and all were soluble in a range of organic solvents.

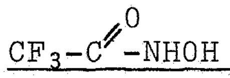
Perfluoroglutaro hydroxamic acid was prepared by the same method, using the ethyl ester, hydroxylamine hydrochloride and sodium methoxide in the molar ratio of 1:2:2 in dry methanol. The crude product was not hygroscopic and showed a melting range due to impurities. Attempted sublimation at 100-120°C under vacuum gave only viscous material as a sublimate. The best method of purification was extraction of the product by ether with subsequent heating of the extracted solid product under vacuum at about 100-100°C. The remaining solid was not hydroscopic and had a sharp melting point.

$(CF_2)_3(COOC_2H_5)_2$ -- 59.2 g (0.2 m)
$NH_2OH \cdot HCl$ -- 27.6 g (0.4 m)
CH_3ONa -- 21.6 g (0.4 m)
Methanol -- 500 ml

Products: NaCl - 18 g (Theor.:23.4 g)
Crude hydroxamic acid: 57 g (Theor.:54 g).

Ether extraction of the crude product at room temperature gave a yield of about 60%.

An attempt to synthesize the hydroxamic acid from the corresponding acid chloride, $(CF_2)_3(COCl)_2$, was not successful; much heat was generated during mixing and the product was a yellow, tacky solid (a mixture of products). Analyses of the perfluoroalkyl hydroxamic acids prepared gave the following results:

a.  $CF_3-\overset{O}{\overset{\|}{C}}-NHOH$ (Sample A-53)

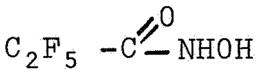
Sublimed under vacuum at 55°C; sublimate-white shining solid; m.p.: fairly sharp, 82-83°C.

Infra-red spectra:

3.12µ (strong doublet; N-H and O-H stretching),
3.28µ

3.4µ, 3.7µ (broad), 5.9µ (strong; C=O stretch),

6.4µ, 7.4µ, etc.



b. $C_2F_5-C(=O)-NHOH$ (Sample A-108)

Sublimed under vacuum at 50°C; sublimate-shining white solid; m.p.; softens at 64-66°C and gives a clear melt at 84-86°C.

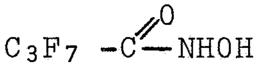
Infrared spectra:

3.15μ (doublet, strong), 3.48μ, 5.85μ (strong),
3.25μ

6.32μ, 6.9μ, 7.45μ, etc.

Elemental analysis:

Element	Theoretical, %	Found, %
C	20.00	20.52
H	1.12	1.25
N	7.8	7.55
F	53.1	53.92



C. $C_3F_7-C(=O)-NHOH$ (Sample A-46

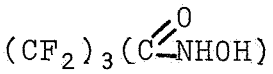
Sublimed under vacuum at 50-55°C; sublimate-shining white solid; m.p: softens from above 66°C, but gives a clear melt only at 96-98°C.

Infrared spectra:

A few peaks in between 3-4μ, the strongest one being at 3.1μ:
5.9μ (strong), 6.55μ, 6.8μ, 7.35μ, etc.

Elemental Analysis:

Element	Theoretical,%	Found, %
C	21.00	21.03
H	0.9	0.9
N	6.1	6.42
F	58.08	57.69



d. $(CF_2)_3(\overset{O}{\overset{/\!/}{C}}-NHOH)$ (Sample A-1161)

Ether extract heated under vacuum at 100-110°C; residue, -white solid; m.p.: 160-163°C. (Fairly sharp).

Infrared spectra:

3.5μ, 3.45μ, 5.9μ, 6.5μ, 6.8μ, 7.5μ, etc. (strong)

Elemental Analysis:

Element	Theoretical, %	Found, %
C	22.2	22.8
H	1.5	1.43
N	10.4	10.19
F	42.2	42.07

2. Preparation of perfluoroalkyl isocyanates:

a. Monoisocyanates:

Altogether three isocyanates, $R_F N=C=O$, have been prepared, R_F being CF_3, C_2F_5 and C_3F_7 respectively. In each case, purified hydroxamic acid was intimately mixed with three to four times its weight of dry phosphorous pentoxide in a glove bag under a flow of dry nitrogen gas. The mixture was placed in a round bottom flask of sufficient size to allow expansion on heating. The flask was fitted with a heating mantle, a glass column and two traps in series, the last one being cooled in a Dry-Ice-acetone bath and guarded from atmospheric moisture and carbon dioxide by soda-lime and Drierite guard tubes. Due to chemical reactivity of perfluoroalkyl isocyanates the connections in the above-mentioned apparatus were made of glass as far as possible and Kel-F grease was used in the joints. For C_2F_5 and C_3F_7 hydroxamic acids, the reaction mixture was slowly heated over several hours to about 180-220° when liquid began to collect in the cooled trap; the mixture was kept at or somewhat above 220° until no more product collected in the trap. Rapid heating always led to an almost explosive reaction with excessive heat generation. The reaction appears to be highly exothermic in nature. For CF_3 hydroxamic acid, the reaction went out of control in most of the cases due to excessive heat generation almost with the start of the reaction at a fairly low temperature (below 100°C). It seems better to use some inert material, such as sand, for dissipation of generated heat.

All the three isocyanates collected as yellowish liquids in the Dry-Ice-cooled trap and they were characterized by their infrared spectra and molecular weights.

[**Ref:** Barr and Hazeldine, J. Chem. Soc. (1956), 3428-for physical properties, not method of preparation]

Literature Values:

Isocyanate	B.P. °C/mmHg	M.W.(Theor)	Infrared Peaks γ_a	γ_s	(Barr & Haszeldine) Others
CF_3NCO	-36	111	4.33μ 4.40μ doublet (strong)	6.84 (strong)	7.50 (weak)
C_2F_5NCO	-9/742	161	-	-	-
C_3F_7NCO	24-26/739	211	4.37 (strong)	6.80 strong)	7.40

γ_a : Antisymmetrical absorption

γ_s : Symmetrical absorption

The overall yield of product collected was 60-80%. During transfer of the product in the vacuum system, it was noticed that the molecular weights of the initial fractions were much lower than expected value; the infrared spectra was the same as reported except for stronger γa peak intensity for C_2F_5NCO and C_3F_7NCO. For CF_3NCO, the infrared spectra always showed an extra peak of moderate intensity at 5.45μ. Evidently some low molecular product was present in the gas. In order to identify the impurity, the gas mixture was passed through a QF1 fluorosilicone (FS 1265) column at room temperature using helium as carrier gas in an 'Autoprep' gas chromatograph; the low molecular weight gas was identified as carbon dioxide (pure carbon dioxide was used as reference sample). The presence of carbon dioxide also explained the stronger γa peak intensity as it absorbs in the same region. The presence of CO_2 in the collected material could not be completely eliminated even after using a soda-lime guard tube. For separation of CO_2 from the mixture, the crude material was kept at a temperature low enough to produce a negligible vapor pressure for the isocyanate under vacuum, but at which the vapor pressure of carbon dioxide was high enough to allow it to be removed. Molecular weight and infrared spectra of the material was checked periodically to insure complete separation.

While transferring isocyanates in the vacuum system, it was noticed that while CF_3NCO could be easily and completely transferred at room temperature, there were colored, higher boiling, fractions left in the traps holding crude C_3F_5NCO and C_3F_7NCO. On examining the end factions of gaseous C_2F_5NCO and C_3F_7NCO coming out in vacuum system, it was noticed that they were of higher molecular weights and showed two extra infrared peaks at 5.3μ and 5.5-5.6μ respectively; these were ascribed to some higher boiling by-product formed during the reaction. In case of CF_3NCO, perhaps this by-product had a boiling point low enough to allow transfer in the vacuum system and the presence of an extra infrared peak at 5.45μ in the spectra was ascribed to its presence.

Separations of the higher boiling by-products from C_2F_5NCO and C_3F_7NCO were made by keeping the traps at -55 to -60°C and -35 to -40°C respectively; under these conditions, the isocyanates came out under vacuum, developing very little vapor pressure; but the higher boiling materials remained in the trap as colored liquids. The isocyanates condensed as colorless material in liquid air-cooled receivers. Complete separation was assured by intermittent checking of the spectra and molecular weight. It was observed afterwards that, for the C_3F_7NCO preparation, this by-product is so high boiling that most of it remained in the reaction vessel. In one experiment, the trap having mostly isocyanate (second trap) was detached from the system at the end of the experiment and the higher boiling material was collected as an almost colorless liquid in the first trap under reduced pressure (water aspirator). The higher boiling material was found to be about 10-20% of the total yield.

Distillation of the higher boiling fractions from the C_2F_5NCO and C_3F_7NCO preparation, using a glass helices-packed column as fractionator and moisture guard tube resulted in collection of almost colorless liquids as main fractions. These were further purified in 'Autoprep' gas chromatograph using QF1 fluoro-silicone column (FS1265) and helium as carrier gas. Separation was not quite satisfactory and it is quite probable that some type of decomposition took place on the column surface, particularly at the higher temperature. At a low temperature, only a fraction of the material emerged. However, the major fraction collected was an almost colorless liquid in both cases and its spectra closely resembled that of the crude material. Both of the samples fumed in air (probably in presence of moisture) and had a very strong and pungent acidic odor.

Sample A108(v) : from C_2F_5NCO preparation

B.P. : 70-72°C; $n^{24.5°C}/_D = 1.2745$

Density: 1.684g/ml (approx at room temperature)

M.W. ≈ 310-315 (Dumas)

Infrared spectra (vapor):

5.3μ , 5.5μ , 6.95μ, (small hump), 7.4μ, etc.

Elemental Analysis:

% C = 24.40

% F = 52.70

% N = 0.36

% H = 0.39

This compound reacted with ammonia (gas) giving a colorless semi-solid mass having infrared peaks at 3.0μ, 3.15μ, 3.3μ, 3.5μ, 5.5-6.3μ(broad having maxima at 5.9μ), 6.9μ, 7.1μ, etc.

Sample A263 (a): from C_3F_7NCO preparation

B.P.: 107-108°C

M.W.: 410-420 (Dumas)

Infrared spectra (liquid on plates):

5.3μ(strong), 5.5μ, 5.6μ, (doublet, strong), 6.9μ(small hump), 7.35μ(strong) etc.

Elemental Analysis:

% C = 23.30

% H = 0.18

% N = 1.55

% P = 0

% F = 58.42

Considering all the possibilities, the available data can best be explained in terms of formation of $(C_2F_5CO)_2O$ for sample A108(v) and $(C_3F_7CO)_2O$ for sample A263(a).

b. Attempted preparation of perfluoroglutarodiisocyanate.

About 30 g of somewhat crude perfluoroglutarohydroxamic acid and 100 g of dry P_2O_5 were intimately mixed and heated to 250 ^{o}C under the conditions described for preparation of perfluoroalkyl monoisocyanates. Initially nothing collected in the Dry-Ice-cooled trap, but under reduced pressure (aspirator), some colored, high boiling liquid collected in the trap. The volatile fraction of the collected material under vacuum showed molecular weight of about 128-130 (Theor. mol. wt of $(CF_2)_3(NCO)_2$ = 234), indicating presence of lower molecular weight substances; the infrared spectra (vapor) showed peaks at 4.21-4.35μ (strong), 5.25μ (strong), 5.5μ, 6.75μ (strong), 7.0μ (strong), etc. The portion of the collected material which could be distilled under vacuum at high temperature was a colorless liquid having infrared peaks at 3.05μ, 4.35μ, 5.55μ, 6.9μ, etc., all the peaks indicating strong absorption. The experiment is to be repeated with pure hydroxamic acid and somewhat different experimental conditions.

3. Reaction of isocyanates with ammonia:

a. Reaction of ammonia and CF_3NCO

Reactants in 1:1 molar ratio were reacted in the gas phase at room temperature or in an ether medium at low temperture; this reaction was also carried out in an excess of one of the components at low temperature. (For experimental details, please see Annual Interim Report, 1967).

The product was a somewhat hygroscopic white solid in all the experiments and in the gas phase reaction, the yield was low. The product was almost insoluble or slightly soluble in ether,ethyl acetate, tetrahydrofuran, acetone, hexafluorobenzene, (and other highly nonpolar solvents) and it did not melt on heating up to 310°C. It began to sublime slowly at about 230°C; above this temperature there was no further change on heating up to 310°C. A portion of the product was soluble in water or methanol and the residue was soluble in sodium hydroxide solution. About 50% of the sample could be sublimed at 120-130°C under vacuum, the sublimate being water soluble and highly hygroscopic. At least a part of the sublimate was probably the ammonium salt (NH_4F) since addition of sodium hydroxide solution to its aqueous solution liberated NH_3. The original sample and residue after sublimation had almost same type of infrared spectra and residue did not sublime or melt on heating up to 310°C. The general pattern of infrared spectra showed the absorption peaks at 3.0μ, 3.2μ, 3.3μ, 4.55μ, 5.6μ-6.1μ (broad), 6.3μ (hump), 7.1μ, etc. The work is in progress.

b. Reaction of ammonia gas with C_2F_5NCO and C_3F_7NCO

Both of the perfluoroalkyl isocyanates were purified and pure samples were characterized by molecular weight determination and infrared spectra. Reaction was carried out in roundbottom flasks of suitable size fitted with a Dry-Ice-cooled cold finger having an inlet tube and guarded by soda-lime and "Drierite" tubes. The flask was cooled in liquid air, and isocyanate and ammonia were condensed in it in measured proportion through the vacuum system. Then the flask originally was kept in a Dry-Ice-acetone bath and slowly warmed up by taking the flask out of the bath. Reaction was very exothermic and unless proper precaution was taken, it became almost explosive, resulting in blowing out of the cold finger.

When the reactants were in a 1:1 proportion, some isocyanate was left in the system suggesting incomplete reaction. Yield was low in such cases (as low as 60-70% based on 1:1 addition product) and the product was a white solid with some viscous, colorless liquid. Similar results were obtained when the reaction was carried out in sealed thick-glass pressure tubes. This suggested some side reactions which consumed more than one mole of NH_3 per mole of isocyanate. When ammonia was in excess, the product was a white, somewhat hygroscopic solid in high yield (almost 90-100%) and no isocyanate was left in the system.

The infrared spectra and melting point of the products indicated that a number of compounds were present. A major portion of the product could be sublimed at 75-95°C under vacuum and the sublimate also was mixture of compounds as indicated by melting point and infrared spectra.

Elemental Analysis:

(1) $C_2F_5NCO + NH_3$ product (1:1.5); sublimed twice at 75-80°C under vacuum; melts over a range of temperature. (Sample A108(VI), Sublimate)

Elements	Sample	$C_2F_5NHCONH_2$(Theor)
%C	15.91	20.2
%H	5.21	1.7
%N	23.82	15.7
%F	41.54	53.4

(2) $C_3F_7NCO + NH_3$ product (NH_3 in excess). Sublimed at 90°C under vacuum; melts over a range of temperature. (Sample A2, Sublimate).

Elements	Sample	$C_3F_7NHCONH_2$(Theor)
%C	17.91	21.05
%H	3.27	1.31
%N	18.3	12.28
%F	50.74	58.33

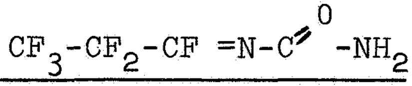
The high N and H content of the sample indicate presence of free ammonium salts. The C:F ratio is approximately 3:5 in (1) and 4:7 in (2) as in the starting isocyanate.

Attempts were made to separate the components of these two products. The reaction product of C_3F_7NCO and NH_3 was found to consist of three fractions: Fraction **1**, highly soluble in ether but insoluble in benzene and petroleum ether was almost a viscous semisolid mass; this part was also soluble in water and might contain some solid and liquid. Fraction **2**, the residue from ether extraction, was a white solid, part of which was sparingly soluble in ether but somewhat more soluble in ethyl acetate, tetrahydrofuran, and methyl alcohol; it was highly soluble in trifluoroacetic acid, aqueous sodium hydroxide and dimethyl sulfoxide, not hygroscopic, and fully sublimable under vacuum at 80-95°C; its melting point was quite sharp: 191-193°C. It was insoluble in water. The best method of separation of Fraction **1** from Fraction **2** was extraction of Fraction **1** completely by ether in a Soxhlet apparatus for a few hours; this method, however, extracted a small amount of Fraction **2** also due to its low solubility in ether. The infrared spectra of Fraction **2** showed peaks at 2.95μ- 3.0μ(strong doublet), 3.1μ (hump), 5.8μ (strong), 6.15μ, 6.65μ, 7.15μ, etc. Fraction **3**, the remaining solid from organic solvent extraction was found to be mostly soluble in water and liberated NH_3 on addition of NaOH to be aqueous solution.

The white crystals separating out of the ethereal solution of Fraction 1 and the major portion of Fraction 3 melts approximately at 145°C and both of them show almost same type of infrared spectra (peaks at 2.9μ, 3.0μ, 3.1μ, 3.3μ, 3.5μ, 6.0μ, 6.2μ, 6.7μ, etc.; two extra peaks at 4.4μ and 4.9μ for Fraction 3). None of the samples were pure enough to send for analysis. All attempts to completely separate the solid from liquid in Fraction 1 failed. However, the absence of any sharp infrared peak at 5.8μ region probably indicate the absence of any carbonyl group in the structure.

The infrared spectra of Fraction 2 indicate the presence of acidamide ($-\overset{O}{\overset{/\!\!/}{C}}-NH_2$) type of grouping in the structure. The nmr spectra of Fraction 2 in (60 MH_Z NMR) either in CF_3COOH solution or in DMSO (d^6) solvent, showed two types of protons in different ratios. However, it is known that N,N, - dimethyl formamide $\left[H - \overset{O}{\overset{/\!\!/}{C}}-N(CH_3)_2\right]$ shows two types of protons due to steric hindrance caused by C=O grouping and it is expected that such hindrance would be more prominent in $-\overset{O}{\overset{/\!\!/}{C}}-NH_2$ grouping (Ref: Application of absorption Spectroscopy of Organic Compounds by John R. Dyer, p 113-114).

Elemental analysis of Fraction 2 (Sample A252 R., recrystallized twice from tetrahydrofuran solution, white shining crystals, m.p. 192-193°C).

Reported	Theor. for  $CF_3-CF_2-CF=N-\overset{O}{\overset{\not\,}{C}}-NH_2$
%C = 23.26	23.1
%H = 1.16	0.96
%N = 13.50	13.46
%F = 50.56	54.80

The infrared spectra or m.p. of the sample was found to be unaltered by treating with either CF_3COOH or anhydrous ammonia in ether medium. The nmr spectra for C-F bonds in the sample, is awaited.

The C_2F_5NCO and NH_3 reaction product, could not be separated by the above procedure. The major portion of the product was found to be soluble in ether or water. The ether soluble part was definitely a mixture as it had a melting point range (135-160°C) and infrared spectra was also indicative of a mixture. The water insoluble part was a white, non-hygroscopic solid, soluble in ether with difficulty and more soluble in tetrahydrofuran. Its infrared spectra was very much like that of fraction 2 of the $C_3F_7NCO + NH_3$ product and the melting point was 175-180°C (not sharp). Further work is in progress.

IV. TABULAR SUMMARY OF RESULTS

[Abbreviations: Hexafluorobutyne-2, HFB-2; Ultraviolet, u.v.: Tetrahydrofuran: THF; Infrared ir; Molecular weight: M.W.; Boiling pt.: b.p. C_6F_6: Hexaflurobenzene]

TABLE I

A. Homopolymerization of Hexafluorobutyne-2(HFB-2)

No. of Expt.	HFB-2 gms	Initiator, gms	Conditions of Expt.	Products
X-a	0.58	PCR supplied sample (Disc. 1 B)0.40	u.v.(100W), room temp.,quartz, 4 hours	Quick initiation. Polyperfluorobutyne-2-0.37g THF soluble gum 0.15g
X-b	1.29	Fractions from PCR sample.Fraction (a):0.22	-do-; 3 hours	No polymerization
		Fraction (b) :0.21	-do-; 4 more hours	No polymerization
		Fraction (c) :0.19	-do; 12 more hours	Immediate initiation. Polyperfluorobutyne-2 :0.65g THF soluble gum :0.08g
X-c	1.25	Fraction c(above 0.32	-do-;16 hours	Immediate initiation. Poly HFB-2 :0.92g
X-8	1.30	chromatographically pure Fraction c 0.15	u.v.(550W),60-80°C quartz, 30 minutes	Poly HFB-2: 0.64 g THF soluble: 0.009 g C_6F_6 soluble: 0.04 g
X-25	1.24	2:3 dichloro hexafluorobutene (same as fraction c) 0.3	Quartz vessel; u.v. (30 W); 18 hrs. irradiation.	Initiation after 10 minutes; white powdered polymer (1.2 g) Residual gas: mainly initiator.

TABLE I (cont'd)

No. of Expt.	HFB-2 gms	Initiator, gms	Conditions of Expt.	Products
X-0	0.86	-d- 0.3	Pyrex vessel; u.v. (550 W); Irradiation: 2 hrs.	No initiation; ingredients recovered unchanged.
X-35	4.48	-d- 0.9	Pyrex vessel with Quartz well and side tube; u.v.(550 W), 5 hrs.; Monomer kept as liquid in side tube (-40 to -45°C)	Some gas phase polymerization observed at the hotter zone (surface of the quartz well); no polymerization in liquid phase; monomer recovered almost fully.
A-127	2.33g	Hexafluoropropylene epoxide: 1.05g	Sealed in thick-walled tube (7-8 atm); $Co^{60}\gamma$ (2000 r/min; 160 hours	White powdered polymer: 2.51g Residual gas: 0.80g; Average mol. wt. : 163; mostly epoxide (unchanged).
A-269	3.80	Hexafluoro acetone: 2.60	Sealed in thick-walled tube (14 atm); $Co^{60}\gamma$ (about 1800 r/min); 20 days.	White powdered polymer: 3.9 g; Residual gas: 2.2g; mol wt:168 (all HFA unchanged).
X-1	0.87	Acid fluoride dimer (M.W.:324) 0.79	-do- 2 hours	Immediate initiation PolyHFB-2: 0.70g (+some loss) white powder (ir #149; shows a little peak at 5.35µ,(adsorbed dimer?). Residual gas: M.W.249 (mainly dimer +some HFB-2)
X-12	1.40	Acid fluoride (M.W.:300)0.208	u.v.(550 W); 30°C; quartz; 17 hours.	Immediate initiation white powdered polymer (PolyHFB-2): 1.15g (ir peak at 5.35µ.
X-K	1.16	Perfluorobutene-2 0.29	-do-	Initiation within 15 mins. Very little polymerization PolyHFB-2 (0.1g). Residual gas: Both reactants present

TABLE I (cont'd)

No. of Expt.	HFB-2 gms	Initiator, gms	Conditions of Expt.	Products
X-15	1.01	Carbon tetrachloride 1.1	u.v.(550 W), 30°C, quartz, 15 hours	Initiation after 10 minutes. Product: Dirty colored solid (0.5-0.52g), smelling of 2,3,4,5 tetrachloro hexafluorobutane. ir spectra same as polyHFB-2.
X-18	1.07	Hexafluorodichlorocyclopentene: 0.716	u.v.(550 W), 30°C, quartz, 3-1/2 hours	Initiation within 5 minutes. Polymer, white mass (0.3-0.4g) Residual gas consisted of both reactants (#182).
X-39	2.49	Di-tertbutyl peroxide (10% molar of monomer).	Taken in a pressure tube with metal valve and kept at 125-135°C for 65 hours.	No polymerization; a little colored liquid (viscous) formed, perhaps due to decomposition of peroxide.
X-42	1.28	chlorodifluoroacetonitrile ($ClCF_2CN$): 0.995	u.v. (140 W), 30°C, quartz, 17 hours.	Quick initiation; slow polymerization; 0.4 g of white polymer, same as polyHFB-2. Almost all nitrile recovered.
X-42a	1.58	0.22	-do-;17 hours	Quick initiation; Product: white powder: 0.51 g, same as polyHFB-2.

TABLE II

Effect of Ultraviolet Radiation on 2,3-Dichloro-1,1,1-4,4,4-hexafluoro-2-butene ($CF_3CCl{=}CClCF_3$; b.p., 68.5°C; M.W., 233; Infrared peak at 6.2μ).

No. of Expt.	Wt. of compound gms.	Conditions of Experiment	Results
X-M	2.07	Pyrex reactor with quartz well (2340 ml) u.v.(550 W). Gas phase; 3 hrs.irradiation.	Colored liquid condenses within few mins. No starting material present in residual gas. Colored product soluble in THF having ir peak (hump) at 5.6-6.2μ.
X-N	0.98	Vycor vessel; u.v. (550 W) at 6" distance; gas phase; 17 hours irradiation	Colored liquid condensed. Residual gas: ir peak (hump) at 5.6-6.2μ.
X-P	0.36	Quartz vessel; u.v. (30 W), gas phase; 17 hours irradiation	Colored liquid condensed. Residual gas: ir peaks at 6.1μ and 6.2μ respectively. Photolysis incomplete.
X-38	1.68	Quartz vessel (75 ml); u.v. (140 W); gas liquid phase; 17 hours irradiation	Colored liquid product. Residual gas (70% of the input) was mainly starting material. After complete degassing under vacuum only about 0.1 g of THF soluble gum was left in the vessel showing ir peaks at 5.5-6.1μ.

TABLE III

Use of Chlorine Gas as Initiator (Cl_2; b.p.:-34°C).

No. of Expt.	Initiator, gms.	HFB-2, gms.	C_2F_4, gms.	Conditions of the experiment	Results
X-17	0.11	2.01	-	Vycor vessel;	Quick initiation and polymerization; white powder (product)=1.6 g. Residual gas shows a small peak at 6.2μ, i.e. some dichloro compound formed.
X-19	0.335	1.24	0.77	Vycor vessel; u.v.(550 W), 18 hours irradiation	Immediate initiations; slow polymerization. Sticky solid product (30-35% yield). M.W. of Residual gas: 158
X-20	0.05	1.72	1.06	Vycor vessel; u.v.(550 W) 18 hours irradiation	Quick initiation; Very little polymerization. Residual gas: 2.79 g; M.W.: 136. Formation of $C_2F_4Cl_2$ is a possibility, thus consuming the initiator.
X-21	0.05	-	0.88	Quartz vessel; u.v.(550 W); 18 hours irradiation	Quick initiation; Polymer, white powder (0.3 g) M.W. of residual gas 116. Probably some $C_2F_4Cl_2$b.p.:3.6°C was. formed.

TABLE IV

Inhibiting action of CF_3NO and CF_3I

No. of Expt.	HFB -2	Other Co-monomer	Initiator	Conditions of Expt.	Products
X-c	0.74g	CF_3NO 0.27g	Fraction C (From PCR sample) 0.346g	u.v.(100 W) 30°C, 30°C, Quartz, 16 hours	No polymer, color of CF_3NO disappeared
X-h	0.51g	CF_3NO 0.23g	Hexafluoro propylene Epoxide 0.62g	-do-; 2 hours	No polymerization; no apparent change visible
X-16	0.73g	CF_3NO 0.31g	Acid fluoride, mostly dimer 0.29g	u.v.(550 W) 30°C; 18 hours	No polymerization; color of CF_3NO not visible
X-40(a)	1.21g	-	Trifluoromethyl iodide: 0.23g (gas)	u.v.(140 W),30°C; 4.5 hours; Quartz	No polymerization; Pressure of gas almost unchanged. Some deposited iodine visible.
(b)			Dichlorohexafluoro butene (initiator) introduced: 0.2g	3 hours more irradiation	No polymerization

TABLE V

Attempted Co-or Terpolymerization of Hexafluorobutyne-2 using Dichloro compound (CF_3-CCl=CClCF$_3$) as Initiator

No of Expt.	Initiator, gms.	HFB-2, gms.	Other monomers, gms.	Conditions of Expt.	Results
X-3	0.18	0.594	C_2F_4: 0.496	u.v.(100 W); 30°C; Quartz vessel; few hours	Initiation within few minutes. Polymer: wax-like (broad ir hump 5.6-6.1μ) Residual gas: M.W. 130 (wt: 0.746g) Polymer softens on heating.
X-5	0.63	1.6	C_2F_4 : 0.7	u.v.(100 W) 30°C, Vycor; 19 hours.	Initiation after 15 minutes. Polymer: sticky white powder + some wax-like material (1.5g + some loss). Residual gas: M.W. 146 (wt: 0.63g). Polymer softens on heating; (shows a hump at 5.8-6.2μ in ir spectra.
X-22	1.5 + 0.3	6.5	C_2F_4:	Pyrex reactor with Quartz well (2340 ml) u.v.(550 W); Initiator injected in two installments; Time of irradiation=10 hours + 17 hours.	Grease like polymer formed, portion soluble in THF 1.27 g product: 0.54 g (THF soluble viscous mass) + 0.73g (sticky white solid), almost completely soluble in C_6F_6). Residual gas: M.W.$\approx$146 & 152.7 (checked after two experiments) 5.8 g; no prominent ir peak at 6.2μ. Product, heated (200°C, 3 hours) Residue tacky solid.

TABLE V (Cont'd)

No. of Expt.	Initiator, gms.	HFB-2 gms.	Other monomers, gms.	Conditions of Expt.	Results
X-23	1.5	6.1	C_2F_4: 3.7	Pyrex reactor (2340 ml); Quartz well covered outside with perforated aluminum foil to reduce dose rate of radiation. u.v. (550 W), 7 hours irradiation.	Initiation within 5 minutes. No further polymerization; but dark liquid visible. Residual gas showed presence of some air. Aluminum foil covered with viscous liquid.
X-24	0.72 g	Part of above gas mixture after removal of air. (approx.2.3.g)		Vycor; u.v. (30 W); 23 hours irradiation	Product: Tacky white polymer (1.80 g)

TABLE V (Cont'd)

No. of Expt.	Initiator, gms.	HFB-2, gms.	Other monomers, gms.	Conditions of Expt.	Results
X-36	0.39 + 0.36	0.66 + 0.68	C_2F_4: 1.05 + 1.04	Quartz-Vycor vessel; u.v. (140 W); Irradiation. 17 hours + 11 hours. Two fresh batches polymerized in one single experiment.	Polymerization: 1st batch (about 80%) + 2nd batch (about 50%). Product: Almost semisolid white mass: 0.36 g (THF soluble viscous liquid) + 1.55 g (C_6F_6 soluble white semisolid). Initiator present in residual gas.
X-37	0.36	-	C_2F_4:	Quartz vessel; u.v. (140 W), 16.5 hours	Product: white mass containing THF soluble viscous liquid = 0.28 g, Rest - white powder 0.82 g) of which C_6F_6 soluble portion is 0.47 g.
X-26	0.3	0.785	C_2F_3Cl: 0.345	Qusrtz; u.v. (30 W); 23 hours irradiation.	White solid product (0.7 g) ir of Residual gas shows presence of all the three components (M.W: 150); Product: 35% soluble in THF semi solid mass.
X-27	0.3 g	0.335	C_2F_3Cl: 0.66	Quartz; u.v. (30 W); 22 hours irradiation.	Very viscous gel-like product completely soluble in C_6F_6; Residual gas: 0.46 g, M.W: 136 (ir shows presence of all the three components).

TABLE V (Cont'd)

No. of Expt.	Initiator, gms.	HFB-2, gms.	Other monomers, gms.	Conditions of Expt.	Results
X-28 (a)	-	1.52	C_2F_3Cl: 1.14	Vycor-Quartz vessel; u.v. (30 W); 4 hours	No initiation
(b)	0.6	-do-	-do-	-do-; initiator introduced; irradiation: 16 hours	White polymer formed
(c)	0.36	0.74	C_2F_3Cl: 0.55	Ingredients introduced in above system. Irradiation 8 hours.	
(d)	0.24	Part of residual gas obtained as above		Quartz vessel; u.v. (30 W), few hours, (Fresh initiation).	White semisolid mass (75% polymerization). Total product: 2.5 g of which about 60% soluble in THF (yellow oil). Rest white powder.
X-34(a)	0.49 + 0.36	1.0	C_2F_3Cl: 1.41	Vycor vessel; u.v.(140 W); irradiation: 6 hours + 12 hours.	Gel like polymer formed (at least 60% polymerization) Residual gas: 1.35 g; M.W: 135. Total product: 3 g of which 2.4 g soluble in THF (yellow viscous oil).
(b)	0.50	1.0	C_2F_3Cl: 1.35	-do-; fresh introduction; 12 hours irradiation.	

TABLE V (Cont'd)

No.of Expt.	Initiator, gms.	HFB-2, gms.	Other monomers, gms.	Conditions of Expt.	Results
X-29	0.07	-	CF_2=CF-CF=CF_2: 0.3	Quartz vessel; u.v.(30 W); 18 hours irradiation	Little colored viscous liquid product.
X-30	0.38	1.25	-do-: 0.865 g	Quartz vessel; u.v.(30 W); 21.5 hours irradiation.	Slow polymerization (about 50%). Residual gas; 1.08 g; Product: white solid partly soluble in THF (colored gum).
X-32	0.36 = 0.36	1.1	C_2F_4 0.61 CF = CF-CF= CF : 0.85	Vycor vessel; u.v.(30 W); irradiation: 17 hours + 5 hours.	Very slow polymerization; Product: very viscous almost colorless semisolid; portion soluble in THF-0.7 g (colored viscous liquid) Remainder 0.4 g sticky white solid.
X-QI	0.24	0.87	C_2F_4: 0.5	Sealed in thick walled pyrex tube; $Co^{60}\gamma$ (2000 r/min)- 6 days.	Partial polymerization; White solid product.
X-QII	0.3	0.77	C_2F_4: 0.47 CF_2=CF-CF=CF_2 0.71	-do-	Very little polymerization.

TABLE V (Cont'd)

No. of Expt.	Initiator, gms.	HFB-2, gms.	Other monomers, gms.	Conditions of Expt.	Results
X-31	0.36	1.2	C_5F_{11}-$CF=CF_2$: 1.65	Quartz vessel; u.v. (30 W), 19 hours.	Quick initiation; White solid product (0.9 g) + a little THF soluble gum.
X-33	0.36	1.33	$(CF_3)_2CO$ (HFA) 1.1	Quartz vessel; u.v. (140 W), 4.5 hours	Quick initiation and polymerization; Product: 0.95 g white powder (about 40% of monomers used) having very little THF soluble gum. HFA might not have reacted at all.

TABLE VI

Attempted Copolymerization of HFB-2 using Acid-Fluorides, derived from Hexafluoropropylene Epoxides as Initiator

No. of Expt.	HFB-2	Other Co-monomer	Initiator	Conditions of	Products
X-2	0.42g	C_2F_4 0.538g	Acid fluoride M.W.: 335 0.488g (mainly dimer) ir peak:5.25μ)	Dried monomers used; u.v.(100 W) Quartz; 30°C; 22 hours	Initiation within few minutes. Polymer: white wax-like solid part soluble in THF, giving slightly colored gum. M.W. of residual gas 182 (0.25g) Polymer softens on heating, shows ir peaks at 5.35μ, 5.6μ, and hump at 5.6-6.2μ (#150)
X-4	1.03g	C_2F_4 1.26g	Acid fluoride (M.W. :340) 0.497g (mainly dimer) ir peak 5.25μ)	Dried monomers used; u.v.(100 W) Vycor; 30°C; few hours	Quick initiation and polymerization; Polymer: white sticky powder (1.43g); about 15% soluble in THF (gum). Polymer properties - same as X-2. Residual gas: M.W. 150 (1.2 g). This polymer formed almost a clear melt at about 200°C.
X-14	1.27g	C_2F_4 0.92g	Acid fluoride (M.W.: 173) mainly monomer. (ir peak at 5.25μ) 0.62g	Dried monomers used: u.v.(550 W) Vycor; 30°C, 20 hours.	Immedicate initiation. Polymer: sticky white powder (1.9g + some loss); softens on heating; ir peaks at 5.35μ. Residual gas: Part non-condensable.