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TECHNICAL REPORT

68-56-CM

POLYMERIZATION STUDIES LEADING TO HIGH-STRENGTH, CHEMICAL-RESISTANT ELASTOMERS SERVICEABLE AT TEMPERATURE EXTREMES

by

D. I. Relyea, H. P. Smith
and A. N. Johnson

Uniroyal, Inc.
Research Center
Wayne, New Jersey

Contract No. DA-19-129-AMC-487 (N)

February 1968

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

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FOREWORD

This is a final report covering research conducted by Uniroyal, Inc., Wayne, New Jersey, from November 30, 1964 to November 29, 1967. The purpose of this project was the investigation of polymerizations leading to chemical-resistant elastomers having high strength and serviceability at temperature extremes. A number of polymers made by using combinations of transition metal catalysts and fluorinated unsaturates were screened. A series of adducts of fluorinated sulfenyl chlorides to cis-polybutadiene was made.

This report was prepared by D. I. Relyea, H. P. Smith and A. N. Johnson of Uniroyal, Inc., under U. S. Army Contract DA19-129-AMC-487(N). Project supervisors for the Army were C. B. Griffis, A. F. Wilson and M. C. Henry. D. I. Relyea served as Project Director for Uniroyal.

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ABSTRACT

The findings of a three-year program of research on the polymerization of fluorinated monomers to form high polymers having random or stereospecific microstructure are described. The objective of this program was the preparation of new elastomeric materials which might be both oil- and chemical-resistant and which might have useful rubbery properties over a wide range of temperatures, from -65° to +300°C.

The initial approach was to apply to several easily-procurable fluorinated olefins some of the stereospecific catalyst systems previously developed for hydrocarbon olefins. Apparatus was constructed for handling the volatile monomers and screening potential polymerization catalysts. The monomers tested included olefins and acetylenes which might undergo 1,2-polymerization, cyclobutenes and norbornenes which might participate in ring-opening polymerization, and conjugated dienes for which several potential polymerization processes are possible. In addition to monomer type, a number of other polymerization variables were explored including (a) the catalyst type, whether cationic, anionic coordination or free radical, (b) the transition metal of the catalyst, (c) the olefin complexing power of the catalyst, (d) solvent, (e) temperature, and (f) monomer ratio in copolymerizations.

It was observed that the fluorinated monomers were generally much less reactive than their hydrocarbon homologs. The most reactive monomers were seen to be the conjugated dienes. Rhodium-initiated polymerization of the conjugated fluorinated dienes was most satisfactory from the viewpoints of rate of conversion to polymer, yield of polymer, ease of copolymerization with hydrocarbon olefins, and insensitivity to water or other polar contaminants. Several fluorinated butadienes are quantitatively converted to polymer by the rhodium catalyst in less than a day at 50°C. The 1:1 copolymer of 1,1,2-trifluorobutadiene and butadiene has Tg of -48°C., is sulfur-vulcanizable, and shows 180 percent swell in ASTM fuel C. At the other end of the monomer-catalyst reactivity range is the combination hexafluoropropene-sesquiethylaluminum sesquichloride + vanadium oxychloride which gives less than 4 percent conversion to polymer in 280 hours.

Some effort was directed toward chemically modifying a stereospecific polymer such as high <u>cis</u>-polybutadiene as an approach to forming stereospecific polymers of improved oil resistance and low temperature properties. Thus, the reaction of pentafluorobenzenesulfenyl chloride with 20 percent of the unsaturation of <u>cis</u>-polybutadiene yields a sulfur-curable rubber of improved oil resistance having Tg of -66°C. and no melting or crystallization phenomena above that temperature.

POLYMERIZATION STUDIES LEADING TO HIGH-STRENGTH, CHEMICAL-RESISTANT ELASTOMERS SERVICEABLE AT TEMPERATURE EXTREMES

I. INTRODUCTION

In recent years there has been an extensive search for an elastomer which might have the combination of properties needed for use at low temperatures or in contact with petroleum or other fuels (1). The most promising product of that search is "nitroso rubber", the 1:1 alternating copolymer of tetrafluoroethylene and nitrosotrifluoromethane. However, even nitroso rubber has some serious deficiencies, notably a vigorously exothermic decomposition above 270°C (2,3) and a glass transition temperature of -51°C. which is 10-20° higher than desirable (4). This report describes the results of a research program whose goal was to develop an elastomer having greater thermal stability and improved low temperature properties and oil resistance. Two approaches were used:

(1) the polymerization of fluorinated olefins, dienes or other unsaturates, mainly by coordination catalyst systems known to be stereospecific with hydrocarbon olefins and diene, and

(2) the chemical modification of <u>cis</u>-polybutadiene by reagents which might improve oil resistance without great harm to thermal stability or glass transition temperature.

Although neither approach was completely successful, several new polymers with some properties approaching the goals were developed.

II. RESULTS AND DISCUSSION

A. FLUORINATED OLEFINS

1. Attempted Homopolymerization by Anionic Coordination Catalysts

One point of departure for obtaining an oil- and freeze-resistant rubber is the polyethylene chain, glass temperature -70° to -110°C (5). This polymer backbone might be modified to improve oil resistance by the introduction of fluorine substituents, either by preparation of a homopolymer of a fluorinated -olefin or by copolymerization of ethylene with a fluorinated -olefin.

The catalyst system ethyl aluminum sesquichloride-vanadium oxychloride was chosen as a starting point for screening stereospecific catalysts in fluoroölefin polymerizations because of the extensive experience at the Uniroyal Research Center in the use of this combination with hydrocarbon olefins. Polymerizations were carried out in various solvents with approximately 4 mole-percent of transition metal catalyst and an Al:V ratio of 2:1 or 5:1. The results are summarized in Table I.

The fluorinated monomers are listed in Table I in an arbitrary order as follows: vinyls, acetylenes, ring compounds, dienes, and heteroatom compounds. Some data for control polymerizations run on simple hydrocarbon olefins are placed at the end of the Table. None of the fluoroölefin homopolymerizations gave more than about 4 percent conversion to polymer during 280 hours at 28°C. The higher ratio of Al:V and the more polar solvents (benzene, methylene chloride) appear to be most favorable to polymerization. These results are reminiscent of those recently reported by Sianesi and Caporiccio (6), who found tetralkyl titanates to be weakly active catalysts for the polymerization of perfluoroölefins, but most effective in halogenated solvents.

In general, each fluorinated olefin monomer was tested for copolymerization with ethylene (two catalysts) and butadiene (two cis-1,4-butadiene catalysts). Those results are described in Section IIA2. Remaining monomer was tried with a tetrabutyl titanate catalyst or a $TiCl_4$ catalyst and as many as four other catalysts. These results are reported in Table I.

Literature results on Ziegler polymerizations of fluorinated monomers indicate general sluggishness, uniformly low rates and low yields, and low molecular weight. The best results in the literature were obtained with aluminum alkyl/tetrabutyl titanate at slightly elevated temperature for hexafluoropropene, but the results for all vinyl monomers reported are quite discouraging. These results were confirmed in that the polymer yields from the 12 vinyl monomers reported are uniformly low to zero and several runs showed evidence of degradation by catalyst attack on the monomer or polymer. Some positive results are shown in the case of two substituted acetylenes and in some of the tests on the five dienes tested.

The readily available monomers hexafluoropropene and vinylidene luoride were studied in the preliminary work when technique of polymer recovery was being developed. These monomers were found to be generally unreactive, even toward catalysts containing electron-rich ligands (7,8). (Experiments 37 and 38). Hexafluoropropene was studied with preformed ethylene propylene rubber (EPR) catalyst from $Et_3Al_2Cl_3$-$VOCl_3$ in two different ratios in three solvents (Experiment 13); with aluminum triisobutyl-tetrabutyl titanate in two ratios and three solvents at 50°; in methylene chloride with premixed catalysts (prepared by prior mixing of reducing agent and transition metal compound) formed from four catalyst combinations in two or more ratios of reducing agent to transition metal; with aluminum triisobutyl-tetrakis (diethylamino-) titanium vs. the latter component alone or vs. triphenyl phosphine; with aluminum triisobutyl-tetrabutyl titanate in four combinations of hydrocarbon and halogenated solvent of different types; with a decyl magnesium iodide-tetrabutyl titanate catalyst in two Mg/Ti ratios in two hydrocarbon solvents vs. three halogenated solvents (Experiment 19); and with a magnesium phenyltetrabutyl titanate catalyst in benzene. No practical yields were obtained.

Similar failures occurred with all vinyl monomers tested containing one unsaturated group, although the other monomers were mostly tested by spot checks consisting of simple trials of typical catalysts in hydrocarbon solution.

1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynyl-cyclobutane polymerized to low molecular weight polymer with several catalysts. The highest yield and molecular weight were obtained with an AlR$_3$TiCl$_4$ catalyst. An attempt to raise the molecular weight by running at -43°C. with varied amounts of catalyst and varied procedures of assembly resulted in no improvement. Low molecular weight is apparently a characteristic of his catalyst (see results of Experiment 63-3 with α-trifluoromethylstyrene, which should have yielded a resin if high molecular weight polymer had been formed).

2,2,2-Trifluoroethyl vinyl ether gave low molecular weight products with VOCl$_3$ and TiCl$_4$ catalysts.

2. Copolymerization with Ethylene by Anionic Coordination Catalysts

Approximately 30 fluorinated monomers of various types were tested or copolymerization with ethylene, usually with the VOCl$_3$ and butyl vanadate catalysts, if sufficient monomer was available, and with other catalysts such as tetrabutyl titanate activated with aluminum triisobutyl or magnesium phenyl, titanium tetrachloride activated with aluminum triisobutyl, or zirconium acetylacetonate catalyst. The results of these experiments are given in Table IV.

The molar ratio was usually two moles of fluorinated monomer to one of ethylene (but one-to-one in the case of liquid F monomers) because of the high reactivity of ethylene, as well as a desire to avoid high pressures in the polymerization tubes. At 0.5 mmole of transition metal in the catalyst, the molecular weight was high enough for an easy separation of product, while the catalyst was in high enough concentration to avoid the effects of adventitious impurities.

Most of the monomers showed a polymerization activity in the presence of ethylene that was far less than the activity of propylene, which is generally considered not to polymerize with an EPR catalyst unless ethylene is present. Copolymers fairly rich in fluorinated monomer were ormed only in the case of hexafluoro-2-butyne, 2-trifluoromethyl butadiene and 1,1-trifluorobutadiene. In four cases a side reaction between catalyst and fluorinated monomer or fluorinated product was indicated by either the infrared spectrum or the color of the product. These monomers were 1,1,2-trifluorobutadiene, vinyl fluoride, 1,1,2-trifluoro-2-chloro-3-vinyl cyclobutane, and 2,2,2-trifluoroethyl vinyl ether. A single trial of 3,3,3-trifluoropropene with ethylene did not give a uniform product as microanalysis indicated 16.96 percent F, while infrared indicated about 1 percent F. So the usual product of a copolymerization was a polyethylene with its typical X-ray diffraction pattern and with an infrared spectrum showing so little fluorine that a microanalysis for F was not considered worthwhile.

The more reactive monomers in copolymerization were hexafluoro-2-butyne and two fluorinated dienes. Specific catalyst effects occurred.

Hexafluoro-2-butyne did not copolymerize with ethylene using $VOCl_3$, butyl vanadate, $TiCl_4$ or tetrabutyl titanate catalysts, but it did respond to magnesium phenyl-tetrabutyl titanate, giving an amorphous resin 6.3 percent F, 25 mole percent butyne, with CF_3 group to every four chain carbons. Replicate runs with slightly increased ethylene feed made with butyne from a different source and a different catalyst composition produced pure poly (hexafluoro-2-butyne) with no hydrogen content, as shown by the infrared spectrum. However, it is doubtful whether a rubber could be produced from ethylene and a comonomer of such an expected high glass temperature.

Control polymerizations with ethylene gave high yields (40-1, 91-9) with the $VOCl_3$ EPR catalyst and lower yields with butyl vanadate (55-1, 5-2) or zirconium acetyl acetonate (42-6) catalysts. No polymerization occurred with a tetrabutyl titanate catalyst (45-3), which is most effective for fluorinated dienes.

Terpolymerizations with Ethylene

Since no rubbers were made in the attempted copolymerizations of fluorinated monomers and ethylene, several approaches were made to this end by combinations of ethylene with two or more monomers (Table V).

As an ethynyl substituted fluorinated cyclobutane had shown some reactivity, it was tested with ethylene and hexafluoropropene (42-6) with the butyl vanadate catalyst. The product was a resinous copolymer of ethylene and the substituted acetylene (like 40-6 Table IV) containing no CF_3 side groups.

In Experiment 71, 2,3-bis(trifluoromethyl) norbornadiene was tested as a fluorine carrier in a mixture with ethylene and propylene. The 71-1 copolymer ($VOCl_3$ catalyst) of ethylene and the norbornadiene incorporated some fluorine. When propylene was used with the other two monomers, a stiff rubber was obtained. The terpolymer, which has a low fluorine content and a glass temperature above that of EPR, appears not to be useful. When the same pair of experiments was repeated with the butyl vanadate catalyst, a copolymer of ethylene and the norbornadiene with a little higher F content than 71-1 was obtained. However, the termonomer mixture made a product (71-4) similar to 71-3 with no incorporation of propylene. Hence, there are specific catalyst and monomer interactions that make behavior of mixed monomers unpredictable. In a control experiment (71-5), a mixture of propylene and ethylene in 2/1 molar ratio made a high propylene EPR in high conversion with no difficulty.

nother approach to a suitable ethylene terpolymer is to use a mix-ure of ethylene with a hydrocarbon diene for low glass temperature and ,1,2-trifluorobutadiene to supply fluorine, since in Table IV mixtures r ethylene and trifluorobutadiene invariably yielded resinous products ver a wide range of monomer ratios. To choose the hydrocarbon diene, utadiene and isoprene were compared at 5° in heptane and benzene using TiCl$_4$ catalyst at two ratios of Al/Ti. Butadiene in benzene at the igher Al/Ti ratio gave the best yield of high *cis* polymer. Then, in xperiment 75 (Table V), also at 5°, mixtures of ethylene and butadiene ere polymerized in benzene-heptane with four types of catalyst (and ome variations in Al/Ti ratios). Infrared spectra indicated no ethyl-ne in the product made with the cobalt catalyst, while mixtures of two ypes of product appeared with the vanadate catalyst. TiI$_4$ catalyst howed ethylene and *cis* butadiene in a copolymer, while TiCl$_4$ catalyst ave a large yield although molecular weight was low.

iI$_4$ and TiCl$_4$ catalysts were selected for trial with ternary mix-ures of ethylene, butadiene and trifluorobutadiene, again at 5° (77 eries, Table V), and with various monomer ratios. The TiCl$_4$ catalyst gain showed ethylene combined with butadiene but no F in the product. n the other hand, the TiI$_4$ catalyst showed a mixture of products, 1) olyethylene containing some butadiene; and 2) polybutadiene containing ome F. In Experiment 79 (Table VII) it was found that with the four ypes of catalyst tested, trifluorobutadiene combines with butadiene at ° only in a small amount. So the choice of temperature to polymerize he terpolymers in the 77 series was unfortunately too low, but the lack r reactivity of trifluorobutadiene as compared with butadiene and ethyl-ne (77-2 and 77-3) and the tendency to form two products (77-4 through 7-6) make it unlikely that a controllable polymerization of the type esired can be achieved.

t is concluded that ethylene is of no value in making the target roduct. It is of marginal utility for freeze resistance, and to meet a 5°F. specification for elastomeric properties, comonomers to decrease crystallinity and impart additional chain flexibility are required. As butadiene is much better than ethylene for freeze resistance, it is more productive to attempt the simple combination of *cis* butadiene units and fluorinated monomer.

B. FLUORINATED DIENES

A second approach to an oil- and freeze-resistant rubber is *via* the *cis* -polybutadiene chain (glass temperature -110°C)(9). A partially or completely fluorinated form of *cis*-polybutadiene might be obtained by proper choice of monomer or comonomer and catalyst. It seemed desirable to use catalysts leading to high *cis*-stereospecificity in polybutadiene (10,11) since *trans* or vinyl polymerization is detrimental (glass temperatures -83°C and -9°C, respectively (12,13)).

1,1,3-Trifluorobutadiene was used in the initial experiments because of its ready availability. Since the diene was much more reactive in anionic coordination polymerization than the olefins, a series of fluorinated dienes was prepared to determine the effect of structure on polymerizability and polymer properties. Synthesis, rather than purchase, was dictated by the limited thermal stability of these diene monomers.

Preparation of Fluorinated Dienes

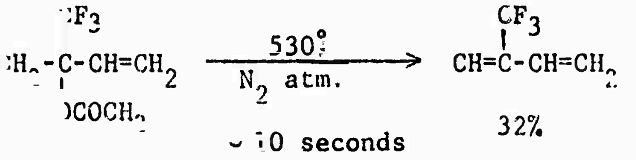
The following synthetic routes were employed:

a) 1,1,2-Trifluorobutadiene by the method of Tarrant and Lilyquist (14):

$$BrCF_2\text{-}CFCl\text{-}CH{=}CH_2 \xrightarrow[\text{i-PrOH}]{Z} CF_2{=}CF\text{-}CH{=}CH_2$$

81 - 92%

b) 2-(Trifluoromethyl)butadiene from an intermediate furnished by Professor Tarrant (15):

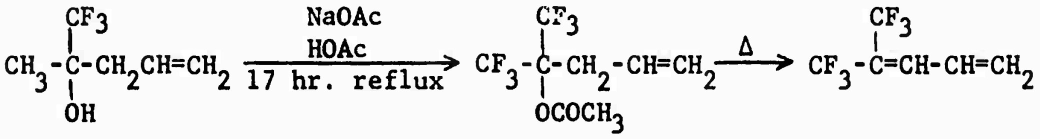


$$CH_3\text{-}\overset{CF_3}{\underset{OCOCH_3}{C}}\text{-}CH{=}CH_2 \xrightarrow[N_2\text{ atm.}]{530°} CH{=}\overset{CF_3}{C}\text{-}CH{=}CH_2$$

~10 seconds

32%

c) 5,5,5-Trifluoro-4-(trifluoromethyl)-1,3-pentadiene from the propylene and hexafluoroacetone adduct (16), furnished by Professor Tarrant:

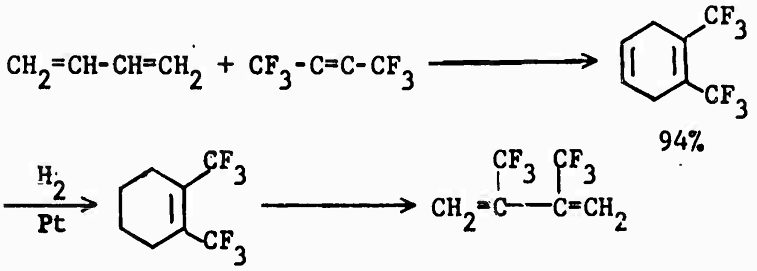


$$CH_3\text{-}\overset{CF_3}{\underset{OH}{C}}\text{-}CH_2CH{=}CH_2 \xrightarrow[\text{17 hr. reflux}]{\text{NaOAc, HOAc}} CF_3\text{-}\overset{CF_3}{\underset{OCOCH_3}{C}}\text{-}CH_2\text{-}CH{=}CH_2 \xrightarrow{\Delta} CF_3\text{-}\overset{CF_3}{C}{=}CH\text{-}CH{=}CH_2$$

80%

62%

d) 2,3-Bis(trifluoromethyl)butadiene by the route of Putnam, Harder, and Castle (17):



94%

53%

52%

2. Homopolymerization by Anionic Coordination Catalysts

Table I shows that attempted homopolymerizations of 1,1,2-trifluorobutadiene with the cis-polybutadiene catalysts titanium tetraiodide/phenyl magnesium (Experiments 22-1, 22-2) or titanium tetraiodide/aluminum triisobutyl (Experiments 22-3, 22-4) gave very low conversions. However, the use of the more nucleophilic catalyst tetrabutyl titanate activated with either phenyl magnesium (Experiments 23-1, 23-2) decyl magnesium iodide (Experiments 23-3, 23-4), or aluminum triisobutyl (Experiments 23-5, 23-6), led to significant conversion to polymer.

This polymer is soluble in methyl ethyl ketone and can be molded easily at 360°F. to a soft film.

It was noted that although 1,1,2-trifluorobutadiene is stable for several months at -78°, it spontaneously polymerized on the walls of a clean vacuum line at room temperature. It polymerized more slowly when the vapor was left in the vacuum line (now polymer coated) at room temperature over a weekend. A thermal polymer (from polymerization in the liquid phase) differs in properties from the titanium catalyst-initiated polymer. The thermal polymer (insoluble in methyl ethyl ketone) has a broader band at 1750 cm.$^{-1}$ than the catalyst-initiated polymer and its absorption in the fluorine region (1000 to 1450 cm.$^{-1}$) is a continuum instead of a series of sharp bands as in the catalyst-initiated polymer. To further demonstrate the effectiveness of the catalyst system, the rates of thermally and chemically initiated polymerizations were compared in Experiments 28 and 32, Table I. The results indicate that the titanium-initiated polymerization is 10 to 20 times faster than the thermal (room-temperature) polymerization.

The tetrabutyl titanate-aluminum triisobutyl initiated polymerization was scaled up to provide a sample of polymer for the U. S. Army Natick Laboratories.

1,1,2-Trifluoro-3-chlorobutadiene and the other fluorinated butadienes were found to be less reactive in homopolymerization than was 1,1,2-trifluorobutadiene (Experiments 81, 91-6, 92 and 119, Table I). Consequently, further anionic coordination polymerization with these monomers was restricted to copolymerizations, mainly with butadiene.

3. Copolymerizations Using Anionic Coordination Catalysts

These were not much more successful than the homopolymerizations and do not appear to offer a practical solution to the present problem. These experiments are described in detail in Table IV and VI.

4. Homopolymerization and Copolymerization with Olefins Initiated by Anionic or Cationic Catalysts

These experiments, summarized in Tables VIII and IX, indicate that the anionic initiators examined (lithium butyl, t-butylmagnesium chloride) are not effective in promoting polymerization of 1,1,2-trifluorobutadiene or its copolymerization with butadiene. Certain comonomer-cationic catalyst combinations produced significant yields of polymer with extensive incorporation of the fluorinated comonomer. These combinations are:

1,1,2-Trifluorobutadiene-isobutylene-$AlBr_3$
1,1,2-Trifluorobutadiene-isobutylene-BF_3
1,1,2-Trifluorobutadiene-methyl vinyl ether-$AlBr_3$

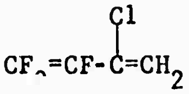
The first two combinations gave obviously low molecular weight products under the conditions used. Probably all of the molecular weights could be increased by increasing the monomer/catalyst ratio.

5. Rhodium Salt-Initiated Emulsion Polymerization

The Uniroyal Research Center discovered the unique ability of rhodium salts to cause the stereospecific trans polymerization of butadiene (18, 19). Rhodium chloride was examined as catalyst in a survey of the reactivity of a range of fluorinated monomers in this type of controlled structure polymerization. Table XII shows that the conjugated dienes 1,1,2-trifluorobutadiene (1), 1,1,2-trifluoro-3-chlorobutadiene (2), and 5,5,5-trifluoro-4-trifluoromethylpentadiene-1,3 (3), are readily polymerized by rhodium chloride in aqueous emulsion.

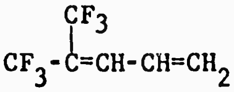
$CF_2=CF-CH=CH_2$

(1)



$CF_2=CF-C(Cl)=CH_2$

(2)



$CF_3-C(CF_3)=CH-CH=CH_2$

(3)

The polymers obtained had the following properties: poly-1, resin, Tg -35°C.; poly-2, rubber, Tg -17°; and poly-3, resin, m.p. 112°.

Exploratory polymerizations of unsaturated fluorine compounds other than conjugated dienes showed them to be much less reactive with the rhodium initiator. The results of these latter experiments, which are presented in detail in Table XII, are briefly summarized as follows:

Monomer	% Conversion to Polymer
3-Chloro-3,4,4-trifluoro-2-isopropenyl-cyclobutene-1	18
α,δ,δ-Trifluorostyrene	3
2,2,2-Trifluoroethyl vinyl ether	0
2-Chloro-2,3,3-trifluorovinylcyclobutane	0
1,2-Bis(trifluoromethyl)-4-methylcyclohexadiene-1,4	0
1,1,2-Trifluoromethyl-1,4-pentadiene	0
1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane	0

Copolymerizations of butadiene (4) or bis-2,3-trifluoromethylbutadiene (5), with monomers 1, 2 and 3 initiated by rhodium trichloride in aqueous emulsion, were studied as possible means of obtaining rubbers with lowered Tg values. Monomer 5 was of particular interest because its free radical-initiated homopolymer has been reported to have good high-temperature stability (17). These polymerizations are described in detail in Table XIII. The most successful ones are summarized below:

Monomer Pair	Mole-% of First Monomer in Polymer	Tg, °C.
-4	51.4	-48
-4	55.1	-35
-4	9.8	-20
-4	31.9	-27
-1	51.4	- 2

Since rhodium-initiated polybutadiene has the trans configuration, it might be expected that the butadiene units of the fluorodiene copolymers and the fluorodienes themselves also have the trans configuration. Preliminary studies of the microstructure of the copolymers have been made using infrared spectroscopy to determine cis, trans and vinyl contents of butadiene portion (20), and nuclear magnetic resonance to establish the presence or absence of unsaturation of certain carbon atoms of the fluorinated monomers. The results indicate that the reactivities of butadiene and 1,1,2-trifluorobutadiene are about the same, since their copolymer has a composition near that of the feed and incorporates 30-35 percent fluorine. The infrared spectrum shows the butadiene is combined in the trans form, as expected. Glass temperatures are -47 to -48°. Since glass temperatures of cis polybutadiene and 1,1,2-trifluorobutadiene are -105° and -35°, respectively, a copolymer of cis butadiene and trifluorobutadiene in equimolal ratio (1 to 2 by weight) would be expected to have a glass temperature of -64°. One possible explanation is that a significant amount of the butadiene monomer has polymerized in the 1,2-manner. Another possibility is that a block or graft copolymer has been formed. This latter explanation would account for the high oil-swelling values which are much larger than would be predicted for a polymer containing 35 percent fluorine. In this case the polymer would consist of soluble polybutadiene chains filled with insoluble poly(trifluorobutadiene) blocks, permitting high oil swelling. Further study would be required to clarify this point.

The monomer pair 4 and 5 was tested at a feed ratio of 1:2 and gave a polymer with nearly the same ratio of combined monomers. All the other monomer pairs were used at a 1:1 feed ratio and gave polymers of about a 1:1 monomer ratio except in the case of the monomer 3 and 4 combination. Monomer 3 appears much less reactive than the others, perhaps because it is highly unsymmetrical, both from electronic and steric viewpoints.

All the successful copolymerizations proceeded with conversion rates of at least 2-3 percent per hour in these prliminary experiments. In several cases it was evident that the reactions proceeded very rapidly, but they were allowed to continue for relatively long periods to insure good yields. In Experiment 99-2, formic acid was added in an attempt to enhance the rate (21, 22). It seems to be an active modifier. Methylene chloride seems to have no particular effect.

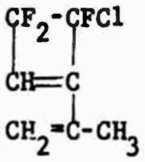
An attempt to make rhodium-catalyzed cis structure by adding KI to the polymerization recipe was unsuccessful with butadiene (Experiment 109).

Three proprietary fluorinated emulsifiers of unknown composition (MMM FC-170, FC-172 and FC-128) failed to support polymerization of butadiene catalyzed by $RhCl_3$.

A bis(1,4-cyclohexadiene chlororhodium) catalyst was compared with rhodium chloride in several runs. As it made similar copolymers at a slower rate (104-3 vs. 99-3, 108-1 vs. 108-2), no further work was done with this catalyst.

6. Iridium-Initiated Polymerization of Fluorine-Containing Dienes

Other work in this laboratory has shown the effectiveness of iridium catalysts in polymerizing norbornenes (18). The close relationship of iridium to rhodium suggested that the iridium catalysts might also be active in polymerization of the fluorinated dienes. A representative group of fluorinated monomers was tested for polymerizability with iridium catalysts in aqueous emulsion. These experiments are summarized in Table XI. As was the case with rhodium catalysts, significant conversions were obtained only with dienes. One comparison was made of the efficacies of ammonium iridium chloride and bis(1,4-cyclohexadienechloroiridium) as catalyst for the polymerization of monomer 6. The salt gave about four times as much polymer as did the complex.

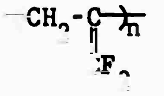


6

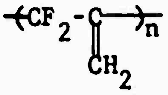
The iridium salt is comparable in activity to rhodium chloride with monomer 6, but much slower than rhodium chloride with monomer 3.

C. PREPARATION AND POLYMERIZATION OF 1,1-DIFLUOROALLENE

A novel fluorine-containing polymer (such as 7 or 8) might be prepared by the polymerization of 1,1-difluoroallene (9) with a nickel (0) catalyst which has recently been reported to polymerize allene (23).



$-(CH_2-C(=CF_2))_n-$



$-(CF_2-C(=CH_2))_n-$

8

Professor Tarrant's observations on the thermal instability of 9 indicated that it would not survive as monomer during shipment. Therefore, Professor Tarrant furnished as the precursor 2-bromo-3,3,3-trifluoropropene-1 (10) which was dehalogenated by the reaction

$$CF_3-CBr=CH_2 \xrightarrow[Et_2O]{BuLi} CF_2=C=CH_2$$

10 9

The product 9 has a boiling point sufficiently close to the ether solvent so that purification by distillation is difficult. Hence, the product was obtained as an ether solution which was suitable for use with a nickel (0) catalyst but not with such anionic coordination catalysts as the $TiCl_4-Al(i-Bu)_3$ pair.

The ether solution of 1,1-difluoroallene was used in several exploratory homopolymerizations (Table X). The highest conversion to polymer (40 percent) was obtained in an azobisisobutyronitrile-promoted free radical polymerization (one week at 50°). Lower conversions (15 percent) were observed in a thermal polymerization (one week at 50°) or in a boron trifluoride-promoted polymerization (one week at -80°). Only [illegible] percent solids were obtained in a t-butylmagnesium chloride-promoted reaction. All of the polymers showed only weak infrared absorption at 760 cm^{-1}, indicating few, if any, pendant $=CF_2$ groups along the chain (structure 7). Possible structures for the polymer include 8 or a repeating cyclopropane unit.

Table X describes the homopolymerization of 1,1-difluoroallene and its copolymerization with allene, both promoted by nickel (0) bis(1,5-

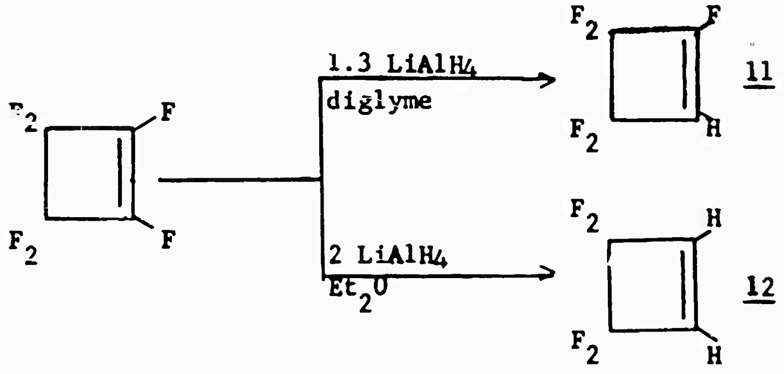
cyclooctadiene). Both proceeded readily to give 81 percent conversion to resins. A homopolymerization of allene under the same conditions gave only 17 percent conversion to a resinous polymer. An analogous series of polymerizations initiated with $VOCl_3$-Al(iBu)$_3$ gave dark resins. The color may possibly be the result of dehydrohalogenation of the polymer. This effect has been previously noted in polymerizations of vinyl chloride with $VOCl_3$ as a catalyst component (24).

It appears that a polymer prepared from allenes as the sole monomers has a chain too rigid to allow rubbery properties. Copolymerization of allenes with dienes might be considered as a route to rubber polymers.

D. PREPARATION AND ATTEMPTED RING-OPENING POLYMERIZATION OF FLUORINATED CYCLOBUTENES

A number of transition metal-catalyzed polymerizations of cyclic hydrocarbon olefins which proceed by opening of the ring to form linear polymers has been described recently. These include polymerizations of cyclobutene (25, 26, 27), cyclopentene (28), norbornene (29), and larger (C_8-C_{12}) rings (30). The application of this polymerization technique to cyclic fluorocarbon olefins could lead to novel fluorinated polymers.

First attempts at this type of polymerization were made with the commercially available perfluorocyclobutene. When these did not succeed (see Table IIA), it was thought that cyclobutenes which did not have fluorine atoms on the double bond might be more reactive in ring-opening polymerization. Hence, the lithium aluminum hydride reduction of perfluorocyclobutene was carried out under two sets of conditions to furnish the potential monomers 11 and 12.

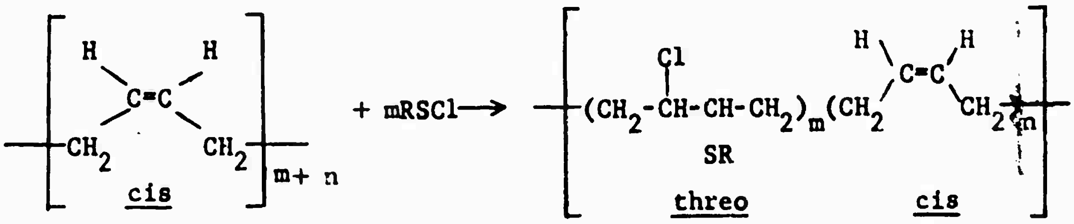


Compound 11 was unreactive in ring-opening polymerization. Compound 12 was obtained only in impure form because of the difficulty of separating it from diethyl ether. An attempt to prepare it in a higher-boiling ether (1,2-diethoxyethane) to permit easier purification was unsuccessful. The polymerizations of 6 promoted with either a $TiCl_4$-based catalyst or Mo or W ring opening catalysts gave only trace yields of polymer (Table IIA). Attempted polymerizations of hexafluoro 1,2-dichlorocyclopentene and 2,3-bis(trifluoromethyl) bicyclo[2.2.1]-heptadiene were also unproductive and this approach was abandoned.

E. CHEMICAL MODIFICATION OF cis-POLYBUTADIENE

1. With Sulfenyl Chlorides

The very low glass transition temperature of the commercially available polymer cis-polybutadiene (Tg = -108°C.) suggested that a rubber meeting the goals of this contract might be prepared from it by adding to the carbon-carbon double bonds one or more reagents which would improve the oil resistance. Sulfenyl chlorides are a class of compounds which add readily to carbon-carbon double bonds, generally adding in the sense $RS^+ Cl^-$. Addition of a fluorinated or other halogenated sulfenyl chloride to cis-polybutadiene might introduce a sufficient number of oil-repelling groups per polymer chain to provide improved oil resistance. This addition was, in fact, found to proceed rapidly at room temperature to give rubbery adducts according to the following equation:



$$\text{Percent Saturation} = \frac{m}{m + n} \times 100$$

The threo configuration of the adduct sites is assigned on the basis of the trans orientation of addition observed in sulfenyl chloride reactions with cyclic olefins (31) and the cis configuration of the unreacted sites is based on the infrared spectrum of the adduct. Thus, the adduct has stereospecificity in its microstructure but a random macrostructure derived from the random location of the sites of addition along the chain. The practical result is a disappearance in the adduct of the crystallization (-64°C.) and melting (-21°C.) phenomena characteristic of cis-polybutadiene.

A preliminary evaluation of these rubbery adducts was made through measurement of glass transition temperature (Tg) with the aid of a Differential Thermal Analyzer. The summary of Tg data given below shows that adducts of perfluorosulfenyl chlorides (CF_3SCl and C_6F_5SCl) display low Tg values to a higher degree of saturation than do the corresponding perchlorosulfenyl chlorides. For the same reason the aliphatic sulfenyl chlorides are preferable to the aromatic analogs.

lass Transition Temperatures (°C.) for Adducts
f cis-Polybutadiene and Sulfenyl Chlorides

ddend	ercent Saturation				
	10	15	20	25	30
F_3SCl	-92	-84	-75	-68	-44
$_6F_5SCl$	-90	-80	-66	-52	-
Cl_3SCl	-85	-50	+28	-	-
Cl_5SCl	-99	-50	+18	-	-

sample of an adduct of pentafluorobenzenesulfenyl chloride and cis-polybutadiene in which sufficient sulfenyl chloride was added to saturate 15 percent of the double bonds of the polymer was examined at the U.S. Army Natick Laboratories. A sulfur-cured specimen showed an R67.5 twist recovery (32) value of -59° which is considered excellent (33). However, the volume swell of 122 percent in 70/30 isooctane/toluene is excessive.

2. With Nitrosyl Fluoride

This reagent was used as the liquid complex with hydrofluoric acid, NOF·3HF. In this form it was found to add to cis-polybutadiene at room temperature to form adducts which varied from rubbers to resins with ncreasing extent of reaction.

lemental analysis of all these adducts indicated more fluorine han nitrogen on a molar basis, corresponding either to addition of HF as well as NOF or to formation of a stable complex between NOF adduct and HF. Although some of these polymers had Tg values near -100°C, they were very difficult to process on a mill, behaving as if cross-linked. Further, they gave low modulus values when cured as gum stocks by dicumyl peroxide. Properties of some typical adducts are summarized below. It appears that extensive further work would be required to develop a practical rubber from the NOF adducts.

Polymer	% N	% F	% Saturation	Tg	Gum Stock Vulcanizate Volume % Swell in Fuel C, 48 hrs, R.T.
cis-Polybutadiene	-	-	0.0	-108	252
NOF·3HF adduct 1	2.17	6.14	19.6	-103	116
NOF·3HF adduct 2	2.66	6.37	20.7	- 99	
NOF·3HF adduct 3	6.2	29.3	148.3		

III. EXPERIMENTAL

A. APPARATUS

The vacuum train shown in Figure 1 was assembled using high-vacuum, hollow-plug stopcocks. This apparatus permits independent loading of two reaction vessels with measured amounts of volatile monomers by means of trap-to-trap distillation through a gas-measuring bulb. Vacuum was obtained with a 3-stage quartz mercury vapor pump and a rotary oil fore-pump. The inert gas was either argon or dry nitrogen which had been deoxygenated over hydrogen-reduced "active copper" (34).

Monomers were measured as ideal gases at room temperatures and one atmosphere pressure. The measuring apparatus had a capacity of 525 ml. (about 22 millimoles). A capillary from the top of the bulb led through a vacuum-tight hypodermic needle to the reaction vessel cap. The gas sample was isolated by means of a mercury cut-off below the measuring bulb. A hand-raised mercury piston was changed to an argon-operated piston with Experiment 89, to avoid exposure of the mercury to air, with consequent trapping of that impurity.

B. MONOMERS

. General

The following monomers were purchased from commercial sources: ethylene (research grade), propylene (research grade), allene, butadiene (instrument grade), isobutylene, vinyl fluoride, vinyl chloride, vinylidene fluoride, tetrafluoroethylene, hexafluoropropene, hexafluorobutadiene, hexafluorobutyne-2, 4-bromo-3-chloro-3,4,4-trifluorobutene-1, perfluorocyclobutene, 2-fluoropropene, 2-(trifluoromethyl)propene, hexafluoro-1,2-dichlorocyclopentene, 3,4,4-trifluoro-4-bromo-2,3-dichlorobutene-1, 1,1,2-trifluoro-2-chloro-3-methyl-3-vinylcyclobutene, α,α,β-trifluorostyrene and 2,2,2-trifluoroethyl vinyl ether.

The following were furnished by other Department of Defense contractors: 2-bromo-3,3,3-trifluoropropene-1, 1,1,1-trifluoro-2-(trifluoromethyl)-4-pentenol-2, 3-(trifluoromethyl)1-butenyl-3-acetate, perfluoro-1,5-hexadiene, 1,1,3,3,5,5,7,7-octafluoro-1,6-heptadiene, 1,1,2-trifluoro-3-vinyl-cyclobutene-2, 2,3-difluoro-2,3-dichlorobicyclo[2.2.1]-heptene-5 and 2,3-difluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]-heptene-5.

Other monomers and precursors were prepared as described below. All monomers were analyzed before use by vapor phase chromatography. Conditions and results of the VPC analyses are summarized in Table XVI.

Butadiene was distilled from a cylinder into a flask at -78°, stored in a stainless steel bomb at 5° over molecular sieve (in later stages redried over molecular sieve or 1/8 spheres of H-151 Alcoa Alumina) and

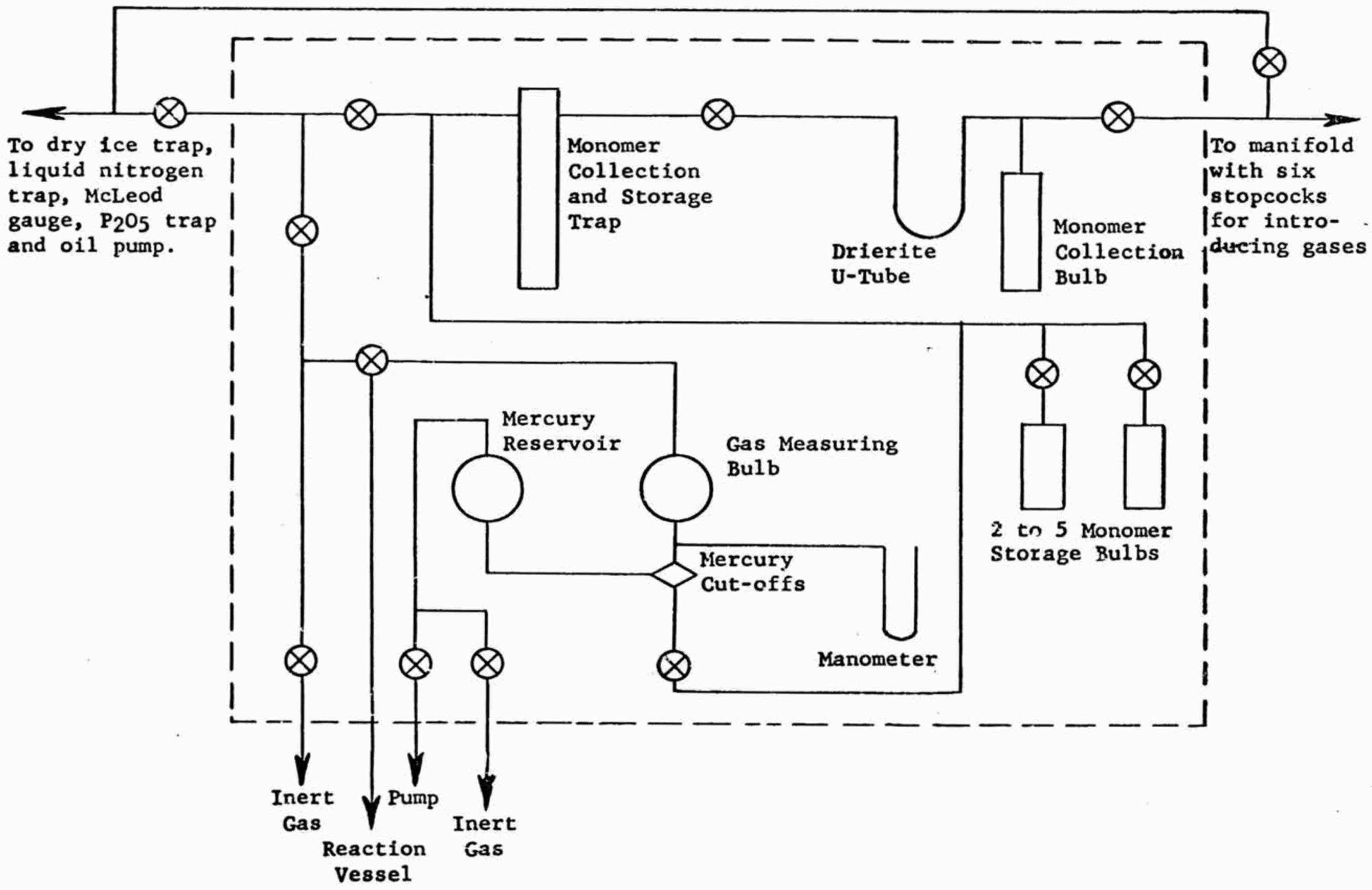


Figure 1. Vacuum Line for Handling Gaseous Monomers. Portion Inside Dotted Lines is in Duplicate

outgassed. Aliquots of 40 to 50 g were condensed in the vacuum line with liquid nitrogen and outgassed by trap-to-trap distillation through Drierite, followed by pumping the frozen monomer until non-condensable gas after a distillation was less than 10^{-3}mm. It was stored in a trap at -78°. Ethylene and propylene were condensed in the vacuum line with liquid nitrogen, dried and outgassed by trap-to-trap distillation through a tube of Drierite, followed by pumping off uncondensable gas from the frozen monomer, and stored at the boiling point of nitrogen until used. Other monomers obtained in cylinders were handled the same way. Cylinders were connected to the vacuum line by 1/4 inch pipe connection to swagelok fitting to a spiral of 1/4 inch stainless tubing with a ₮ 10/30 joint, metal to glass of the vacuum line. The connection was pumped out to 10^{-5}mm. as a leak test before introducing monomer to the line.

Monomers boiling near room temperature were best handled under argon by syringe as solutions in the polymerization solvent, and chilled a little if necessary.

Liquid monomers were dried with Linde 5A molecular sieve, outgassed with argon and stored in the refrigerator under argon. Where inhibitor was to be removed, this was done by chromatography with Al_2O_3 under argon, followed by flushing with argon (1,1,2-trifluoro-3-vinylcyclobutene-2). Trifluoroethyl vinyl ether was distilled into the vacuum line, outgassed and dried over Drierite, and loaded as vapor (with difficulty due to condensation).

Monomer densities (of liquids) not given in the literature were calculated by the Schroeder correlation (35) plus an approximate correction for temperature difference between the boiling point and temperature of use. This procedure was tested on four fluorinated dienes for which density data are given. The average difference between literature-reported density and that calculated at the boiling point by the correlation was 1.9 percent, a satisfactory agreement for our purposes.

2. 1,1-Difluoroallene

A solution of 51.2 g. (0.294 mole) of 99.7 percent 2-bromo-3,3,3-trifluoropropene-1 in 200 ml. of ethyl ether was cooled to -90° with liquid nitrogen and treated dropwise with 132.2 g. (0.314 mole) of 15.2 percent butyllithium-in-_n_-hexane and 76.7 g. of ethyl ether. The addition, carried out under a nitrogen atmosphere, required two hours at -87 to -97°. Distillation with a flash temperature up to 30° gave a total of 23.5 g. of volatile liquid product. Vapor phase chromatography (VPC) showed the following components: 0.9 percent nitrogen, 0.9 percent carbon dioxide, 28.6 percent 1,1-difluoroallene, 7.0 percent n-butane, 2.8 percent n-hexane and 59.8 percent ethyl ether.

The higher-boiling residue was swept with nitrogen overnight to entrain 140 g. of dry ice-condensable liquid. Vapor phase chromatography of this distillate showed it to contain 3.6 percent of 1,1-

difluoroallene.

The total yield of 1,1-difluoroallene was 53 percent.

3. Preparation of 1,1,2-Trifluorobutadiene

This material, b.p. 7.8-9°, was prepared from 4-bromo-3-chloro-3,4,4-trifluorobutene-1, in 81-92 percent yield by the zinc-promoted dehalogenation method of Tarrant and Lilyquist (14).

4. 5,5,5-Trifluoro-4-(trifluoromethyl)-1,3-pentadiene

The precursor 1,1,1-trifluoro-2-(trifluoromethyl)-4-pentenyl-2-acetate was prepared as follows: a mixture of 124 g. (0.60 mole) of 1,1,1-trifluoro-2-(trifluoromethyl)-4-pentenol-2, 183.8 g. (1.80 moles) of acetic anhydride, 56.8 g. (0.693 mole) of sodium acetate and 222.7 g. (3.71 moles) of glacial acetic acid was refluxed for five hours. The clear solution was cooled to room temperature and stirred with 466 g. of water. A lower layer of 109 g. was separated, washed with water and dried to give 90.8 g. of crude ester, n_D^{21}1.3332. Vapor phase chromatography showed this to be 75 percent ester, 21 percent unreacted alcohol and 4 percent unknown.

Fractionation of 89.8 g. of the crude product and 13.6 g. of trichlorobenzene in a spinning-band column gave the following fractions:

Fraction	Weight, g.	b.p., °C. (mm.)	n_D^{21}	VPC Analysis		
				% Ester	% Alcohol	% $C_6H_3Cl_3$
1	2.9	56 (730)	1.3995	0.4	21	-
2	69.8	103-92(500-400)	1.3485	71.3	27.7	1.0
3	13.2	84 (400-300)	1.3488	92.7	6.5	0.8
4	1.4		1.3495	96.6	3.1	0.3

These fractions constitute a 43 percent yield of the ester corrected to 100 percent purity.

A second preparation of the acetate was carried out with a 17-hour reflux period. Isolation of the crude acetate, as described above, gave a yield of 86.5 percent of 94 percent pure product, n_D^{21} 1.3494.

1,1,1-Trifluoro-2-(trifluoromethyl)-4-pentenyl-2-acetate was pyrolyzed by passage through a Vycor column packed with 4-mm. glass Raschig rings and heated at 525-535° over a 22-cm. length. The rate of addition of ester to the tube and the flow of nitrogen carrier gas were adjusted to give a residence time in the heated zone of about 10 seconds. The crude product was collected in a dry ice trap, warmed to room temperature, washed with water, dried and distilled at reduced pressure. The following fractions were collected:

Fraction	Weight, g.	b.p., °C. (mm.)	n_D^{25}	% Purity by VPC
	9.5	38 (240)	1.3410	94.9
	13.0	33 (200)	1.3413	93.6
	0.8	30 (135)	1.3425	77.7
	5.2	dry ice trap	1.3418	90.4

Fractions 1-4 represent a 62 percent yield of the diene corrected to 100 percent purity. The reported refractive index for the diene is n_D^{20} 1.3447 (36), which may be extrapolated to 1.3422 at 25°.

Anal. Calcd. for $C_6H_4F_6$: C, 37.91; H, 2.12; F, 59.97

Found: C, 38.74; H, 2.21; F, 56.93.

5. Attempted Catalytic Dehydration of 1,1,1-Trifluoro-2-(trifluoromethyl)-4-pentenol-2

A 20 mm. I.D. Vycor tube was packed for a length of 23 cm. with 70 ml. of Alcoa 6-8 mesh F-1 activated alumina. The alumina was pretreated by heating overnight at 305° under a slow stream of nitrogen. The column was then heated at 270-280° while the alcohol (23.8 g., 0.113 mole) was dropped into the column during three hours under a 50 ml./minute stream of nitrogen. The pyrolysate (13.2 g.) was condensed in a dry ice trap. Negligible condensate was observed in a second dry ice trap. Extensive char formation occurred in the heated tube. Vapor phase chromatography of the condensate showed the presence of 30 percent unreacted alcohol. No diene could be detected.

6. Attempted Phenyl Isocyanate-Promoted Dehydration of 1,1,1-Trifluoro-2-trifluoromethyl-4-pentenol-2

A mixture of 10.4 g. (0.050 mole) of the alcohol, 13.8 g. (0.115 mole) of phenyl isocyanate, 0.2 ml. of dibutyl tin dilaurate and 37.5 g. of xylene was heated overnight at 123° with stirring under a nitrogen atmosphere. After the first hour of heating, 0.41 g. (0.0044 mole) of aniline was added. No carbon dioxide evolution was noted. Volatile material (23.7 g.) swept into a dry ice trap during reaction was shown by vapor phase chromatography to contain no diene.

7. 2-(Trifluoromethyl)-butadiene-1,3

Forty-four and six-tenths grams of 3-(trifluoromethyl)-1-butenyl-3-acetate (84.7 percent pure containing 10 percent of the parent alcohol) was pyrolyzed under the conditions described above to give 39.5 g. of dry ice-condensable products. Distillation gave the following fractions:

raction	Weight, g.	b.p., °C.	Diene Content (by VPC)
	3.9		67% + 32% low boiler
	7.7	30	90%
	10.0	50-60 (75 mm.)	0.4% + 54% HOAc

Anal. Calcd. for $C_5H_5F_3$: C, 49.19; H, 4.13

Found C, 49.66, 59.77; H, 4.22, 4.44

The total yield of diene was 32 percent.

1,2-Bis(trifluoromethyl)-1,4-cyclohexadiene

The method of Putnam, Harder and Castle (17) was used to prepare this compound from hexafluorobutyne-2 (HFB) and excess butadiene (BD) with the following results:

Run No.	HFB, g.(moles)	BD, g.(moles)	Hrs.	°C.	Weight g.	b.p. °C.	n_D^{20}	Yield %
	98 (0.602)	58 (1.07)	39	25	122.6	135	1.3783	94
	160 (0.99)	90 (1.67)	64	25	176.7	135	1.3792	82

The products of both runs were 99.9 percent pure by vapor phase chromatographic assay. The reported n_D^{25} is 1.3778 (17).

Hydrogenation of 1,2-Bis(trifluoromethyl)-1,4-cyclohexadiene

This reaction was run in a model 3911 Parr hydrogenation apparatus to prepare 1,2-bis(trifluoromethyl)cyclohexene, following the procedure of Putnam, Harder and Castle (17). The following runs were made at 20-40 psig in a 435 ml. pressure bottle:

					Product		
Diene, g.(mole)	Conditions	% Hydrogen Uptake	% Yield	n_D^{19}	% Olefin Component	% Aromatic Component	% Other Components
97.7(.452)	Reactor cooled	34	69	1.3782	55	38	7
56.1(.260)[a]	Reactor not cooled	56,77,102	85	1.3753	67	10	23
24.5(.113)[b]	120g. THF solvent	84,93	56	1.3756	94	4	1
12.0(.056)[c]	-	88,91,33					

a. Added in increments of 42.5, 5.1 and 8.5 g.
b. Added in increments of 9.1 and 15.4 g.
c. Added in increments of 12, 10.9 and 20 g.

Preparative vapor phase chromatography of the product of the third run gave a sample of the aromatic component whose infrared spectrum in the 2000-1600 cm^{-1} region indicated m-disubstitution (37).

10. 2,3-Bis(trifluoromethyl)butadiene by Pyrolysis of 1,2-Bis(trifluoromethyl)cyclohexene

A Vycor reaction tube of 22 mm. I.D. was packed with quartz rods and heated to 815-830°C. over a 12-in. length. A vacuum of 3 to 6 mm. was maintained during addition of 57.6 g. (.246 m.) 1,2-bis(trifluoromethyl)-cyclohexene (93.2 percent purity by vapor phase chromatography) over a period of five hours. A condensate of 3.5 g. was obtained in the collection flask at room temperature, while the two dry ice traps contained 12.7 g. and 1.6 g. for a total of 17.8 g. The traps were rinsed with cold trichlorobenzene to give 91.9 g. solution to which was added 0.2 g. t-butyl catechol. The mixture was stored in dry ice and distilled three days later in a 12-inch packed column.

Fraction No.	Weight grams	B.P., °C.	n^{21}	% Diene (by VPC)	Yield, %
	0.1		-	-	
	2.4	52-58	1.3388	83.7	5.2
	0.6	70-74	1.4040	31.7	
	1.3	83-86	1.4058	-	
	2.0	112-135	1.4010		
	8.0	178-198	1.4972		
	4.0	198-200	1.5557		
	9.6	213	1.5680		
		Residue	1.5692		

A second reaction run at 725°C. under 3-5 mm. gave 15.4 g. (54 percent) of product which was 96 percent pure.

1. 1.1,2-Trifluoro-3-chloro-1,3-butadiene

n a one-liter 3-neck flask were placed 62.3 g. (0.865 m.) 90 percent zinc dust. 1.4 g. zinc chloride, and 118.7 g. n-butanol. The mixture was heated to 84°C. with agitation under 250-300 mm. vacuum. Addition of 48.3 g. (0.188 m.) 3,4,4-trifluoro-4-bromo-2,3-dichlorobutene-1 was carried out over 20 minutes and 63.6 g. of condensate was trapped with a dry ice condenser. Another 47.8 g. (0.185 m.) of the dichloro compound was added over 43 minutes to give 48 g. crude product. A second dry ice trap used in both runs contained 11.4 g. (21.5 percent) of crude diene.

The three main fractions were combined and distilled at 40-60°C. pot temperature and 75-150 mm. There was obtained 34.3 g. (64 percent) of diene which was redistilled through a 12-inch long packed column at 184-188 mm. to give 17.2 g. (30 percent) of the diene of 92.8 percent purity. The major impurities were 4.8 percent of a low boiler and 0.5 percent of a high boiler believed to be n-butanol.

12. Reaction of Isopropenylacetylene and Chlorotrifluoroethylene

A 2-l. Parr bomb was alternately evacuated to 100 mm. and pressurized to 50 psig with argon. The evacuated bomb was then charged with 190 g. (2.88 mole) of freshly distilled isopropenylacetylene and 1 g. of 4,4'-thiobis-(6-*t*-butyl—2-ethylphenol) (inhibitor). The bomb was chilled in dry ice and charged with 429 g. (3.69 moles) of chlorotrifluoroethylene.

The reactor was agitated for 30 hours, mainly at 94-104°C. and at about 215 psig maximum pressure. An exotherm developed at about 95°C. and lasted for about five hours with decrease in pressure from about 92 to 100 psig. On cooling to 26°C., the pressure was 25 psig. Cooling and venting gave a liquid residue of 614 g. which decreased to 507 g. weight on standing three hours in the hood.

The reaction was repeated on approximately the same scale. Distillation of the combined residues gave 299 g. (28.5 percent) of 1,1,2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, b.p. 40-43° (26-29 mm.) followed by 112 g. (10.7 percent) 1,1,2-trifluoro-2-chloro-3-isopropenylcyclobutene-3 and then by 147.9 g. (7.9 percent) of 1,1,2-trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl)cyclobutane, b.p. 59-61° (1.3 mm.). There was a residue of 97 g.

13. 3,3,3-Trifluoropropyl Chloride

In a 5-l. 3-necked stainless steel flask were placed 500 g. (2.80 moles) of antimony trifluoride and 112 g. of antimony pentachloride. There was an exotherm from 16° to 38°. The mixture was warmed to 49° and 252.3 g. (1.39 moles) of 1,1,1,3-tetrachloropropane was added over a period of three and one-third hours. During this time the flask temperature was 65-88° and gentle reflux occurred. Volatile products formed during the reaction were collected in a dry ice condenser and were combined with the material distilled off when the flask temperature was raised to 110°. The crude product was washed with 7.5 *N* hydrochloric acid and redistilled to give 43.6 g. (27 percent) of 3,3,3-trifluoropropyl chloride, b.p. 44-47°, n^{20} 1.3280-1.3282.

Vapor phase chromatographic analysis of the product showed it to be 98.2 percent pure with 1.4 percent of a more volatile component.

14. 3,3,3-Trifluoropropyl Iodide

In a 750 ml. stainless steel bomb were placed 1.2 g. azobisisobutyronitrile and 250 g. of methanol. The bomb atmosphere was replaced with nitrogen by five times evacuating to 0.2 mm. and refilling with nitrogen to 20 psig at dry ice temperature. The bomb was reevacuated and charged with 133 g. (0.682 mole) of trifluoromethyl iodide.

The bomb was stirred and heated at 66-67° with incremental addition of ethylene whenever the pressure dropped to 80 psig. The total ethylene uptake was 29 g. (152 percent of theory for a 1:1 adduct). The bomb was cooled and the methanol solution diluted with 1000 ml. of water to give 114.6 g. of heavy oil which was 86 percent 3,3,3-trifluoropropyl iodide by vapor phase chromatography. Distillation through a 12-inch packed column gave product, b.p. 88-89°, n_D^{25} 1.4170, 99.5 percent pure by vapor phase chromatography.

15. 3,3,3-Trifluoropropene

a). By dehydrochlorination of 3,3,3-trifluoropropyl chloride - A solution of 17.8 g. (0.134 mole) of 3,3,3-trifluoropropyl chloride in 69.2 g. of 95 percent ethanol was treated with 30 ml. of 1.7 N ethanolic potassium hydroxide followed by another 90 ml. after 20 minutes. The solution was heated to 67° during 90 minutes to give 11.5 g. of volatile product collected in a dry ice condenser. Distillation of the crude product gave 10.9 g. (85 percent) of 3,3,3-trifluoropropene, b.p. -22°. A second reaction gave 11.4 g. (89 percent) of product, b.p. -22°.

(b). By dehydroiodination of 3,3,3-trifluoropropyl iodide - The method described above gave 78 percent yield of the olefin, b.p. -22°, when applied to the corresponding iodo compound.

16. 1,1,2,2-Tetrafluoro-3-vinylcyclobutane

The cycloaddition of butadiene and tetrafluoroethylene was carried out under conditions similar to those reported (38) except that a solvent (240 g. o-dichlorobenzene) was used, reducing the pressure of 85 g. (1.57 moles) of butadiene and 38 g. (0.38 mole) of tetrafluoroethylene in a 750 ml. stainless steel bomb to less than 200 psig. The solution was heated eight hours at 130°, cooled and distilled to give 40 g. (68 percent) of adduct containing 3 percent of butadiene as determined by vapor phase chromatography.

17. Preparation of 2,3-Bis(trifluoromethyl)norbornadiene

A 1-l. Parr autoclave was cooled with dry ice, evacuated to 1 mm. pressure and charged with 23.1 g. (0.350 mole) of freshly distilled cyclopentadiene, 269 g. of petroleum ether and 64.0 g. (0.395 mole) of hexafluoro-2-butyne. The reactor was allowed to warm to room temperature overnight. The homogeneous mixture was freed of petroleum ether by distillation at reduced pressure to leave a residue of 71.4 g. (99.4 percent) of crude 2,3-bis(trifluoromethyl)norbornadiene, n_D^{21} 1.3695.

Two fractional distillations gave 47.1 g. (59 percent) of pure diene, b.p. 38° (28 mm.), 23° (10 mm.), n_D^{19} 1.3692-1.3704, whose infrared spectrum showed maxima at 1690 cm.$^{-1}$ (CF_3-C=C), 1570 cm.$^{-1}$ (strained C=C) and 1190-1110 cm.$^{-1}$ (very strong, C-F). Vapor phase chromatography indicated the presence of eight minor components totalling 1.2 percent; one component amounted to 0.6 percent. The nuclear magnetic resonance spectrum is consistent with the assigned structure and does not allow a four-membered ring structure.

18. Reduction of Hexafluorocyclobutene to 2,3,3,4,4-Pentafluorocyclobutene

In a 2-l. 3-necked flask were placed 1117 g. of diethylene glycol dimethyl ether (Ansul Ether 141) and 30.6 g. (0.81 mole) of lithium aluminum hydride. The mixture was cooled to -62° with stirring and treated with 100.8 g. (0.623 mole) of gaseous hexafluorocyclobutene over a period of 65 minutes. The mixture was stirred two hours while the temperature rose to 10° and then quenched by the successive addition at 20-33° of 32 ml. of water, 29.3 g. of 20 percent sodium hydroxide, 50 ml. of water and 30 g. of 20 percent sodium hydroxide. Partial distillation of the hydrolyzed product gave 38.2 g. of crude product. Redistillation through a spinning band column gave 19.0 g. (21 percent) of product, b.p. 32-33°, n_D^{26} 1.3225. Vapor phase chromatography assay indicated a purity of 98.4 percent.

19. Reduction of Hexafluorocyclobutene to 3,3,4,4-Tetrafluorocyclobutene in Ethyl Ether Solvent

In a 2-l. flask were placed 794 g. of ethyl ether and 42.2 g. (1.11 moles) of lithium aluminum hydride. The mixture was cooled to -75°. Hexafluorocyclobutene (92.0 g., 0.568 mole) was added during 105 minutes and the mixtures allowed to stand 30 minutes at -75°. The reaction mixture was quenched by addition of 150 ml. of water (temperature rose to -35°) and 382 g. of 46 percent sulfuric acid at -40° to -50°. The mixture was stirred overnight at room temperature. The lower aqueous layer was extracted twice with 100-ml. portions of ether and combined with the upper organic layer. The combined organic products were dried over magnesium sulfate and distilled through a spinning band column to give 3,3,4,4-tetrafluorocyclobutene containing some ethyl ether. Calculation from vapor phase chromatographic analysis showed the yield of pure tetrafluorocyclobutene was 17.9 g. (25 percent).

20. Attempted Reduction of Hexafluorocyclobutene to 3,3,4,4-Tetrafluorocyclobutene in 1,2-Diethoxyethane Solvent

In a 2-l. three-necked flask were placed 602 g. of 1,2-bis-(ethoxy) ethane and 29.2 g. (0.77 mole) of lithium aluminum hydride. The mixture was cooled to -70°. Hexafluorocyclobutene (98.1 g., 0.605 mole) was added at -70 to -72° over a period of 95 minutes. The reaction mixture was allowed to stand another 30 minutes at -70° and then was treated with a solution of 117 g. of n-butanol and 21 g. (1.17 mole) of water. This addition required 10 minutes and produced a slight exotherm. Excess water (125 g., 7 moles) was added. As the mixture was warmed to 40°, an exotherm to 60° occurred with some loss of volatile products. The reaction mixture was acidified with 100 ml. of sulfuric acid in 200 ml. of water and stirred overnight at room temperature under a slow stream of nitrogen. Passing the nitrogen stream through a dry ice trap condensed 42 g. of volatile product, of which 13 g. boiled below room temperature. Vapor phase chromatography of both fractions showed little if any product of the C_4HF_5 or $C_4H_2F_4$ type, nor could any be found upon distillation of the acidified hydrolysis residue.

21. 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynyl cyclobutane

The monomer was prepared from isopropenylacetylene and chlorotrifluoroethylene according to the procedure of Sharts and Roberts (39). A portion of the product was fractionally distilled to give 105 g. of n_D^{21} 1.4035 (lit. n_D^{25} 1.4039) b.p. 41.0 - 43.0 (36 mm.).

C. CATALYST COMPONENTS

1. General

The following were purchased from commercial sources: aluminum triisobutyl, ethyl aluminum sesquichloride, vanadium oxychloride, molybdenum pentachloride, tungsten hexachloride, vanadium acetylacetonate, tetra-*n*-butyl titanate, cobalt octoate (12 percent polymerization grade) and titanium tetrachloride. Commercial butyl vanadate was used until Experiment 55, when material prepared as described below was used. Titanium tetraiodide was first prepared as a 0.5 percent suspension in ethylbenzene as described below. Beginning with Experiment 50 an 0.018 *N* solution in benzene was used. From Experiment 90 the solution was prepared from commercially available titanium tetraiodide. Other catalyst components were prepared as described below.

2. *n*-Butyl Vanadate

This material, b.p. 128-129° (1.5 mm.), was prepared in 41.3 percent yield from vanadium pentoxide and dried *n*-butyl alcohol by the method of Orlov and Voronkov (40).

3. 5 Percent Suspension of Titanium Tetraiodide in Diethylbenzene

A preparation of a 0.1 *M* TiI_4 suspension in inert solvent was made according to the directions of Dr. Walter Nudenberg (41).

4. Dehydration of Zirconium Acetyl Acetonate (42)

Zirconium $(acac)_4.10H_2O$ (K. & K.) was dehydrated by pumping at room temperature on 59 grams of starting material at 2 x 10^{-4} mm. (the vapor pressure of water at -78°C.) as long as water was evolved. The dried material was dissolved in 200 ml. benzene and considerable brown sludge filtered out. To the clear benzene solution was added 700 ml. petroleum ether to precipitate the complex. After filtration, washing with petroleum ether and vacuum drying, a yield of 20.6 gm. was obtained.

5. Tetrakis (diethylamino)titanium

The method of Bradley and Thomas (43) was used to prepare this material on a scale of 0.20 mole. The product, b.p. 94-96° (0.1 mm.), $n_D^{19.5}$ 1.5357, was obtained in 18 percent yield.

6. Nickel (0) Bis(1,5-cyclooctadiene)

A Soxhlet extraction apparatus was assembled with 12.85 g. (0.050 mole) of nickel (II) acetylacetonate in a 20 x 80-mm. thimble and a boiling flask containing 72 ml. (63.4 g., 0.586 mole) of 1,5-cyclooctadiene, 25 ml. (19.9 g., 0.100 mole) of aluminum triisobutyl, and 150 ml. of ether. After refluxing the ether solution in the boiling flask for 24 hours, 3.8 g. of nickel (II) acetylacetonate remained in the thimble. Large yellow crystals of nickel (0) bis(1,5-cyclooctadiene) had formed in the flask. The mixture was chilled in an ice-water mixture and the liquid drawn off. The residue was washed with 10 ml. of ether and dissolved in 100 ml. of dry benzene to give a catalyst solution found to be effective in causing polymerization of allene.

X-ray fluorescence analysis of the catalyst solution showed the yield to be 5 g. or 52 percent based on nickel (II) acetylacetonate used.

7. Decyl Magnesium Iodide in Heptane

A baked, two-liter flask was equipped with stirrer, reflux condenser, pressure equalizing dropping funnel, heating mantle, and nitrogen blanket. In it was placed 26.7 g. (1.1 mole) of ether washed magnesium. There were added 100 ml. ethyl ether, 15 ml. of 1-iododecane, and a crystal of iodine. After the iodine color was gone, ether was added to cover the magnesium. The remainder of 450 ml. of ether and 258 g. (1 mole) of 1-iododecane was added over 3/4 hour while the flask was chilled with ice water. Stirring and refluxing were continued for another half hour after all the halide was added.

The magnesium was separated by decantation in the dry box. With stirring, the ether was stripped off under vacuum, ending by heating with an oil bath at 150°C. at a pressure of 15 mm. After the slurry had cooled to 50°C. it was taken up in 500 ml. dry heptane by stirring under argon. The flask was rinsed out with 200 ml. heptane, while the slurry was split into two equal parts in the dry box, and stored in 26 ounce beverage bottles.

Addition of excess HCl and back titration with N/10 NaOH gave a value of .834 meq./ml. for the suspension of decyl magnesium iodide in heptane.

D. SOLVENTS

Benzene (reagent grade) and heptane (pure grade) were chromatographed through a 15-cm. layer of coconut charcoal and a 45-cm. layer of silica gel under dry nitrogen. They were stored in dried bottles over 9.6 percent sodium-lead alloy under argon or oxygen-free nitrogen. Methylene chloride was chromatographed through Linde 5A molecular sieve and stored in a dry tank over Linde 5A molecular sieve.

E. POLYMERIZATION TECHNIQUES

1. With Transition Metal Compound and Aluminum Alkyl (Ziegler-Natta Catalyst)

In a typical early experiment (11-C, Table I), a 100-ml. test tube tooled at the top for a soda bottle cap was baked for 48 hours at 130°C. The tube was then cooled under a stream of argon and charged with 10 ml. of 0.05 M tetra-n-butyl titanate in dried benzene and 2.0 ml. of 0.95 M aluminum triisobutyl in dried benzene. It was sealed with a bottle cap having a gasket of 0.050-inch fabric-reinforced butyl rubber and a liner of 0.020 inch nylon, shaken and then heated for 15 minutes at 40°C. to develop the catalyst. The tube was chilled in dry ice and connected under a blanket of nitrogen to the vacuum train shown in Figure 1. The tube was evacuated to 0.001 mm. in two minutes and charged with 23.5 +/- 1.0 moles of hexafluoropropene. It was pressured to 4 psig with argon and transferred to a 49°C. water bath where it was gently agitated for 329 hours. The final pressure was measured, the tube vented, uncapped and solvent allowed to evaporate. The residue in the tube was digested overnight at room temperature with a solution of 5 parts isopropanol - 1 part concentrated HCl. After soaking, it was given a water soak, isopropanol soak (with phenyl β-naphthylamine if unsaturation was present in the polymer), and was vacuum dried at room temperature. Decantation and/or centrifuging were used to recover small amounts of material. The insoluble product was dried after decantation of the hydrochloric acid. There remained a trace of brown polymer in the form of a film.

From Experiment 16 on, the general practice was to form the catalyst (i.e., mix the two components) in the presence of monomer. This procedure frequently gives a more active catalyst and a catalyst which makes amorphous polymer with certain monomers. In this procedure one of the catalyst components was the last ingredient loaded into the tube and was added immediately after the cold tube had been loaded with monomer and pressurized with dry nitrogen. The tube was warmed at once with continuous shaking to room temperature and then stirred 15 minutes at room temperature for catalyst development. At the end of the polymerization period the tube was vented and its contents poured into isopropanol/hydrochloric acid (80:20, by volume). The polymerization tube was rinsed with the same acidic alcohol solution. The mixture was allowed to stand 24 hours. The product was separated by decantation, washed with distilled water and soaked in it one day. After a third day of soaking in isopropanol, and a methanol wash, the product was vacuum dried at room temperature. Other variations, such as centrifuging, were resorted to if necessary. Where the product was unsaturated, 15 to 50 mg./l of phenyl-beta-naphthylamine were added to both isopropanol solutions. The weighed, recovered polymer was tested by X-ray diffraction, if a solid or resin, and by infrared, as a film or KBr pellet. After sampling, 2 parts phenyl β-naphthlyamine were added to rubbery polymers on a mill. Fluorine analyses were run by Microanalysis, Inc. or Schwarzkopf Microanalytical Laboratory. Differential thermal analyses and swelling tests were run by standard methods.

Beginning with Experiment 16, the use of nylon liners was discontinued because of plasticizer extraction; Teflon liners were found to be satisfactory. After some experimentation with Paracril gaskets for liner backing in the case of vinylidene fluoride only, a return was made to butyl gaskets.

Beginning with Experiment 27, the gas blanket for all purposes was high purity nitrogen deoxygenated over active copper and dried with 5A molecular sieve. The use of an argon atmosphere in earlier experiments had led to difficulty in evacuating tubes frozen in liquid nitrogen.

2. With Rhodium- or Iridium-Based Initiator

These were carried out by the aqueous emulsion technique described by Rinehart, Smith, Witt and Romeyn (27).

F. CHEMICAL MODIFICATION OF CIS-POLYBUTADIENE

1. Materials

Trifluoromethanesulfenyl chloride and trichloromethanesulfenyl chloride were purchased from commercial sources. Pentachlorobenzenesulfenyl chloride and pentafluorobenzenesulfenyl chloride, b.p. 38° (20 mm.), n_D^{25} 1.4925, were prepared from the corresponding thiophenols by the method of Almasi and Gants (44). Nitrosyl fluoride was used as a complex of the empirical formula $NOF \cdot 3HF$.

2. Addition of Pentafluorobenzenesulfenyl Chloride to *cis*-Polybutadiene

Typically, a 5 percent solution of *cis*-polybutadiene in carbon tetrachloride was treated at room temperature with a solution of pentafluorobenzenesulfenyl chloride in carbon tetrachloride. Reaction appeared to be complete in five minutes as judged by fading of the sulfenyl chloride color. Removal of the carbon tetrachloride solvent left a rubbery residue.

3. Addition of Nitrosyl Fluoride-Hydrogen Fluoride (NOF-3HF) to *cis*-Polybutadiene

A solution of 6.55 g. (0.121 mole) of *cis*-polybutadiene in 145.7 g. of *n*-heptane was placed in a polyethylene bottle, diluted with 337 g. of reagent chloroform, and treated with 6.30 g. (0.575 mole, 0.475 equiv.) of $NOF \cdot 3HF$. The bottle was closed and the mixture was stirred overnight at room temperature. A slight pressure rise was noted. An insoluble solid (0.75 g.) was removed. A 94-g. aliquot of the reaction mixture was stirred into 1200 ml. of *n*-heptane to precipitate 1.10 g. of brown rubber.

Anal. Calcd. for $[(C_4H_6)_{10}NOF \cdot HF]_n$: N, 2.30; F, 6.24

Found: N, 2.66; F, 6.37

A 210-g. aliquot of the reaction mixture was stirred into methanol to precipitate 2.78 g. of brown rubber of Tg -99°.

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TABLE [illegible]

HOMOPOLYMERS OF FLUORINATED MONOMERS WITH [illegible] COORDINATION CATALYSTS

Monomer[a] Expt. No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
Vinyl Fluoride							
43-5	1r	30H	89	.025	Black semi-solid		Degraded; unsat. 1700, 1665, 955 cm.^{1}
43-6	2At	30H	89	0	-		-
43-7	3Bt	30H	89	0	-		-
43-8	4Ar	30B	89	0	-		-
43-9	9At	30B	89	0	-		-
Vinylidene Fluoride							
12-A	3C	10H	305	-	Trace fluid		
12-B	3D	10H	305	-	Brown semi-solid		
12-C	3C	10B	305	-	Trace semi-fluid		
12-D	3D	10B	305	-	Brown solid		
12-E	3C	10M	305	-	Trace semi-fluid		
12-F	3D	10M	305	-	Buff solid		
17-1	at right	10B	400	-	Trace white resin		1 mM. $P(C_6H_5)_3$ at 25°
17-2	at right	10B	400	.204	Resinous material mostly catalyst		1 mM. $P(C_6H_5)_3$ at 4°
17-3	at right	10B	400	.093	White product insoluble in i-propanol		1 mM. $(Net_2)_4Ti$ at 4°
1704	at right	10B	400	-	Trace		1 mM. $(Net_2)_4Ti$ at 25°
17-5	10t	10B	400	-	Trace white matl. insol. in HCl		
17-6	10At	10B	400	.445	Solid catalyst residue		
33-1	4Ar	22B	64	0	Solid + .2 ml.oil		Additive .25 mM. anisole
33-2	4Ar	22B	64	.043^{d}	Solid + 0 oil		Additive .25 mM. diphenyl ether
33-3	4Ar	22B	64	0	Solid + .1 ml. oil		Additive .25 mM. triphenyl phosphine
33-4	4Ar	22B	64	0	Solid + .25 ml. oil		Additive .25 mM. tributyl phosphite
33-5	4Ar	22B	64	0	Solid + .2 ml. oil		Additive .25 mM. thiophene
33-6	4Ar	22B	64	0	Solid + .13 ml. oil		Additive .25 mM. ethyl sulfide
33-7	4Ar	22B	64	0	Solid + .45 ml. oil		Additive .25 mM. triethyl amine
33-8	4Ar	22B	64	0	Solid + .40 ml. oil		Additive .25 mM. $[N(CH_3)_2]_3P{=}O$
33-9	4Ar	22B	64	0	Solid + .17 ml. oil		Additive none
34-1	15r	27B	160	0	Solid + .182 gm. oil		Additive .25 mM. anisole
34-2	15r	27B	160	.010	Am.solid + .098 gm.oil		Additive .25 mM. diphenyl ether

Table I (Cont'd.)

Monomer[a] Expt. No.	Cata- lyst[b]	Ml. Sol- vent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
34-2	15r	27B	160	0	Solid + .150 gm. oil		Additive .25 mM. triphenyl phosphine
34-4	15r	27B	160	0	Solid + .170 gm. oil		Additive .25 mM. tributyl phosphite

On addition of M/2 $TiCl_4$ there was reaction with $CH_2=CF_2$ vapor to form black streaks on the tube wall in the 34 series.

36-1	15r	27B	140	.007[e]	Solid + .201 gm. oil		Additive .25 mM. anisole
36-2	15r	27B	140	.005[e]	Solid + .114 gm. oil		Additive .25 mM. diphenyl ether
36-3	15r	27B	140	0	Solid + .135 gm. oil		Additive .25 mM. triphenyl phosphine
36-4	15r	27B	140	0	Solid + .133 gm. oil		Additive .25 mM. tributyl phosphite
36-5	15r	27B	140	0	Solid + .084 gm. oil		Additive .25 mM. thiophene
36-6	15r	27B	140	0	Solid + .072 gm. oil		Additive .25 mM. ethyl sulfide
36-7	15r	27B	140	0	Solid + .084 gm. oil		Additive .25 mM. triethyl amine
36-8	15r	27B	140	0	Solid + .177 gm. oil		Additive .25 mM. $[N(CH_3)_2]_3P=O$
36-9	15r	27B	140	0	Solid + .088 gm. oil		Additive none
35-1	4At	32B	112	.0147	Oil		.115 mM. added water
35-2	4At	32B	112	.0117	Oil		.173 mM. added water
35-3	4At	32B	112	.0098	Oil		.233 mM. added water
35-4	4At	32B	112	.0079	Semi-solid		.338 mM. added water
35-5	15t	32B	112	.0213	Oil		.115 mM. added water
35-6	15t	32B	112	.0204	Oil		.173 mM. added water
35-7	15t	32B	112	.0196	Oil		.233 mM. added water
35-8	15t	32B	112	.0190	Oil		.338 mM. added water

In the 35 series $TiCl_4$ solution was diluted with solvent and frozen before the addition of $CH_2=CF_2$. While there was black reaction product at the interface between monomer and frozen solution of $TiCl_4$, the amount of reaction product was much less than in the 34 series.

37-1	3t	28H	160		None		Additive .25 mM. n-butyl amine
37-2	3t	28H	160		Trace black scum		Additive .25 mM. diethyl amine
37-3	3t	28H	160		Trace black scum		Additive .25 mM. pyridine
37-4	3t	28H	160		-		Additive .25 mM. n-butanol
37-5	3t	28H	160		Trace black scum		Additive .25 mM. diphenyl ether
37-6	3t	28H	160		Trace black scum		Additive none
38-1	3t	28H	138	.001	Black solid		Additive .25 mM. n-butyl amine
38-2	3t	28H	138	0	-		Additive .25 mM. diethyl amine
38-3	3t	28H	138		Trace black smear		Additive .25 mM. pyridine
38-4	3t	28H	138		Trace black smear		Additive .25 mM. n-butanol
38-5	3t	28H	138	.001	Black smear		Additive .25 mM. diphenyl ether
38-6	3t	28H	138	.001	Black smear		Additive none
42-8	9At	30B	148	0	-		-

Paracril gaskets in the 37 series; butyl gaskets in the 38 series.

Table 1 (Cont'd.)

Monomer[a] Expt. No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
Tetrafluoroethylene							
59-3	1r	30H	40	0			
59-4	2t	30H	40	0			
64-1	3t	30B	90	trace	Brown resin		
64-2	4Dt	30B	90	.014	Buff resin		
64-3	5t	30B	90	0.048	Soft, black gum		
2-Fluoropropene							
48-4	1r	18H	64	.012	White resin	Resembles polyethylene	Not clear, continuum
48-5	2t	18H	64	0	-	-	-
48-6	3At	18B	64	0	-	-	-
48-7	5At	18B	64	0	-	-	-
2-Trifluoromethylpropene							
49-4	1r	18H	19	.004	White powder	Faint lines 4.15A 3.70A	Impure
Hexafluoropropene							
13-1	1A	10H	280	-	Trace brown solid		Preformed catalyst heated 15 min. at 45°C
13-2	1	10H	280	-	Trace brown solid		Preformed catalyst heated 15 min. at 45°C
13-3	1A	10B	280	-	Black solid		Preformed catalyst heated 15 min. at 45°C
13-4	1	10B	280	.124	Black solid		Preformed catalyst heated 15 min. at 45°C
13-5	1A	10M	280	-	Trace brown solid		Preformed catalyst heated 15 min. at 45°C
13-6	1	10M	280	.123	Black solid		Preformed catalyst heated 15 min. at 45°C
11-A	3C	10H	329	-	-		Preformed catalyst heated 15 min. at 45°C, run at 49°C
11-B	3D	10H	329		Trace brown film		Preformed catalyst heated 15 min. at 45°C, run at 49°C
11-C	3C	10B	329	-	-		Preformed catalyst heated 15 min. at 45°C, run at 49°C
11-D	3D	10B	329		Trace brown film		Preformed catalyst heated 15 min. at 45°C, run at 49°C
11-E	3C	10M	329		Trace brown grease		Preformed catalyst heated 15 min. at 45°C, run at 49°C
11-F	3D	10M	329		Trace brown gum		Preformed catalyst heated 15 min. at 45°C, run at 49°C

Table I (Cont'd.)

Monomer[a] Expt. No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
14-1	11	10M	240		Little brown resin		Preformed catalyst heated 15 min. at 45°C.
14-2	12	10M	240		Little green brown fluid		Preformed catalyst heated 15 min. at 45°C
14-3	13	10M	240	-	Trace brown solid		Preformed catalyst heated 15 min. at 45°C
14-4	3A	10M	240	.114	Buff solid		Preformed catalyst heated 15 min. at 45°C
14-5	11A	10M	240	-	Trace green-brown solid		Preformed catalyst heated 15 min. at 45°C
14-6	12A	10M	240	-	Little brown solid		Preformed catalyst heated 15 min. at 45°C
14-7	13A	10M	240	-	Trace gray solid		Preformed catalyst heated 15 min. at 45°C
14-8	3E	10M	240	-	Trace brown semi-solid		Preformed catalyst heated 15 min. at 45°C.
15-1	3F	10M	240	-	Little buff solid		Preformed catalyst heated 15 min. at 45°C
15-2	3G	10M	240	-	Little buff solid		Preformed catalyst heated 15 min. at 45°C
16-1	at right	10B	360	-	Buff resinous material		1 mM. $P(C_6H_5)_3$ at 25°
16-2	at right	10B	360	.181	Mostly $P(C_6H_5)_3$		1 mM. $P(C_6H_5)_3$ at 4°
16-3	at right	10B	360	-	Trace brown fluid		1 mM. $(Net_2)_4Ti$ at 4°
16-4	at right	10B	360	-	Trace brown fluid		1 mM. $(Net_2)_4Ti$ at 25°
16-5	10t	10B	360	-	Trace red-brown powder		
16-6	10At	10B	360	.267	Grayish resinous catalyst residue		
18-1	3Kt	20	320	-	Red brown powder		Solvent 50 heptane - 50 CH_2Cl_2
18-2	3Kt	20	320	-	Trace black powder		Solvent 50 heptane - 50 CH_2Cl_2
18-3	3Kt	20	15	-	Black solid		Solvent 50 heptane - 50 CCl_4
18-4	3Kt	20	15	-	Black solid		Solvent 50 heptane - 40 CCl_4
18-5	3Kt	20	320	-	Trace buff & black solid		Solvent 50 heptane - 50 Freon 113
18-6	3Kt	20	320	-	Brown powder		Solvent 50 heptane - 50 Freon 113
18-7	3Kt	20	320	-	Small amt.red brown resin		Solvent 38 heptane - 62 CH_2Cl_2
18-8	3Kt	20	320	-	Small amt.dark powder		Solvent 38 heptane - 62 CH_2Cl_2
19-1	14t	14H	268		1 & 2 combined		Solvent 100 heptane
19-2	14At	12H	268	.123	Buff resin	Amorphous	Solvent 100 heptane
19-3	14t	14	268		3 & 4 combined		Solvent - 72 benzene - 28 heptane
19-4	14At	12	268	.145	Buff resin	Amorphous	Solvent - 83 benzene - 17 heptane
19-5	14t	14	268		5 & 6 combined		Solvent - 72 CH_2Cl_2 - 28 heptane

Table I (Cont'd)

[illegible]^a Expt. No.	Catalyst^b	Ml. Solvent^c	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
19-6	14At	12	268	.037	[illegible] resin	Amorphous	Solvent - 83 CH_2Cl_2 - 17 heptane
19-7	14t	14	268		7 & 8 combined		Solvent 72 CCl_4 - 28 heptane
19-8	14At	12	268	.042	Buff resin	Amorphous	Solvent 83 CCl_4 - 17 heptane
19-9	14t	14	268		9 & 10 combined		Solvent 72 Freon 113 - 28 heptane
19-10	14At	12	268	.056	Buff resin	Amorphous Some TiO_2	Solvent 83 Freon 113 - 17 heptane
20-1	4Er	22B	18	.256	Light brown resin turns to black residue after treatment with conc. HCl	Amorphous	Infrared spectrum unlike polyhexafluoropropene
Hexafluoro-2-butyne							
44-5	1r	30H	64	0	-	-	Infrared spectrum of 44-10
44-6	2t	30H	64	0	-	-	Shows 4 peaks around 1625 cm.$^{-1}$
44-8	3t	30H	64	0	-	-	Also a weaker doublet at 1695
44-10	4Ar	30B	64	.219	Light brown resin	Amorphous rings at 3.5 & 6.8A	Strong bands are located at 1180, 1205, 1270, and 1280. There are also bands at 710, 770 & 875 cm.$^{-1}$
65-3	5t	30B	18		Trace black solid		
1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane							
39-1	1Bt	12H	64	.300	Brown powder		
39-2	2BT	12H	64	.129	Brownish		Sl. exotherm 22% Recovered by $\underline{i}$-PrOH
39-3	3t	12H	64	.084	Light brown		10% treatment, balance by
39-4	5t	12H	64	2.903	Br.fluid polymer		Exotherm 11% addition of water
39-5	9Bt	13B	64	0			0%
63-6	4Dt	20B	117	.003	White resin	Catalyst residue	Catalyst assembled cold in presence of
61-1	5c	12H	16	.98	Semi-fluid		monomer, run at -43°C
61-2	5Bt	12H	16	.50	Semi-fluid		Catalyst assembled at 25°, chilled
61-3	5	12H	16	.73	Semi-fluid		before monomer added. Run at -43°C
61-4	5B	12H	16	.41	Semi-fluid		Catalyst assembled at 25° in presence of
61-5	5t	12H	16	2.67	Semi-fluid		monomer, sl. exotherm, run at 25°C

Table I (Cont'd.)

The infrared spectrum of the ethynyl cyclobutane monomer shows strong ≡C-H absorption at 3305 cm.$^{-1}$, also bands at 2280 and 2122. Strong bands at 1312, 1225, 1140, and 1108 are presumed to be due to fluorine structures. The bands at 998, 965, 950, 900 and 890 are in the cyclobutane ring region, also the weaker lines at 992 and 975.

39-4 polymer has only a trace of absoprtion at 3310. It has the strong bands at 1310, 1232 and 1105, but the band at 1150 is gone. Bands are also present at 1000, 984, 975 (shoulder) and 942.

Monomer[a] Expt. No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
α-Trifluoromethylstyrene							
63-1	3At	8B	117	Trace	White solid		
63-2	4Dt	20B	117	.089	Yellow semi-fluid		
63-3	5t	7B	23	.309	Dark brown gum		
α,β,β-Trifluorostyrene							
63-7	4Dt	20B	117	Trace	Yellow resin		
63-8	5t	7B	117	Trace	Brown resin		
1,1,2-Trifluoro-2-chloro-3-vinylcyclobutane							
46-4	2t	12H	88	0			
46-5	3At	12B	88	0			
46-6	5Ar	12B	88	.018	Brown resin	Amorphous	
1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane							
70-3	5t	10B	22	.005	Brown resin		
70-4	3At	10B	96	Trace	Gum		
70-5	4Ft	10B	96	Trace	White gum		
1,1,2,2-Tetrafluoro-3-vinylcyclobutane							
112-5	3Hr	11B	64	0			
112-6	5Er	11B	64	0			
1,1,2-Trifluorobutadiene							
22-1	17t	18B	64	.003	White resin		
22-2	17At	20B	64	.001	White resin		
22-3	6t	11B	64	.01	White polymer		
22-4	6At	12B	64	.21	Brown powder	Amorphous	
23-1	4Ct	12B	184	.545	Gray resin	Crystalline	4.45A v. strong; 4.0A strong; 2.35 A weak
23-2	4Dt	12B	184	.350	Gray resin	Crystalline	Like 23-1 plus weak lines at 2.2A, 1.7A
23-3	14At	12B	184	trace			
23-4	14t	12B	184	.401	Gray resin	Crystalline	Like 23-1 plus weak lines 3.4A, 2.2A,1.7A

TABLE II (Cont'd.)

Monomer[a] Expt.No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
1,1,2-Trifluorobutadiene (Cont'd.)							
23-5	3Bt	12B	160	1.32	Gray resin	Crystalline	Like 23-1 52% conv. Ziegler polymerization rate .325% conv./hr.
23-6	3At	12B	160	1.02	Brown resin	Crystalline	Like 23-1 plus weak lines at 3.4A, 1.7A
28-1	None	5B	208	.255	10% conversion		Thermal polymerization rate .048% conv./hr.
28-2	None	5H	208	.187	7.4% conversion		Thermal polymerization rate .036% conv./hr
32-1	3B	12B	23	.242	9.5% conversion		Ziegler polymerization rate .41% conv./hr.
32-2	3B	12B	89	1.556	61.5% conversion		Ziegler polymerization rate .69% conv./hr.
27-4f	3IT	10H	112	.836	7.05% conversion		Ziegler polymerization rate .063% conv./hr.
25-1f	3Bt	22B	16	2.83	31.5% conversion		Ziegler polymerization rate 1.85% conv./hr.
68-6	2t	30H	2	.178	Yellow brittle resin		
24-1	4Ar	22B	160	.203	Buff resin	Crystalline like 68-6	I. R. like 27-4

Spontaneously polymerized CF_2=CF-CH=CH_2 (no solvent) is gelled, amorphous, and shows a much more diffuse infrared spectrum than Ziegler or emulsion polymer.

32-2 failed to give a satisfactory unsaturation value as iodine number determined by using mercuric acetate catalyst in chlorobenzene solution. A blend of samples likewise failed when a bromine method was tried.

Infrared spectra were run on 23-1, 23-4, 23-5, 24-1, 25-1, 27-4 and 68-6. Characteristic bands were 3120, 2950, 1730, 1630, 1430, 1380, 1290, 1240, 1180, 1120, 1055, 1020, 920, 875, 680, 645. Between samples there were small differences in the ratio of 1730 to 920 and 1730 to 1630 (water?) but the spectra were almost identical. No very thick films were run to show up C and H more.

Poly(1,1,2-trifluorobutadiene) was tested for solubility in many solvents, M. E. K., chloroform, benzene, chlorobenzene, methylene chloride, cyclohexanone.

The 920 band is probably not vinyl as there is no 990. 1,1,2-Trifluoro-1,4-pentadiene has strong bands at 921 and 986.

Table I (Cont'd.)

Monomer[a] Expt.No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum
2-Trifluoromethylbutadiene							
91-6	3Jr	11B	67	.04	Viscous fluid		Strong bands at 888 cm.$^{-1}$ and in fluorine region
only 7.3 mM. monomer, added as vapor							
1,1,2-Trifluoro-3-chlorobutadiene							
119-4	1t	29H	66	.069	Light brown resin		Feed 4.1 mM. monomer
119-5	1t	25H	66	.355	Light brown resin	Amorphous	Feed 10.5 mM. monomer
Monomer added as a solution 31% by weight in benzene. Conversions are 12% and 24% respectively. Experiment was primarily a test for detonation (cf. chloroprene with this catalyst). Infrared spectrum on 119-5 shows a weak F region, -C≡C- at 2335, 2355, enhanced -CH-, unsaturation 1596-1650, evidence of dehalogenation as compared with 119-1, made with rhodium catalyst.							
5,5,5-Trifluoro-4-(trifluoromethyl)-1,3-pentadiene							
81-3	1t	14H	18,24	.018	Powder		12 mM.monomer .8% conv.run at 25°,then 50°
81-4	3At	9B	18,24	.158	Resin		12 mM.monomer 6.9% conv.run at 25°,then 50°
81-5	14t	9B	18,24	.005	Powder		6.9 mM.monomer 0.4% conv.run at 25°, then 50°
81-6	5At	8B	18,24	.034	Powder		<3.4 mM.monomer >5% conv.run at 25°,then 50°
92-2	6Cr	6B	19	.016)			11.6 mM. monomer run at 60
92-3	6Cr	6B	19	(combined)			11.6 mM.monomer run at 25
92-6	7t	6B	19	.010			11.6 mM.monomer run at 60
92-7	7t	6B	19	0			11.6 mM.monomer run at 25
92-8	7t	12B	19	1.10			22 mM.monomer Butadiene blank 92% conv. at 25°
1,1,2-Trifluoro-3-vinylcyclobut-2-ene							
47-5	3At	10B	138	.399	Brown resin + yellow resin	Amorphous Amorphous	Almost identical Almost identical
Infrared spectrum - 1770 cm.$^{-1}$, 1720, 1450 shoulder, 1415, 1320, 1285, 1220, 1168, 1130 (1070-1080), 1040, 975 shoulder, (920), 895, 835, 725, 650							
47-6	Distillation residue				White resin		Like 47-5 plus weak 950, 690 cm.$^{-1}$

Table I (Cont'd.)

Monomer[a] Expt.No.	Catalyst[b]	Ml. Solvent[c]	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	Remarks and Infrared Spectrum			
2,2,2-Trifluoroethyl vinylether										
59-7	1r	30H	40	.239	Black rubber semi-fluid					
59-8	2t	30H	40	0						
63-4	4Dt	21B	117	.036	Light brown grease					
63-5	5At	7B	117	.681	Brown grease					
Infrared spectrum of 63-5- 2940 cm.$^{-1}$, (1962), 1430, (1388), 1283, 1167, 1128, 996 shoulder, 972, (855), (832), 665										
Ethylene										
40-1	1r	30H	16	.625	95% conv.to white resin	Highly cryst.	Polyethylene spectrum			
Polymer formed while the tube was being thawed, before the catalyst had been stirred.							Starting pressure 48 psi.			
42-6	9At	30B	148	.246	White resin	Sharp polyethylene pattern	Regular polethylene spectrum			
45-3	3At	30H	210	trace	Oily scum					
55-1	2Ct	30H	16	.297	White resin 50% conv.		Test of catalyst preparation			
55-2	2Dt	30H	16	.198	White resin 30% conv.		Test of catalyst preparation			
91-9	1t	29H	17	.661	White resin 105% conv.					
Butadiene								% cis	% trans	% vinyl
24-3	3I	3B	240	.080	Sticky gray rubber			14	26	60
46-9	6At	8.5B	18	.384	Brown rubber		Conv. 32%	31	46	6
46-10	7At	8.5B	18	.751	White rubber, gelled		Conv. 63%	34	64	3
53-5	6Ct	10B	6	.742	Brown rubber		Conv. 62%	82	15	3
53-6	6Bt	10B	21	.641	Brown rubber		Conv. 54%	-	-	-
58-4	6Cr	10B	16	.943	Soft rubber		Conv. 79%	66	28	6
58-5	8rt	10B	16	1.121	Soft rubber		Conv. 94%	79	17	4
65-5	6Dt	15B	19	.968	Soft rubber		Conv. 81%	69	27	4
91-1	6Kr	12B	68	1.14	Rubber		Conv. 96%	80	16	3
91-2	6Kr	12B	68	1.16	Rubber		Conv. 97%	.05 mM. I_2 added		
								63	31	6
92-8	7t	12B	19	1.10	Rubber		Conv. 92%	64	8	28
90-5	6Ir	18B	18	.50	Soft rubber		Conv. 37	78	17	4
90-6	6Ir	18B	18	.90	Fluid rubber		Conv. 67	63	33	4
90-7	26r	18B	18	1.05	Fluid rubber		Conv. 78	88	8	4
90-8	7t	18B	18	1.06	Soft crumb		Conv. 79	60	16	24
90-10	6Lr	12B	18	1.08	Fluid rubber		Conv. 80	67	29	4
90-11	6Ir	18B	18	2.23	Soft rubber		Conv. 83	69	27	4
90-12	6Lr	12B	18	1.13	Fluid rubber		Conv. 84	67	29	4
90-5 and 90-6 through -12 used two different TiI_4 samples. 90-8 had a trace of gel.							90-11 used 44 mM. monomer.			

Table I (Cont'd.)

Monomer[a] Expt.No.	Catalyst[b]	Ml. Solvent	Time hrs.	Yield gm	Product	Remarks and Infrared Spectrum			
							% Cis	% Trans	% Vinyl
101-4	7t	12B	70X[g]	1.064	H. M. wt. rubber	Conv. 89%	67.8	6.5	25.7
101-8	7t	2B10M	70X	1.035	H. M. wt. rubber	Conv. 87%	56.0	10.0	34.0
112-4	7t	12B	65X	1.088	Soft rubber	Conv. 92%	60	7	26
115-1	7t	10B	14 mins. X	.735	Gelled rubber	Conv. 62%	65	14	21
115-2	7Et	10B	5 mins. XX	.979	Soluble rubber*	Conv. 82%	96.9	1.3	1.8
115-3	7Ft	10B	2 hrs. 8 mins.	.219	Soluble rubber*	Conv. 18%	80.6	13.2	6.2
115-4	7Gt	10B	1 hr. 13 mins.	.459	Soluble rubber*	Conv. 39%	81.6	14.4	4.1

*Good clean-up of cobalt - polymer soluble in CS_2.

a. Monomer is 22 millimoles (mM.) unless otherwise stated.
b. All Ziegler catalyst compositions are given in Table XV. Each combination of reducing agent and transition metal compound is referred to by a number. A capital letter is added for each different set of starting amounts of the two components. An "r" or "t" is added to indicate whether the reducing agent or transition metal compound is added first. Nearly all catalysts were formed in the presence of monomer, so the orders of addition are either 1) reducing agent, monomer, transition metal compound; or 2) transition metal compound, monomer, reducing agent. If no "r" or "t" is present in the code, the catalyst is preformed, that is, reducing agent and transition metal were stirred together before the addition of monomer.
c. Solvent codes.
    B represents benzene
    H represents heptane
    M represents methylene chloride
d. Infrared spectra of the solid and liquid products of 33-2 are similar but do not resemble that of high molecular weight polyvinylidene fluoride.
e. X-ray patterns 36-1-amorphous
    36-2-slightly crystalline
f. For 25-1 the feed was 83 mM.; for 27-4 the feed was 110 mM. monomer. 25-1 product was a moldable soft resin
g. X = exotherm XX = strong exotherm

Table IIA

RING-OPENING POLYMERIZATIONS OF FLUORINATED MONOMERS

Expt. No.	mM. Monomer	Catalyst	Ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Powder Pattern	[illegible]
2,3-Bis(trifluoromethyl)bicyclo (2,2,1)-2,5-heptadiene								
41-1	25	5Ct	8B	187	3.89	Viscous oil	-	Blank
41-2	25	5Ct	7B	187	.22	Brownish resin	-	Additive - 2 mM. α-picoline
41-3	25	16t	7B	187	0	-	-	Additive - 2 mM. α-picoline
41-4	25	3Bt	8B	167	.279	Brownish resin	-	Blank
41-5	25	3Bt	7B	187	.060	Brownish resin	-	Additive - 2 mM. α-picoline
Perfluorocyclobutene								
26-1	22	1Ct	6H	306	0	-	-	Run at 25°
26-2	22	1Ct	6H	306	.002	Black polymer	-	Run at 50°, leaked
26-3	22	5Bt	6HB	306	0	-	-	Run at 25°
26-4	22	5Bt	6HB	306	.014	Black polymer	-	Run at 50°
26-5	22	6Et	6B	306	.003	Brown polymer	-	Run at 25°
26-6	22	6Et	6B	306	.005	Brown polymer	-	Run at 50°
26-7	22	3It	6B	306	0	-	-	Run at 25°
26-8	22	3It	6B	306	.003	Brown solid	-	Run at 50°
31-1	22	18t	6H	281	0			
31-2	22	19t	6H	281	0			
31-3	22	20t	6H	281	0			
31-4	22	21t	6H	281	0			
31-5	22	22t	6H	281	0			
31-6	22	23	6H	281	.011	Red powder	Amorphous Very,very faint line at 3.5 Angstroms	
31-7	22	2B	6H	281				
2,3,3,4,4-Pentafluorocyclobutene								
76-1	25	19t	21B	94		Trace brown scum		Assembled & run at 5°
76-2	25	20t	21B	94		Trace brown scum		Assembled & run at 5°
76-3	25	5t	22B	94		Trace brown scum		Assembled & run at 5°
Hexafluoro-1,2-dichlorocyclopentene								
29-1	14.5	19t	1B	287	.020	Brown powder	Amorphous ring 6-6.5 Angstroms	
29-2	14.5	20t	1B	287	.010	Brown powder	-	
29-3	14.5	5t	1B	287	.012	Brown powder	Amorphous ring Faint line at 5 Angstroms	

TABLE [illegible]

EMULSION AND SOLUTION RING-OPENING POLYMERIZATIONS OF HEXAFLUORO-1,2-DICHLOROCYCLOPENTENE -1 AND PERFLUORO-CYCLOBUTENE AT 50° WITH NOBLE METAL CATALYSTS

Expt. No.	30-1	30-2	30-3	30-4	30-5	30-6
Rhodium chloride trihydrate, gm.	.05	.05	-	-	-	-
Ruthenium chloride, gm.	-	-	.59	.59	.59	.59
Distilled water, ml.	10	10	10	10	.75	.75
Nacconol NRSF, gm.	.5	.5	.5	.5	-	-
Absolute ethanol, ml.	-	-	-	-	9.25	9.25
Hexafluorodichlorocyclopentene, mM.	19.5	-	19.5	-	19.5	-
Nitrogen flush & seal						
Perfluorocyclobutene, mM.	-	31	-	31	-	31
Polymerization temperature, °C.	50	50	50	50	50	50
Total time, hrs.	762	204	762	204	762	204
Final pressure, psig	-	37	-	34	-	30
Yield, mg.	1	-	17	31	21	28
X-ray powder pattern	-	-	(	All	amorphous	)

In 30-5, the X-ray pattern shows an amorphous ring centered on 5.6 and a very, very faint larger ring. In 30-6, over 25 lines show an inorganic material resembling Na_2SiF_6.

Table III

ZIEGLER COPOLYMERIZATIONS OF FLUORINATED MONOMERS USING THE THREE COMBINATIONS OF 1,1,2-TRIFLUOROBUTADIENE, HEXAFLUOROPROPENE AND VINYLIDENE FLUORIDE

Catalyst - Type 3t, 2.5 mM. Al(i-bu)$_3$; 1 mM. Ti (OBu)$_4$ prepared by stirring at room temperature in presence of monomer.
Solvent - 40 ml. heptane
Polymerization temperature - 25°

Code	Monomers	Time hrs.	Residual pressure psi	Product	Conversion %	% F	Remarks
27-1	.11 mole $C_4F_3H_3$ .110 ± .002 more C_3F_6	88	55	5.2 gm. White resin Highly crystalline Stronger X-ray pattern at 4.8 Angstroms than the blank 27-4	34	51.53	Too low for significance* Infrared shows more intense F bands at 1040 and 1170 cm.^{1} and a higher ratio of F to unsaturation (1170/1740) than in 27-4 $C_4F_3H_3$ homopolymer
27-2	.11 mole $C_4F_3H_3$ .13 mole $C_2H_2F_2$	88	120	3.7 gm. White resin Highly crystalline X-ray pattern like 27-4 except no line at 4.8 Angstroms	29	50.09	Too low for significance* Infrared shows more intense F bands at 1040 and 1170 and a higher ratio of F to unsaturation (1170/1740) than in 27-4 $C_4F_3H_3$ homopolymer
27-3	.11 mole C_3F_6 .125 ± .005 mole $C_2H_2F_2$	406	144		0		
27-4	.11 mole $C_4H_3F_3$	112	10	.84 gm. White resin	11	52.56	Catalyst 25% of that given above

*Theoretical F contents

$C_4F_3H_3$	52.56
C_3F_6	76
$C_2H_2F_2$	59.4

[illegible]

[illegible] WITH [illegible]

[illegible] Expt. N.	[illegible] Ratio M/E a	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X ray Pattern	Remarks [illegible] Infrared Spectra [illegible]
Vinyl fluoride								
43-1	23.5/11	1r	30H	89	.283	Brown resin	Polyethylene	Polyethylene plus additional pip at 950
43-2	same	2At	30H	89	.131	White resin	Polyethylene	Polyethylene plus weak 911 & 990 Vinyl present
43-3	same	3At	30H	89	.006	White resin	Impure Polyethylene	-
43-4	same	4Ar	30B	89	.087	Greasy fluid	-	Degraded copolymer shows unsatura-tion at 1726
Vinylidene Fluoride								
40-2	23-5/11	1r	30H	16	.242	White resin	Polyethylene	Polyethylene
40-3	same	2t	30H	16	.195	White resin	Polyethylene	Polyethylene
40-4	same	3At	30H	16	.001	-	-	-
42-7	same	9At	30B	148	.010	White resin	Polyethylene in detail but without 4.55 line	$CH_2 = CF_2$ a minor component
Tetrafluoroethylene								
59-1	22/11	1r	30H	40	.237	White solid	Polyethylene	Polyethylene
59-2	22/11	2t	30H	40	.091	White solid	Polyethylene	Polyethylene
2-Fluoropropene								
48-1	22/11	1r	30H	64	.331	Buff resin	Weakened Poly-ethylene	Trace F at 1155, 1230
48-2	22/11	2t	30H	64	.200	White resin	Polyethylene in detail	No significant F
48-3	22/11	4Ar	30H	64	.030	Off-white resin	Polyethylene + line at 4.90A	Trace F at 1155, 1215
3,3,3-Trifluoropropene								
105-1	5.38/11.2	1t	30H	64	.162	White resin	Polyethylene + weak line at 4.9A	I.R. - about 1% F indicated by shallow peaks in F region probabl not homogeneous, as %F (Schwarzkopf) is 16.96 by weight, 10.5 mole %. Conversion is 20%.

Table IV (Cont'd.)

Monomer Expt. No.	Molar Ratio H/E ^{a}	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
2-Trifluoromethyl Propene								
49-1	22/11	1r	30H	19	.336	White powder	Polyethylene in detail	No significant F
49-2	22/11	2t	30H	19	.153	White powder	Polyethylene in detail	No significant F
Hexafluoropropene								
42-1	24/12	1r	30H	16	.294	Creamy resin	Polyethylene in detail	Polyethylene
42-2	24/12	2t	30H	16	.117	White resin	Polyethylene in detail	Polyethylene
42-3	24/12	3At	30H	148	trace	Oil	-	-
42-5	24/12	4Ar	30B	16	.065	Grayish white resin	Polyethylene in detail	Polyethylene
α - Trifluoromethylstyrene								
54-7	25/12	1Cr	30H	65	.017	White resin	Polyethylene in detail	-
54-8	25/12	2Ct	30H	65	.164	White resin	Polyethylene in detail	Trace F
α, β, β - Trifluorostyrene								
68-4	25/22	1t	30H	2	.241	Gray resin	Polyethylene	Polyethylene with trace phenyl, F
68-5	25/22	2t	30H	2	.532	Hard white resin + thin rubbery streamers	Polyethylene Polyethylene	Polyethylene very little F Polyethylene with slightly more F than the resin
Hexafluoro-2-butyne								
44-1	22/11	1r	30H	64	.286	White resin	Polyethylene in detail	Polyethylene plus very weak 1145, 1180
44-2	22/11	2t	30H	64	.234	White resin	Polyethylene in detail	Polyethylene plus minor component at 1175, 1195, 1240
44-3	22/11	5t	30H	64	.247	Buff resin	Polyethylene in detail	Polyethylene plus weak 1145, 1230 bands
44-4	22/11	3t	30H	64	0		-	-
44-9	22/11	4Ar	30B	64	.590	Lt.Br. resin	Mixed	Amorphous ring 6-7A, weak Polyethylene lines at 4.10 & 3.75. New faint 3.5A line 46.33% F: 25 mole % butyne

Table IV (Cont'd.)

Monomer Expt. No.	Ratio M/E [a]	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	Infrared Spectrum cm.$^{-1}$
Hexafluoro-2-butyne (Cont'd.)								
65-1	22/13	4Dr	30H	18	.135	Yellow resin	Amorphous like 65-2, but weaker	No H in spectrum - missing are 2840, 2920, 1460, 720-730 doublet
65-2	22/14.5	4Dr	30H	18	.913	White resin	Amorphous faint rings at 3.7 & 7 angstroms	No H in spectrum like 65-1
Infrared shows in 44-9 roughly 30% ethylene combined								
Infrared shows in 65-1, 65-2 nearly 100% $CF_3C = C CF_3$ Combined								
1,1,2-Trifluoro-2chloro-3-methyl-3-ethynyl-cyclobutane								
40-5	24/24	1r	30H	16	.692	Yellow resin	Polyethylene pattern	2.19% F
40-6	24/24	2t	30H	16	.540	White resin	Faint Polyethylene pattern	1.75% F
40-7	24/24	3At	30H	16	.005	White resin	Amorphous	-
68-1	50/22	2t	30H	2	.404	Hard White resin	Polyethylene	About 1% F by I.R.
68-2	75/22	2t	30H	2	.494	White resin	Polyethylene	About 1.5% F by I.R.
68-3	38/11	2t	30H	2	.384	White resin	Weak polyethylene pattern	2.26% F
2,3-Bistrifluoromethylbicyclo (2.2.1) 2,5 - heptadiene								
41-6	22/23.5	1r	26H	43	.502	Buff resin	Polyethylene in detail	The norbornadiene is a moderate constituent of the copolymer (12.8% F; 4.1 mole % $C_9H_6F_6$). Unsaturation shows at 1750 & 1785. The Polyethylene crystallinity bands at 725 & 735 are strong. 1140 & 1170 F bands are very strong, with 1210, 1245, 1270 & 1290 bands also present.
2,3-Dichloro-2,3-difluorobicyclo (2.2.1) heptene-5								
54-5	25/12	2Ct	30H	65	.334	White resin	Polyethylene + Amorphous ring at 5.5A	Very little F

[illegible] (Cont'd.)

Monomer Expt. No.	Molar Ratio M/E [a]	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum [illegible]
2,3-Difluoro-2,3-bis trifluoromethylbicyclo (2.2.1) heptene - [illegible]								
54-6	25/12	2Ct	30H	65	.146	White resin	Polyethylene in detail	Trace F
1,1,2-Trifluoro-2-chloro-3-vinylcyclobutane								
46-1	22/11	1r	30H	16	.334	White crumb	Polyethylene	Minor Amt. cyclobutane, 2.17%
46-2	22/11	2t	30H	16	.125	White resin	Polyethylene 4.55A line weak	Less cyclobutane than in 46-1
46-3	22/11	4Ar	30H	88	.067	Transparent yellowish resin	Polyethylene 4.55A line gone	Cyclobutane like 46-1 some vinyl 911, 990
67-7	50/22	1t	30H	16	.675	Soft gray resin	Weak Polyethylene pattern	1.52% F
67-8	100/22	2t	30H	16	.307	Soft white resin	Polyethylene	Less F than 67-7
1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane								
70-1	50/22	1t	30H	3	.689	Gray-brn.resin	Polyethylene	Very little F
70-2	50/22	2t	30H	3	.310	White resin	Polyethylene	No F
1,1,2-Trifluoro-2-chloro-3-methyl-3-(3,3,4-Trifluoro-4-chlorocyclobutenyl)-cyclobutane								
67-3	25/22	1t	30H	16	.710	Buff resin	Weak Polyethylene pattern	Slight F
67-4	25/22	2t	30H	16	.694	Buff resin	Polyethylene pattern	5.67% F: more than 67-3
1,1,2-Trifluorobutadiene								
45-1	19/11	1r	30H	18	1.830	Orange resin	Faint Polyethylene pattern	20.5% F: mole % $C_4H_3F_3$, 14.2

Table [illegible] (Cont'd.)

Monomer Expt. No.	Molar Ratio M/E [a]	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
1,1,2-Trifluorobutadiene (Cont'd.)								
45-2	19/11	2t	30H	18	.712	Light brown resin	Polyethylene in detail + faint 2.35A line	34.0% F; mole % $C_4H_3F_3$, 32.0
45-4	7/21	5At	30H	18	.513	Light brown resin	Polyethylene in detail	6.15% ~~F; mole %~~ $C_4H_3F_3$, 3.31
45-5	15/11	4Ar	30B	210	.416	White skins + brn.grease	- -	Ethylene rich Trifluorobutadiene rich
68-7	22/22	2t	30H	2	.751	Yellowish resin crumb	Weakened Polyethylene	Strong F, strong unsaturation at 1725 on Polyethylene pattern. 12.26% F makes ethylene content 77% From feed and yield maximum ethylene content is 82%; mole % $C_4H_3F_3$, 6.74
5,5,5-Trifluoropentadiene-1,3								
54-9	25/12	2Ct	30H	65	.089	White resin	Polyethylene	-
2-Trifluoromethylbutadiene								
91-7	9.7/11	1t	30H	17	.56	Resin	37% crystalline lines 5.94, 5.15, 5.47 4.15 3.85 3.74 3.44, 3.30, 2.96, 2.56	3[illegible] conversion F 3.35, 2.64% Schwarzkopf

Infrared indicates 16.15% F, 34.1% $CH_2 = C(CF_3)-CH{=}CH_2$ and checks the yield

Monomer Expt. No.	Molar Ratio M/E [a]	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
Hexafluorobutadiene								
50-1	22/11	1r	30H	16	.311	Soft, white resin	Polyethylene	Trace F
50-2	22/11	2t	30H	16	.148	Soft, white resin	Polyethylene	Pure Polyethylene
50-3	22/11	4Ar	30H	88	.041	Brown, friable resin	Weakened Polyethylene Pattern	Lean copolymer 2.51% F· .6 mol % C_4F_6

Table IV (Cont'd.)

Monomer Expt. No.	Molar Ratio M/E [a]	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
5,5,5-Trifluoro-4-trifluoromethyl-1-3-pentadiene								
94-5	25/11.4	1t	30H	16	.25	Brownish white resin	Polyethylene	3.61% F
94-6	25/11.4	2r	28H	16	.27	Brownish white resin	Polyethylene	1.36% F
2,3-Bis (Trifluoromethyl) butadiene								
94-3	19/11	1t	30H	16	.293	Brown-white resin	Polyethylene	Polyethylene + faint F at 1130; 1.91% F
94-4	19/11	2r	27H	16	.281	Brown-white resin	Polyethylene	Polyethylene + faint F at 1130; 1.71% F
1,1,2-Trifluoro-3-vinylcyclobutene-2								
47-1	22/11	1r	30H	18	.326	Yellow powder	Amorphous Polyethylene lines 4.10 & 3.65 barely show	Strong F, unsat. at 1725 13.1% F; 8.5 mole % butene
47-2	22/11	2t	30H	18	.342	White powder	Polyethylene in detail except 4.55 line faint	About 10% F by Comparison of 47-1 & 47-2 spectra
1,1,2-Trifluoro-2-chloro-3-isopropenylcyclobutene-								
67-1	25/22	1t	30H	16	1.778	Brownish white resin	Polyethylene pattern	Polyethylene w/unsat. around 1700, moderate F - some loss in work up
67-2	25/22	2t	30H	16	1.140 + .174	Brown resin + white resin Brown grease ppt'd fr. CH_3OH by H_2O	Polyethylene pat'n. Polyethylene pat'n. -	Polyethylene like 67-1 but richer in F monomer; 8.56% F -
1,1,2-Trifluoro-1,4 - pentadiene								
54-3	25/12	1Cr	30H	65	.011	Off-white powder	Polyethylene in detail	-

Tabl[illegible] (Cont'd.)

Monomer Expt. No.	Mole Ratio M/E [a]	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	[illegible] Pattern	[illegible] Infrared Spectrum [illegible]
1,1,2-Trifluoro-1,4 - pentadiene (Cont'd.)								
54-4	25/12	2Ct	30H	65	.010	White powder	Polyethylene in detail	-
1,5-Perfluorohexadiene								
54-1	25/12	2Ct	30H	65	.214	White powder	Polyethylene in detail	[illegible]ylene, very little F
1,1,3,3,5,5,7,7-Octafluoro-1,6-Heptadiene								
54-2	25/12	2Ct	30H	65	.166	White powder	Polyethylene in detail	Polyethylene, trace F
1,2-Bistrifluoromethylcyclohexadiene-1,4								
67-5	25/22	1t	30H	16	.706	White resin	Weak Polyethylene	Trace F
67-6	25/22	2t	30H	16	.857	White resin	Weak Polyethylene	Trace F

Both 67-5 and 67-6 had an appreciable fraction (1/3 and 3/4 respectively) of low molecular weight material recovered by precipitation with water from isopropenol solution.

Monomer Expt. No.	Mole Ratio M/E [a]	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	[illegible] Pattern	[illegible] Infrared Spectrum [illegible]
2,2,2-Trifluoroethyl vinyl ether								
59-5	12/11	1r	30H	40	.476	Transparent semi-fluid	-	Ether polymer, little evidence [illegible] ethylene. 1460 weak· 1280, 1165 112[illegible] very strong. Bands at 1720, 1695, 1680, 1640, 1620 suggest CF_2= CH-
59-6	22/11	2t	30H	40	0	-	-	-
1,1,2,2-Tetrafluoro-3-vinylcyclobutane								
111-1	50/11.6	1t	29H	18	.33	Brn. wh. resin	Strong Polyethylene pattern	3.5% conversion

By comparison with monomer spectrum about 12 wt. %, 2.4 mole % butene in product.

a. M is monomer in experiment heading
   E is ethylene. Quantities are millimoles.

TABLE V

TERPOLYMERIZATIONS OF FLUORINATED MONOMERS WITH ETHYLENE BY ANIONIC COORDINATION CATALYSTS

Monomers Expt. No.	Molar Ratio $M_1/M_2/E^*$	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X ray Pattern	Remarks and Infrared Spectrum cm.
Hexafluoropropene (M_1) + 1,1,2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane (M_2) + ethylene (E)								
42-4	22/25/11	2t	30H	16	.265	Creamy resin	Polyethylene in detail	The yne monomer a minor constituent - no indication of CF_3-$CF=CF_2$ in product - resembles 40-6, Table IV
2,3-Bis(trifluoromethyl) norbornadiene (M_1) + propylene (M_2) + ethylene (E)								
71-1	25/0/11	1t	30H	16	.358	White resin	Polyethylene	Copolymer blank - polyethylene containing some F
71-2	25/22/11	1t	30H	16	1.336	Stiff rubber	Polyethylene	Roughly a 50-50 copolymer of ethylene and propylene containing F equivalent to 71-1
71-3	25/0/11	2t	30H	16	.249	White resin	-	Copolymer blank - F content 2.4 x that in 71-1
71-4	15.4/22/11	2t	30H	16	.180	White resin	-	Ran out of M_1 qualitatively Similar to 71-3 ethylene copolymer with a high norbornadiene content. No propylene present
71-5	0/24/12	1t	30H	16	1.149	Stiff rubber	-	Copolymer blank - a high propylene rubber - 68% propylene 86% conversion
1,1,2-Trifluorobutadiene (M_1) + butadiene (M_2) + ethylene (E) run at 5°								
75-1	0/20/20	5Fr	9B9H	16	0	-	-	-
75-2	0/20/20	5Gr	9B9H	16	.755	Soft resin	-	Bad cleanup; poor spectrum
75-3	0/20/20	7t	9B9H	16	.512	Fluid rubber	-	No polyethylene crystallinity at 720-730 Calculated as polybutadiene 72% *cis*, 19% vinyl, 9% *trans*

Table V (Cont'd)

Monomers Expt. No.	Molar Ratio $M_1/M_2/F^a$	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum [illegible]
75-4	0/20/20	2t	9B9H	16	.243	Brown polymer + white resin	-	Trans and vinyl polybutadiene + polyethylene
75-5	0/20/20	6Ft	8B10H	16	.683	Dead soft resin	-	
75-6	0/20/20	6Gt	9B9H	16	.949	Dead soft resin	-	Strong polyethylene crystallinity band at 720-730 is also wide, indicating cis-polybutadiene. Cis + $-CH_2-CH_2-$ is 75%, 3.5% vinyl, 19% trans
77-1	[illegible]3/11.5	5Gt	9B9H	20	.022	Lgt. brn. powder	-	No spectrum taken
77-2	7/33/7	5Gt	9B9H	20	.478	Buff crumb	-	No F in product - trans 33%, vinyl 7, cis 31-0, ethylene 0-26
77-3	7/33/7	5Ht	9B9H	20	.278	Buff crumb	-	No F in product - trans 27, vinyl 7.5, cis 47-0, ethylene 0-38
77-4	7/33/7	6Ft	9B9H	20	.636	Light brn. rubber + white resin (minor)		Trace F in high cis polybutadiene Polyethylene
77-5	7/33/7	6Gt	9B9H	20	1.046	Light brn. rubber + white resin (quite minor)		Trace F in high cis polybutadiene Polyethylene containing trans and cis butadiene, some vinyl
77-6	[illegible]5/23/11.5	6GT	9B9H	20	.692	Light brn. rubber + white resin (about one-half)		Trace F in high cis polybutadiene containing $-CH_2-CH_2-$ Polyethylene containing trans and cis butadiene

a. Amounts are given in millimoles.

Table VI

COPOLYMERIZATIONS OF FLUORINATED MONOMERS (EXCEPT 1,1,2-TRIFLUOROBUTADIENE) AND BUTADIENE BY ANIONIC COORDINATION CATALYSTS

Monomer Expt.No.	M/B mM.Ratio	Cata- lyst	ml. Sol- vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.^{1}
64-4	22/22	6Dt	16B	90	.502	Fluid polymer	-	At 20 hrs.booster of .25 mM.Al(i-bu)$_3$ 64 cis, 31 trans, 6 vinyl,trace F
64-5	11/22	8At$_1$t$_2$	15B	90	.513	Fluid polymer	-	At 20 hrs.booster of .25 mM.Al(i-bu)$_3$ 65 cis, 30 trans, 5 vinyl, trace F
64-6	11/22	7t	15B	90	0	-	-	-
2-Fluoropropene								
48-8	22/22	6At	8B	64	0	-	-	-
48-9	22/22	7At	8B	64	.051	White resin	Amorphous ring About 5A One line at 2.10A	High trans polybutadiene 2.43% F; 7.2 mole % propene
2-Trifluoromethylpropene								
49-8	22/22	6At	8B	112	1-2	Low mol.wt. oil	-	Discarded
49-9	22/22	7At	8B	112	.011	White gum	Amorphous ring at 5A	A little F shows in high trans polybutadiene
α-Trifluoromethylstyrene								
62-4	25/22	7t	12B	22	.638	Plastic + gelled polybutadiene	-	Slight F Spoiled by improper assembly
α,β,β-Trifluorostyrene								
62-5	25/22	7t	12B	22	.476	White soft resin	Amorphous	A little F, a little phenyl in 50 trans 50 cis polybutadiene
Hexafluoro-2-butyne								
65-4	22/22	7t	15B	18	Trace	White solid	-	-
65-7	19.5/22	7Bt	17B	18	.043	Brown resin	-	Very impure, shows F and trans $-CH_2-CH=CH-CH_2$
65-8	17/22	24t$_1$t$_2$	17B	18	.006	Brown resin	-	-

Table [illegible] (Cont'd)

Monomer Expt. No.	M/B mM. Ratio	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane								
62-7	25/22	7t	12B	22	.02[illegible]	Buff resin	Amorphous	-
62-8	25/22	6Dt	13B	18	.0[illegible]	Trace oil	-	-
62-9	25/22	8At$_1$t$_2$	13B	18	.0[illegible]	Trace oil	-	-
2,3-Difluoro-2,3-dichlorobicyclo(2.2.1)heptene-5								
62-3	37/22	7t	12B	22	.917	Gelled polybutadiene	-	Small amount of F Not properly assembled
2,3-Difluoro-2,3-bis(trifluoromethyl) bicyclo(2.2.1)heptene-5								
62-2	25/22	7t	12B	22	.488	Soft gray rubber + some white specks	-	Not properly assembled On dissolving, filtering, and reprecipitating the rubber, it was a high cis polybutadiene containing no F.
1,1,2-Trifluoro-2-chloro-3-vinylcyclobutane								
46-7	25/22	6At	8B	18	[illegible]	[illegible] powder	Many [illegible]	Inorganic
46-8	25/22	7At	8B	114	.107	Soft tacky gum	-	Shows slight F and unsaturation at 1710-1725 as well as 1640 in a high trans polybutadiene
70-9	50/22	7t	4B	68	1.063	Gelled white rubber	-	Some F Strong unsaturation at 1725 Vinyl 910, 990 Dihydrohalogenation of ring
1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane								
70-6	50/22	6Ht	9B	68	.219	Fluid rubber	-	Polybutadiene, no F, like 70-7
70-7	50/22	6It	9B	68	.349	Fluid rubber	-	Polybutadiene, no F, 66 cis, 29 54 ans 4 vinyl
70-8	50/22	7t	4B	68	1.118	Gelled white rubber	-	Like 70-9

Table VI (Cont'd.)

Monomer Expt. No.	M/B mM.Ratio	Cata- lyst	ml. Sol- vent	Time hrs.	Yield gm.	Product	X-ray Pattern	[illegible] Infrared Spectrum cm.$^{-1}$
1,1,2,2-Tetrafluoro-3-vinyl cyclobutane								
112-7	25/44	6C	18B	43	2.163	Soupy rubber	-	Str.exotherm;trace F by I. R.; 0 by micranal. cis 75, vinyl 4, trans 21; Tg -105
112-4	0/22	7t	12B	65	1.088	Soft rubber	-	Blank, exotherm, 92% conversion 68 cis, 26 vinyl, 7 trans
112-9	25/44	7t	18B	43	2.546	Soft rubber	-	Exotherm; trace F by I. R. No F by microanalysis 60C, 22V, 18T; Tg -97 Soluble in $CHCl_3$
5,5,5-Trifluoromethyl-1,3-pentadiene								
62-1	25/22	7t	12B	22	.319	White resin + soft,lgt.brn.gum	Amorphous Amorphous 2 rings	Some F; trans, vinyl and cis Slightly more F than in resin Not properly assembled
2-Trifluoromethyl-1,3-butadiene								
91-3	44/0	6Cr	18B	68	2.27	Solid rubber	-	Blank-exotherm, 98% conversion -73 cis, 23 trans, 4 vinyl
91-4	44/9.6	6Cr	18B	68	.018	Flaky soft resin	-	Impure monomer changed catalyst to red color. About 6.3% $C_5F_3H_5$ in a mostly trans butadiene
91-5	22.2/10.4	7t	18B	67	1.21	High mol. wt.rubber	-	2.26% F Schwarzkopf 2.2 mole % $C_5H_5F_3$ Cis 70, trans 20, vinyl 10
Hexafluorobutadiene								
50-10	22/22	6At	8B	88	.014	Brown resin + 1 to 2 ml. oil	Amorphous	1-2 ml. of oil discarded Weak F band in mainly trans polybutadiene
50-11	22/22	7At	8B	88	.029	White gum	Amorphous ring centered at 5A One line at 2.05A	16.13% F; 8.8 mole % C_4F_6 in mainly trans polybutadiene

Table VI (Cont'd.)

Monomer Expt. No.	M/B mM. Ratio	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-Ray Pattern	Remarks and Infrared Spectrum
5,5,5-Trifluoro-4-(trifluoromethyl)-1,3-pentadiene								
81-1	25/22	6Dt	12B	40	.976	Yellow oil	-	Run at 50°; 20% conversion 41.14% F; 38.4 mole % $C_6H_4F_6$
81-2	25/22	7t	12B	40	.135	White gum	-	Run at 50°; 3[illegible] conversion 38.50% F; 33.9 mole % $C_6H_4F_6$
In both these copolymers the 725 band is intense and sharp as in poly $(CH_2=CH-CH=C(CF_3)_2)$ itself; conclusion - butadiene is trans (from 967 band) and the structure of the pentadiene portion is unknown.								
2,3-Bis(trifluoromethyl) butadiene								
94-1	20/22	6Cr	18B	46	.004	Brown oily scum	-	-
94-2	20/22	7t	18B	46	.63	Sticky rubber	-	5.72% F; 2.9 mole % $C_6H_4F_6$ Butadiene portion 79 cis, 13 vinyl, 8 trans, strong bands in F region 1130 etc.
1,1,2-Trifluoro-3-vinylcyclobutene-2								
47-3	25/22	6At	8B	18	.455	Brown powder + soft dark gum	Amorphous ring about 5A	Resin = gum in spectrum Some F and strong 1710 in trans rubber. 4.04% F; 4.1 mole % butene
47-4	25/22	7At	8B	138	4.5	Yellow gum	-	More F than 47-3, less 1710 in trans rubber. 12.53% F; 14.5 mole % butene
62-10	25/22	7t	12B	22	.229	Buff resin	Amorphous	Strong F Unsaturation at 1710 Cis butadiene minor, a little vinyl
$C_6H_5F_3$ may polymerize only through the vinyl group.								
1,1,2-Trifluoro-3-chlorobutadiene-1,3								
119-6	22.9/33	17Dr	16B	66	0			Catalyst destroyed by polar impurity. Catalyst was doubled and still not active. V.P.C. identified traces of butanol in monomers.
2,2,2-Trifluoroethyl Vinyl Ether								
58-1	11/22	6Dr	20B	93	0	-	-	-
58-2	11/22	17Cr	20B	93	0	-	-	-
62-6	25/22	7t	12B	22	.022	Trace brown oil	-	-

Table VII

COPOLYMERIZATIONS OF 1,1,2-TRIFLUOROBUTADIENE WITH BUT[illegible] [illegible] [illegible]ONIC COORDINATION CATALYSTS

Expt. No.	$C_4H_3F_3$/B mM. Ratio	Catalyst	ml. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm.$^{-1}$
24-3	0/22	3It	3B	240	.080	Sticky rubber	-	60 vinyl, 26 trans, 14 cis
24-4	21/21	3Bt	6B	240	.374	Semi-solid	-	1710, 1625, 1430, 1340, 1175, 1150, 970, 905 - copolymer of $C_4H_3F_3$ and trans butadiene 40.09% F = 76.3% $C_4H_3F_3$
24-5	21/21	3Dt	6B	240	.628	Semi-solid Softer than 24-4	-	Replication of 24-4 with a different catalyst ratio
24-6	21/21	6Jt	6.5B	160	.473	Orange resin	Amorphous	Strong F, strong trans, a little vinyl, unsat. 1640 and 1715, replication of 24.7 at different catalyst ratio
24-7	21/21	6At	7B	240	1.02	Black resin	Amorphous	21.0% F = 39.9% $C_4H_3F_3$ Infrared shows unsat. 1715, 1630. Strong F 1060, 1175; trans butadiene 975, trace vinyl 911, trace ? cis.
60-1	0/22	6Cr	10B	18	.002	-	-	Catalyst destroyed Someway unknown.
60-2	22/22	6Cr	10B	18	.268	Rubber	-	Some gel. No F Cis 81, trans 14, vinyl 4
60-3	22/22	6Cr	20B	18	.334	Rubber		Some gel. No F Cis 85, trans 11, vinyl 4
60-4	22/22	6Dr	13B	18	.511	Rubber	-	Some gel. No F Cis 72, tranc 24, vinyl 4
60-5	22/22	8rt	10B	18	.190	Rubber	-	Gelled. 20-30% $C_4H_3F_3$ + trans butadiene Unsaturation 1640, 1720 Alkylation 690.
57-1	0/22	7At	8B	65	0	-	-	Blank
57-2	0/22	7At	1B7M	65	.40	Sticky rubber	-	Blank. M is CH_2Cl_2. 30% conv. High cis + appreciable trans & vinyl
57-3	11/33	7Ct	2B14M	65	1.23	White rubber	-	Gelled - 36.5% conversion 1.4% F = 2.66% $C_4H_3F_3$ Cis, trans, and vinyl present

Table VII (Cont'd.)

Expt. No.	$C_4H_3F_3$/B mM. Ratio	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectra, cm.$^{-1}$
57-4	22/22	7Ct2B	14M	65	.42	White rubber	-	Gelled - 10% conversion 8.56% F = 16.26% $C_4H_3F_3$ Cis, trans and vinyl present
57-5	33/11	7Ct2B	14M	65	.54	White rubber	-	Gelled - <11.4% conversion 15.02% F = 28.6% $C_4H_3F_3$
57-6	22/22	7Ct16B		65	1.21	White rubber	-	Mostly vinyl and trans ~~Gelled ~30% conversion~~ 4.55% F = 8.65% $C_4H_3F_3$ High cis rubber with appreciable trans and vinyl
Polymerizations 79-1 through 79-10 run at 5°								
79-1	7/18	7t	9B9H	19	.273	Short soft rubber	-	% F 0.95 - 1.8% $C_4H_3F_3$ High cis, appreciable trans & vinyl
79-2	5/20	7t	9B9H	19	.011	Short soft film	-	-
79-3	7/18	6Gt	9B9H	19	.014	Stiff film	-	-
79-4	5/20	6Gt	9B9H	19	.747	Liquid polymer	-	% F 0.59 - 1.12% $C_4H_3F_3$ 62% cis, 31 trans, 5 vinyl
79-5	7/18	2t	9B9H	19	.062	White soft resin	-	-
79-6	5/20	2t	9B9H	19	.031	White soft resin	-	-
79-9	7/18	5Gr	9B9H	19	.209	Soft white film	-	% F 0.67 = 1.27% $C_4H_3F_3$ Mostly trans, 13% cis, 3% vinyl
79-10	5/20	5Gr	9B9H	19	.071	Soft white film	-	-
Sums of Yields by Catalysts (gms.)								
	Cobalt Octoate	TiI$_4$		VO(OBu)$_3$		TiCl$_4$		
	.284	.761		.093		.280		
102-1	22/22	7Dt	26B	16	1.160	Rubber	-	Exotherm; I. V. 73; Tg -84; 33% conv. 31% $C_4H_3F_3$, 45 cis, 11 trans, 44 vinyl

[illegible]

Expt. No.	$C_4H_3F_3/B$ mM. Ratio	Catalyst	m. Solvent	Time hrs.	Yield gm.	Product	X-ray Pattern	[illegible] and Infrared Spectra
102-2	11/33	7Dt	26B	16	1.720	Rubber	-	Exotherm; 59% conv. Tg -82 22% $C_4H_3F_3$, 42 cis, 12 trans, 46 vinyl
102-3	33/11	7Dt	26B	16	.726	Rubber	-	Exotherm; 18% conv. 44% $C_4H_3F_3$, 24 cis, 20 trans, 56 vinyl
102-4	22/22	7Dt	26B	16	1.060	Rubber	-	No exotherm; I.V. .82, 630% conv. 34% $C_4H_3F_3$, 9 cis, 20 trans, 71 vinyl
102-5	33/11	7Dt	26B	16	.579	Rubber	-	No exotherm; 14% conv. 60% $C_4H_3F_3$, 7 cis, 25 trans, 68 vinyl
102-6	11/33	7Dt	26B	16	1.539	Rubber	-	No exotherm; 50% conversion 34% $C_4H_3F_3$, 13 cis, 22 trans, 65 vinyl

Sum of cis, trans, and vinyl is normalized to 100%.
Sum of yields - in benzene 3.606 - in CH_2Cl_2 3.178.

F analysis by comparison of absorbance of 1050 and 1150 bands with those of 27-4 polytrifluorobutadiene.
Samples were sticky rubbers with poor cobalt cleanup. Except for 102-1 and 102-2, they had resinified by the time a DTA test was made.

Conclusion - Water contamination of butadiene indicated by cis butadiene blanks with low yield and high vinyl. In CH_2Cl_2, as compared with benzene, yield decreases, cis content decreases, vinyl content increases, trifluorobutadiene content of product increases. Trifluorobutadiene itself may affect a polymerization in the same way as a halogenated solvent.

Table VII (cont'd)

Expt.No.	$C_4H_3F_3/B$ mM.Ratio	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	Ex. [illegible] Cat.Color	[illegible] Infrared Spectrum
116-1	0/33	17Dr	19B	15-1/2	1.671	Solid rubber	+ Dark brown	[illegible].9, trans 3.0, vinyl 4.8
116-5	22/33	17Dr	17B	15-1/2	0	-	0 Light brown	- - -
116-3	0/33	6Kr	18B	15-1/2	1.534	Solid rubber	+ Dark brown	Cis 81, trans 15, vinyl 4
116-7	22/33	6Kr	18B	15-1/2	0	-	0 Red	Catalyst destroyed at once
116-4	0/33	7Et	9B9H	15-1/2	1.833	Solid rubber	+ Light blue	Gelled - run too long Cis 73, trans 19, vinyl 8
116-8	22/33	7Et	9B9H	15-1/2	1.723	Solid rubber	+ Yellow	Gelled - run too long Cis 87, trans 8, vinyl 5 No F.

1,1,2-Trifluorobutadiene changed the catalyst color of three polymerizing solutions as compared with a blank made with butadiene only. V.P.C. on the residue in the storage tube after distilling out most of the trifluorobutadiene showed isopropanol in the trifluorobutadiene. On treating the remaining monomer with NaOH at 0°, a fair amount of brownish polymer was formed, of normal infrared spectrum.

Runs below are with 1,1,2-trifluorobutadiene (94 gm.) purified by NaOH treatment at -25, 7-1/2 hrs., followed by treatment with .25 ml. neat aluminum triisobutyl (6 times the theoretical amount to use up .06 mole % isopropanol not removed by NaOHO at -78, followed by holding at -25 for 1 hour, and redistilling to storage over molecular sieve. A small amount of polymer was a by-product of the $Al(i\text{-}bu)_3$ treatment. VPC still showed isopropanol.

Expt.No.	$C_4H_3F_3/B$ mM.Ratio	Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	Ex. [illegible] Cat.Color	[illegible] Infrared Spectrum
126-1	0/43	17Er	21B	60	2.317	V. soft rubber	+ Dark brown	Cis 91, trans 5, vinyl 4
							0	Cis 36, trans 6, vinyl 57
126-2	43/43	17Fr	21B	60	.125	Yellow solid	Light brown	Catalyst destroyed
							++	
126-3	0/43	63Cr	20B	60	2.056	V. soft rubber	Dark brown	Cis 64, trans 31, vinyl 5
							0	
126-4	43/43	6Dr	21B	60	2.344	Sticky brown Soft rubber	Dull brown	
							0	Gelled in 1-1/2 hrs. at 5°, run too long.
126-5	0/43	7Er	21B	60	2.323	Gelled rubber	Clear	Cis 98.1, trans .6, vinyl 1.3 Cobalt octoate not added
126-6	43/43	7Hr	21B	60	2.823	Orange brn. resin	-	

As soon as trifluorobutadiene was added to butadiene standing on frozen $Et_3Al_2Cl_3$ solution in benzene, cationic polymerization started as shown by yellow, then strong red color as a plug of gel was formed in the reaction tube. With this catalyst, cobalt octoate must be added first (with butadiene the order is immaterial). 126-2, 126-4, 126-6 all show alkylation at 694 in infrared spectrum, typical of polar contamination of catalyst. Butadiene portion is nearly equal cis and trans with 5-6% vinyl. There is little F. Weak bands around 2300 suggest -C≡C- ? and bands 1640-1800 suggest -C=CF- .

Table VIII

ANIONIC EXPLORATORY POLYMERIZATIONS AND COPOLYMERIZATIONS OF 1,1,2-TRIFLUOROBUTADIENE

Expt. No.	Molar Ratio $M/C_4H_3F_3$ [a]	M Moles Cata-lyst	ml. Sol-vent	Time hrs.	Yield gm.	Product	Remarks	
Trifluorobutadiene alone								
80-4	0/21	.1LiBu	10THF	89	.271	Lgt. brown film	Run at 50°	10% conversion
80-7	0/21	.1LiBu	10B	89	.049	White crumbs	Run at 50°	2% conversion I.R. Poly(trifluorobutadiene)
80-5	0/21	1 t-BuMgCl	10THF	89	.372	Tan lumps	Run at 25°	14% conversion I.R. poly(trifluorobutadiene)
80-6	0/21	1 t-BuMgCl	10THF	89	.199	Tan lumps	Run at 50°	7% conversion
With 2,2,2-Trifluorovinyl ether								
80-1	24/0	1LiBu	10THF	89	.009	Gummy white resin	Run at 25°	.3% conversion
80-2	24/0	1LiBu	10THF	89	0	-	Run at 50°	
80-3	24/21	1LiBu	10THF	89	.096	White bits of film	Run at 25° poly(trifluorobutadiene) only	1.7% conversion
With Butadiene								
72-1	118/11	.1LiBu	10 toluene	63	.014	Clear resin	.13% conversion - run at -30°	
86-1	22/22	.16LiBu	15B	69	.061	Brown rubber	Catalyst added at 25 polymerized at 50	1.5% conversion
86-2	22/22	.16LiBu	15THF	69	.033	Brown Rubber	Catalyst added at 25 polymerized at 25	.8% conversion
86-3	22/22	.8LiBu	15THF	69	.033	Brown rubber	Catalyst added at 25 polymerized at 50°	
86-4	11/33	.8LiBu	15THF	69	.104	Brown rubber	Catalyst at -65° polymerized at 50	
86-5	33/11	.8LiBu	15THF	69	.035	Black rubber	Catalyst at -65° polymerized at 50	
86-6	22/22	-	15THF	143	.136	Transparent rubber	No catalyst	
86-9	11/33	.8LiBu	15THF	68	.162	Brown rubber	Catalyst at -65° polymerized at 50	

LiBu reacts immediately with monomer vapor to give instant polymer and a black coloration. The addition of catalyst to the frozen tube at -65° eliminated the black coloration, but did not prevent the destruction of the catalyst. Spectra of 86-1, 86-3 and 86-9 have a close resemblance to 86-6, which must be free radical polymer, and shows trans butadiene only.

a. Amounts in millimoles.

Table IX

CATIONIC EXPLORATORY POLYMERIZATIONS AND COPOLYMERIZATIONS [illegible]

Comonomer Expt. No.	Molar Ratio $M/C_4H_3F_3$ [a]	Mmoles Catalyst	ml. Solvent	Time hrs.	Temp °C	Yield gms.	Conv. %	Remarks
Butadiene								
72-2	117/12.5	.1AlBr$_3$	10Te*	63	-30	.022	.33	Brown oil - no F - cis & trans polybutadiene
72-3	112/11.9	1.4BF$_3$**	10Te	63	-30	3.83	52	Reddish brown brittle resin - some F trans & vinyl polybutadiene
73-2	85/19.3	.1AlBr$_3$	10M*	96	-80	.15	2.2	White resin - little F trans polybutadiene mostly
73-3	90/28.7	17BF$_3$	10M	96	-80	4.43	55	White resin -2.64% F ratio $C_4H_3F_3$ in product to feed .08
Isoprene								
72-7	28/28	1.4BF$_3$	10Te	63	-30	.066	13.4	Resin some F, copolymer
72-8	29/20	.1AlBr$_3$	10Te	63	-30	3.57	85	Resin some F, copolymer
73-6	40/19.3	.1AlBr$_3$	10M	96	-80	.18	4	White resin - 0.22% F ratio $C_4H_3F_3$ in product to feed .010
73-7	41/19.3	.7BF$_3$	10M	96	-80	2.38	52	White resin - 1.65% F ratio $C_4H_3F_3$ in product to feed .05
Isobutylene								
72-4	85/8.9	.14BF$_3$	10Te	63	-30	.717	12.5	Oil plus a little gel - slight F copolymer
72-5	98/24.1	.2AlBr$_3$	10Te	63	-30	.578	7.1	Semi-fluid copolymer moderate F
73-4	87/19.3	.1AlBr$_3$	10M	96	-80	2.45***	36	Semi-fluid - 4.12% F ratio $C_4H_3F_3$ in product to in feed .23
73-5	87/19.3	.7BF$_3$	10M	96	-80	2.51	37	Semi-fluid - 4.23% F ratio $C_4H_3F_3$ in product to in feed .23
Isobutyl vinyl ether								
72-6	18.9/12.0	.1AlBr$_3$	10Te	63	-30	3.54	100	Transparent rubber - some F copolymer, mostly ether, T_g 5° C

a. Amounts in millimoles.

Table IX (Cont'd.)

Comonomer Expt. No.	Molar Ratio M/$C_4H_3F_3$ ^{a}	Mmoles Catalyst	ml. Solvent	Time hrs.	Temp °C	Yield gms.	Conv. %	Remarks
Methyl Vinyl Ketone								
73-8	44/19.3	.1$AlBr_3$	10M	96	-80	.72	18	Stiff yellow rubber - 12 [illegible] ratio $C_4H_3F_3$ in product to [illegible]
2,2,2-Trifluoroethyl vinyl ether								
73-9	37/19.3	.1$AlBr_3$	10M	96	-80	trace	-	-
Homopolymer								
80-8	0/22	.1$AlBr_3$	9M	.5	-80	.029	1	Tan lumps - polymer partly degraded (by I.R.)

* Te = Tetrachloroethylene; M = Methylene chloride

**BF_3 as etherate

*** One half of polymer yield was recovered by evaporation of solvent and precipitant

Table X

NICKEL BIS(CYCLOOCTADIENE)-INITIATED POLYMERIZATIONS OF 1,1-DIFLUOROALLENE AND RELATED EXPERIMENTS

Monomer Expt. No.	Molar Ratio $M_1/C_3H_2F_2$ [a]	Cata- lyst	ml. Sol- vent	Time hrs.	Yield gm.	Product	X-ray Pattern	Remarks and Infrared Spectrum cm^{-1}
Difluoroallene Homopolymerizations								
85/1	0/8.4	AIBN	8H28E*	167	.320	White grease	-	.01 gm. AIBN catalyst Run at 50° - mixed structure
85-2	0/8.4	None	8H28E	167	.122	White grease	-	Run at 50° - mixed structure
85-3	0/8.4	At rt.	8H28E	18	.024	Trace brown grease	-	Run at 50° - catalyst 1.4 mM. t-Butyl Mg. Cl in THF
85-4	0/8.4	At rt.	8H28E	167	.126	White soft resin	-	Run at 50° - catalyst .25 ml. 47% BF_3·etherate .820 shows very high content $-CF_2-C(=CH_2)-$
87-4	0/8.8	3At	9B8H-E*	99	.254	Light brown resin	-	39% conversion - no 820 Mostly $-CH_2-C(=CF_2)-$ by 1740
Copolymers with Allene (M_1)								
87-1	0/8.8	At rt.	6B8H-E*	22	.526	White resin	Cryst.	81% conversion - .18 mM. Ni(C)$(COD)_2$ catalyst $-CH_2-C(=CF_2)-$ structure by 1730
87-2	22/8.8	Same	6B8H-E	22	.326	Brown resin	Cryst. Type II	81% conversion Copolymer - poor spectrum
87-3	22/0	Same	6B10H	22	.171	Grey brown resin	Cryst. Type II	17% conversion Polyallene spectrum str. 880
87-5	0/8.8	25	19H-E	99	.054	Light brown resin	-	8% conversion Degraded - no F
87-6	22/8.8	25	19H-E	99	.162	Light brown resin	-	10% conversion Copolymer - degraded - no F
87-7	22/0	25	19H-E	99	1.390	Light gray resin	Very cryst. Type II	139% conversion Polyallene spectrum

[illegible]

[illegible] Expt. No.	Molar Ratio $M_1/C_3H_2F_2$[a]	Catalyst	Solvent	Time hrs.	Yield gm.	[illegible]	Pattern	[illegible] Infrared Spectrum
Homopolymerizations of 1,1,2-Trifluorobutadiene (M_1)								
88-1	22/0	as 87-1	16B	66	.179	Gray resin	-	Polytrifluorobutadiene spectrum
88-4	22/0	as 87-1	16B	19	.108	Purple gray resin		
88-5	22/0	as 87-1	1B15H	18	.197	White resin + Ni	-	.18 mM. added 1,5-COD
88-6	22/0	as 87-1	1B15H	18	.366	White resin + Ni	-	.36 mM. added 1,5-COD
88-7	22/0	as 87-1	1B15H	18	.151	White resin + Ni	-	.54 mM. added 1,5-COD
88-8	22/0	as 87-1	1B15H	18	.176	White resin + Ni	-	.90 mM. added 1,5-COD
88-9	22/0	as 87-1	1B15H	18	.160	White resin + Ni	-	1.80 mM. added 1,5-COD
Vinylidene Fluoride (M_1)								
88-2	22/0	as 87-1	16B	66	.249	Trace black scum + salts		-
88-3	22/0	as 87-1	16B	19	.078	Salts only	-	-
Vinyl Fluoride (M_1)								
88-11	22/0	as 87-1	1B15H	18	.703	Trace dark scum + salts	-	Clean-up instructions violated
88-13	22/0	1t	44H	18	.077	Salts	-	-
Vinyl Chloride (M_1)								
88-10	22/0	as 87-1	1B15H	18	.062	Trace dark scum + salts	-	Clean-up instructions violated
88-12	22/0	1t	44H	18	.595	Gray brown powder plus lumps black inside	-	Dehalogenated

*E = ethyl ether. In the 87 series the monomer was furnished in a mixture of heptane and ether, the proportions of which were not exactly known.

a. Amounts in millimoles.

Table XI

IRIDIUM CATALYZED HOMOPOLYMERIZATIONS OF FLUORINATED MONOMERS IN EMULSION

All polymerizations run 240 hrs. at 50°C.

Recipe - Catalyst; distilled water, 8 ml.; 20% Novulphor O, 1.25 Ml.; 20% Aquarex ME, 1.25 ml.; 40% formaldehyde, .5 ml.; 25 mM. monomer. Catalyst-.075 gm. ammonium iridium chloride (Recipe A) or .055 gm bis(1,4 cyclohexadienechloroiridium) (Recipe B).

Expt. No.	Monomer	Recipe	Yield gm.	Conv. %	Product
106-1	3-Chloro-3,3,4-trifluoro-2-isopropenyl-cyclobutene-1	A	2.83	77	Amorphous white resin Infrared unsaturation at 1695 cm.^{1} Many F lines
106-10	"	B	.727	20	Amorphous white resin Infrared like 106-1
106-2	1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane	A	.008	<1	Amorphous white resin Unsaturation at 1693, 1625 cm.$^{-1}$
106-3	1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene	A	.007	<1	Gray resin
106-4	1,1,2-Trifluoro-2-chloro-3- methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl) cyclobutene	A	0	-	-
106-5	α,β,β-Trifluorostyrene	A	0	-	-
106-6	1,1,2-Trifluoro-2-chloro-3-vinylcyclobutane	A	0	-	-
106-7	1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane	A	0	-	-
106-8	2,2,2-Trifluoroethylvinyl ether	A	0	-	-
106-9	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	A	.560	12	White resin Some crystallinity plus inorganic contamination. Unsaturation 1670 cm.$^{-1}$ Strong F at 1120, 1150, 1205, 1235 cm.$^{-1}$.

Table XI (Cont'd.)

[illegible] No.	Monomer	Recipe	Yield gm.	Conv. %	Product
Copolymer with Butadiene					
110-2	44 mM. Butadiene 25 mM. 1,1,2,2-Tetrafluoro-3-vinyl cyclobutane	See below	.040		F bands in polymer are different from those in the cyclobutane monomers. Unsaturation shows at 1719 cm.$^{-1}$. With the low conversion, apparently dehydrohalogenation preceded polymerization.

Recipe - .055 gm. of bis(1,4-cyclohexadiene) chloroiridium, 7 ml. distilled water, 1 ml. 20% Nacconol NRSF (no formaldehyde).

TABLE XXX

RHODIUM CHLORIDE CATALYZED HOMOPOLYMERIZATIONS OF FLUORINATED MONOMERS IN EMULSION

Recipe - $RhCl_3 - 3H_2O$ .020 gm. distilled water, 7 ml.; 20% Nacconol NRSF, 1 ml.; monomer; Argon flush and run under Argon at 50°C.

Expt. No.	mM.	Monomer	Time hrs.	Yield gm.	Conv. %	Product
96-1	64.5	1,1,2-Trifluorobutadiene Infrared identical with that of 25-1 Zeigler catalyzed A mull in $CCl_2 = CCl_2$ shows no vinyl at 3020 and 3070	67	6.915	100	Slightly cryst. resin Partly sol. in $CHCl_3$ Tg -35°; Tm 56, 79
97-1	25	β,β,β-Trifluoroethyl vinyl ether	162	0	0	-
97-2	25	α,β,β-Trifluorostyrene	42	.134	3	Resin - strong F, phenyl in I. R.
97-3	25	1,1,2-Trifluoro-2-chloro-3-vinylcyclobutane	42	trace	-	-
97-4	25	4,5,5-Trifluoro-1,4-pentadiene	162	0	0	-
103-1	21.4	1,1,2-Trifluoro-2-chloro-3-isopropenylcyclobut-3-3n3	65	.817	18	Amorphous resin*
103-2	20	1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane	65	.051	1+	Slightly crystalline resin*. Lines 6.2 & 8.2A, amorphous ring under 6.2A
103-3	25	1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene	65	0	0	-
103-6	25	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	65	4.00	84	Amorphous resin* Ring at 5-6A Swells a little in $CHCl_3$ Tm + 112
119-1	20.8	1,1,2-Trifluoro-3-chlorobutadiene (added as a solution 31% by weight in benzene) Infrared spectrum of polymer has bends at 3020, 2956, 1675, 1420, 820, and 660 cm.$^{-1}$ like polychloroprene Strongest bands 1675, 1420, 1352, 1334, 1314, 1260, 1210, 1166, 1125, 400 cm.$^{-1}$ Theoretical % C, 33.7; % H, 1.41; % Cl, 24.86	65	3.059	100	V. smooth milling tacky rubber $CHCl_3$ soluble % C 33.11; 32.90 % H 1.40; 1.39 % Cl 26.62; 26.74 Tg -17°C.
123-1	22	Hexafluorobutadiene	385	0	-	Above recipe except run with ml. distilled water and 2 ml. 20% Nacconol NRSF.

*103-1 shows a band at 1700 cm.$^{-1}$ nearly as strong as the bands in the F region.
103-2 has a very similar spectrum but a close doublet 1698 and 1702. Bands are in the same locations in both spectra. Most ident differences are qualitative at 1250, 1300, 1386, 1545, 1700 cm.$^{-1}$
103-6 has several peaks close to 1678. Strongest bands are at 1400, 1325, 1240, 1210, 1150, 1120, 975, 946 and 714 cm.$^{-1}$.

Table XII (Cont'd.)

Expt. No.	[illegible]	Monomer	Time hrs.	Yield gm.	Conv. %	Product
93-1**	12.[illegible]	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	187	.027	1	Waxy solid
93-2**	22	1,1,2-Trifluorobutadiene	187	.154	6	Buff resin, for NMR****
124-1***	22	1,1,2-Trifluorobutadiene	12	2.283	98.5	White resin, for NMR****

** Recipe - $RhCl_3 \cdot 3H_{20}$ .015 gm.; absolute ethanol, 7.5 ml.; add monomer if liquid; real; add monomer if vapor; freeze with liquid nitrogen, uncap and recap under N_2; rotate in 50° bath.

*** Recipe - Azobisisobutyronitrile, .025 gm.; distilled water, 7 ml.; 20% Nacconol NRSF, 1 ml.; flush with argon; t-octyl mercaptan, .20 ml.; seal under argon and freeze to -80°; 1,1,1-trifluorobutadiene, 22 mM; recap; polymerize at 50° overnight.

**** NMR tests - 93-2 had an infrared spectrum like 25-1 (Ziegler polymer). It was $CHCl_3$ soluble and was examined by proton and F_{19} NMR in $CDCl_3$, tetramethylsilane reference. On solution in $CHCl_3$, by heating to 80°, 124-1 dissolved completely. On cooling down to 25°, only a trace of polymer precipitated. The polymer was examined by H_1 resonance in $CDCl_3$ = tetramethyl silane reference, and compared with 93-2. The main features of both spectra are H in $CHCl_3$ at 726% 8, two triads centered at 551 and 520 respectively; a sextet centered at 297; a broad band at 234, and a sharp band (impurity?) at 128. The peaks at 551 and 520 represent H_J resonance on a double bond carbon of the trans polymer split by F on the adjacent double bond carbon, with a HF of 31 cps, and split by the adjacent CF_2 with a $H\text{-}CF_2$ of 8 cps. The sextet centered at 290 corresponds to a splitting of CH_2 by adjacent CF_2 with a $J_{CH_2\text{-}CF_2}$ of 16 cps, and split by F with a $J_{CH_2\text{-}F}$ of 7 cps. A cis structure would require $J_{CH_2\text{-}F}$ of one-half of this value.

The main structure is trans (as expected with a rhodium catalyst) but distortion of the main bands indicates other structures are present. Band at 234 is not explained. No $-CF{=}CF_2$ or $-CH{=}CH_2$ were present. Conditions -100 megacycles, 23,000 gauss for H spectrum; 94.1 megacycles for F_{19} spectrum.

Now the infrared spectra of poly(1,12-trifluorobutadiene) made with Ziegler, $RhCl_3$ or free radical catalysts are alike, so all catalysts must give mainly trans structure.

[illegible]

ttempt to make R[illegible] catalyzed cis-polybutadiene - ba[illegible] ecipe t t.p of tabl

Expt. No.	mM.	Monomer	mM. Added KI	Time hrs.	Yield gms.	Product
109-1	44	Butadiene	.075	160	.388	Gelled rubber, insol. in $CHCl_3$
109-2	44	Butadiene	.15	160	.398	Gelled rubber, insol. in $CHCl_3$
109-3	44	Butadiene	.225	160	.117	Gelled rubber, insol. in $CHCl_3$
109-4	44	Butadiene	.45	160	.026	
109-5	44	Butadiene	1.06	160	.050	

Infrared on 109-2 shows trans-polybutadiene except for a maximum of 4% vinyl and 8% cis.

Tests of fluorinated emulsifiers in polymerization of Butadiene catalyzed by $RhCl_3$.

Recipe - $RhCl_3 \cdot 3H_2O$ .020 gm.; distilled water, 8 ml.; emulsifier; dissolve; argon flush, seal; butadiene 72 mmoles; pressurize with 4 psi N_2 at -80°; double cap; thaw and polymerize at 50°C. for 167 hrs.

Expt. No.	Emulsifier	Yield gms.	Product
98-1	M & M FC-170 .2 ml.	.060	Insoluble black hard resin
98-2	M & M FC-172 .2 ml.	.028	Dark brown powder
98-3	M & M FC-128 .2 gm.	.014	Greasy brown powder

Table XIII

RHODIUM CATALYZED COPOLYMERIZATIONS OF FLUORINATED MONOMERS [illegible]

Recipe - A - .020 gm. rhodium chloride trihydrate; 7 ml. distilled water; [illegible] ml. 20% Naconol NRSF. flush with argon; seal; add 20-25 mmoles monomer and double cap or reseal under N_2. Polymerize at 50°.

Recipe - B - .05gm. Bis (1,4-cychohexadiene chlororhodium)· 13 ml. distilled water· 2.5 ml. 20% Naconol NRSF· 5 ml. formic acid: argon flush: seal; add 20-25 mmoles monomer and double cap or reseal. Polymerize at 50°.

Expt. No.	mM. M_1	mM. M_2	Recipe	Time hrs.	Yield gm.	Conv. %	Product
Copolymerizations of Butadiene (M_1) and 1,1,2-Trifluorobutadiene (M_2)							
99-1	22 C_4H_6	22 $C_4H_3F_3$	A	17	1.498	43	Tough nervy brown rubber swells in $CHCl_3$, CH_2Cl_2 32.9% F; 45.4 mole % $C_4H_3F_3$; Tg -47; Tm
99-2	22 C_4H_6	22 $C_4H_3F_3$	A	17	.455	13	.25 ml. HCOOH added Soft brown rubber 32.3% F; 44.1 mole % $C_4H_3F_3$
99-3	22 C_4H_6	22 $C_4H_3F_3$	A	17	2.068	59	5 ml. CH_2Cl_2 added Tough nervy brown rubber swells in $CH\ Cl_3$, CH_2Cl_2 35.8% F; 51.4 mole % $C_4H_3F_3$; Tg -48; Tm +5
99-4	22 C_4H_6	22 $C_4H_3F_3$	see right	143	0	0	15 ml. CH_2Cl_2 +.020 gm. $RhCl_3 \cdot 3H_2O$ only.
104-3	22 C_4H_6	22 $C_4H_3F_3$	B	65	.628	18	5 ml. $C\ H_2Cl_2$ added Logey rubber 35.03% F; 49.8 mole % $C_4H_3F_3$; Tg -48; Tm +5

Table [illegible] (cont'd)

Expt. No.	mM. M_1	mM. M_2	Recip.	Time hrs.	Yield gm.	[illegible] %	Product
Other Copolymerizations with Butadiene (M_1)							
103-4	22 C H	25 5,5,5-Trifluoro-4-methyl-1,3-pentadiene	A	115	.70+	?	Tube leaked during experiment with double capping. Product two rubbers of differing molecular weight, of moderate F content and of similar infrared spectrum.
108-2	22 C_4H_6	18 5,5,5-Trifluoro-4-trifluoro-methyl-1,3-pentadiene	A	115	1.695	37	Leathery rubber swells in $CH Cl_3$ Infrared-strong trans butadiene; strong F 1150 etc.; unsaturation 1670 & 1710; 16.63%F; 9.8 mole% $C_6H_4F_6$; Tg -20; Tm +55
104-1	22 C_4H_6	25 5,5,5-Trifluoro-4-trifluoro-methyl-1,3-pentadiene	B	64	1.343	28	5 ml. CH_2Cl_2, added, some leakage Product - syrupy trans polybutadiene + black resin containing some F.
108-1	22 C_4H_6	18 5,5,5-Trifluoro-4-trifluoro-methyl-1,3-pentadiene	B	283	1.5±		Leathery resin Tm + 69
114-1	22 C_4H_6	11.7 2,3-Bis(trifluoro-methyl)-butadiene	A	18	.490	14.5	[illegible] 5 ml. [illegible] Nervy rubber Infrared shows very strong F in copolymer with trans butadiene; 37.3% F; [illegible]1.8 mole % $C_6H_4F_6$; Tg -27
119-2	22 C_4H_6	20.8 1,1,2-Trifluoro-3 chloro-butadiene	A	65	2.548	60	Nervy rubber 41.47% C, 3.82% H, 19.04% Cl, both components show by I.R.; band on Cl, 55.1 mole % $C_4H_2ClF_3$; Tg -35
123-2	22 C_4H_6	22 Hexafluorobutadiene	see right	385	.153	4	.020 gm. $RhCl_3 \cdot 3H_2O$ Products - red brown greasy resin plus brown resin 15 ml. distilled water ? ml. Nacconol NRSF

Table XIII (Cont [illegible]

Expt. No.	mM. M_1	mM. M_2	Recipe	Time hrs.	Yield gm.	[illegible] %	Product
Other Copolymerizations with [illegible]diene (M_1) (Cont'd.)							
110-1	44 C_4H_6	25 1,1,2,2-Tetrafluoro-3-vinyl cyclobutane	A	64	.83	13%	[illegible]ene (I.[illegible]) Tm. + 65°, + 130°
Other Copolymerizations with 1,1,2-Trifluorobutadiene (M_2)							
103-5	25 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	22 $C_4H_3F_3$	A	65	6.44	91	Tough white rubber swells [illegible] $_3$ yield indicates 26% C H F [illegible] 56.61% F; 60.1 mole % $C_4H_3F_3$; 46.1 [illegible] % $C_4H_3F_3$; Tg -17; Tm +103
104-2	25 5,5,5-Trifluoro-4 trifluoromethyl-1,3-pentadiene	22 $C_4H_3F_3$	B	65	2.508	42	5 ml. CH_2Cl_2 added. 55.3% F I.R. contradicts F analysis and indicates more M_1 in 104-2 than in 103-5. Brown tough rubber -75.8 mole % $C_4H_3F_3$; Tg +2; Tm +108.
119-3	20.8 1,1,2-Trifluoro-3 chlorobutadiene	22 $C_4H_3F_3$	A	65	5.126	97	Sl. sticky tough rubber 39.00% C, 2.24% H; 14.51% Cl; based on Cl, 48.6 mole % $C_4H_3F_3$; Tg -26 Both components show up strongly in infrared spectrum
123-3	22 Hexafluorobutadiene	22 $C_4H_3F_3$	see right	385	2.782	47	.020 gm. $RhCl_3 \cdot 3\ H_2O$ 15 ml. distilled water 2 ml. Nacconol NRSF By yield product should contain 16.6% C_4F_6 C analysis 44.12%; H analysis 2.79%; comparing with 125-4 as a blank; C analysis indicates 4% C_4F_6 in product, H analysis indicates none. Tg -34°C; Tm 56°C, 83°C. Tg of -34 is probably a good value for poly (trifluorobutadiene)

[illegible] (Cont'd.)

Expt. No.	mM. M_1	mM. M_2	Recip	Time hrs.	Yield gm.	Conv. %	Product
Coordinated Free Radical-Catalyzed Copolymerization of Butadiene (M_1) and 1,1,2-Trifluorobutadiene (M_2)							
Recipe - Mn $(C_5H_7O_2)_3$. 2 gm; distilled water, 18 ml.; 20% Nacconol NRSF, 2.5 ml; flush with argon; 1% by volume MTM-4 in flushed CCl_4, 3 ml.; argon flushed CCl_4, 5 ml.; seal; monomer; recap; polymerize at 50° 12 hrs.							
125-2	$78C_4H_6$/ 0	$C_4H_3F_3$		12	2.929	69	Gelled rubber cis 17 at most, trans 63, vinyl 20 used too much Mn in this series
125-4	$0C_4H_6$/58	$C_4H_3F_3$		12	6.51	100	Soluble in warm $CHCl_3$, not in cold $CHCl_3$. 44.70% C; 2.685% H infrared spectrum typical $(C_4H_3F_3)$
125-6	$39C_4H_6$/39	$C_4H_3F_3$		12	6.938	100	Tg. -51°C.

BUTADIENE - TRIFLUOROBUTADIENE COPOLYMERIZATIONS IN EMULSION WITH R[illegible] EXPERIMENTS.

Code		122-1	122-2	122-3	122-4	122-5	122-6	122-7	99-1	118-2	118-[illegible]	121-1	127-1	128-1	128-[illegible]
Reaction Volume	ml.	50	50	50	50	50	50	50	50	640	100	250	250	250	250
Recipe Volume	ml.	24.4	24.3	24.4	24.4	24.4	12.2	12.3	12.2	121	86	121	120	120	120
$RhCl_3 \cdot 3H_2O$	phm.	.574	.574	.576	.576	.576	.574	.574	.574	.548	.511	.554	.568	1.140	.875
Distilled Water	phm.	224	455	458	451	456	224	224	224	214	200	216	447	447	447
Maconol NRSF	phm.	5.74	5.74	5.76	11.5	5.76	5.74	5.74	5.74	5.48	5.11	5.54	11.4	11.4	11.4
Methylene Chloride	phm.	-	94	-	-	-	-	-	-	183	-	171	-	-	-
Sodium Carbonate	phm.	-	-	-	-	2.56	-	-	-	-	-	-	-	-	-
Formic Acid	phm.	-	-	-	-	4.42	-	-	-	-	-	-	-	-	-
1,5-cyclooctadiene	phm.	-	-	-	-	-	3.2	-	-	-	-	-	-	-	-
Styrene	phm.	-	-	2.2	2.2	-	-	-	-	-	-	-	-	-	-
Butadiene	phm.	33	33	33	33	33	33	33	33	42.8	33.2	42.4	34	33.3	33.3
1,1,2-Trifluorobutadiene	phm.	67	67	67	67	67	67	67	67	57.2	66.8	57.6	66	66.7	66.7
Butadiene	mmoles	43.5	21.75	26.1	26.1	26.1	21.75	21.75	21.75	202	168	198	132	130	130
1,1,2-Trifluoro-butadiene	mmoles	43.5	21.75	26.1	26.1	26.1	21.75	21.75	21.75	135	169	135	129	130	130
Free space ml./	gm.monomer	3.6	7.2	6.0	6.0	6.0	7.2	7.2	7.2	20.25	.51	5.1	6.16	6.16	6.16
Water gm/	gm.monomer	2.2	4.45	4.51	4.46	4.48	2.2	2.2	2.2	2.14	2.0	2.16	4.47	4.47	4.47
Emulsifier gm/	gm.monomer	.057	.057	.057	.114	.057	.057	.057	.057	.055	.051	.055	.114	.114	.114
Emulsifier gm/	gm. water	.0255	.0126	.0126	.0256	.0126	.0255	.0255	.0255	.0255	.0255	.0255	.0254	.0254	.0254
Agitation			end		over	end				sloshing			end over end		
Polymerization Time at 50°hrs.		19	19	19	19	19	19	8	17	20	41	71	39	35	66
Appearance at 10 hrs.		*	*	*	*	*	-	-	-	-	-	-	-	-	-
final		-	-	-	-	-	-	*	*	-	floc**	floc**	floc**	floc**	floc**
Yield	gm	4.322	1.762	.732	3.460	3.566	.251	.176	1.498	3.8	9.1	14.1	8.99	?	4.9
Conversion %		61	50	17	82	85	7	5	42	15	33	56	42	41	23
%F										31.82	18.74	(26) I.R.	(37.33 on blend)		
Mole % $C_4H_3F_3$										43.4	21.7				
Tg										-51		-53			
Tm										+51		-			

* 122-1 Massive flock
122-2 Latex over milky CH_2Cl_2
122-3 Latex - 2 cm monomer layer
122-4 Latex - no monomer layer
122-5 Latex - no monomer layer a little flock on stirrer
122-6 Floc + monomer layer + turbid coarse latex
99-1 Flocced suspension plus a little oil layer

[illegible] (Cont'd.)

** Scale-up recipe 118-2, 118-3, and 121-1 is 7 times recipe A, Table 13, except for slight variation in the amount of monomer. 118-2 and 121-1 had 35 ml. CH_2Cl_2 in addition. 118-2 was run in a stainless steel bomb which was etched by the $RhCl_3$. The polymer was a smooth milling dark low mooney rubber. 118-3 was nervy and sheeted very rough. Infrared confirms F analysis of 118-2, 118-3. 118-3 sampled to Natick. Tests reported in letter of Angus Wilson to D. I. Relyea, August 10, 1967.

121-1 stopped after 15 hours. It had prefloc early, and was at end a blob of jelly in a little water.

127-1 was stopped earlier than intended in trying to get a stuck capper die off the cap. Rubber sheeted with holes and bad shrinkage.

128-1 had a large lump of prefloc. Conversion 41% by solids (polymer spilled in work-up). .342 gm. soft polymer recovered.

128-2 had six ½" magnetic stirrers instead of the usual single one. It was mounted for maximum end-over-end agitation. After 3 hours, it was an almost transparent emulsion. Floc started at 18 hours and was increased at 26 hours. Solids were 7.1% at 42 hours and 7.0% at 66 hours. Polymer rough on milling test.

Physical Properties of Cured Polymer 127-128 Blend

A blend of 127-1 (9.33 gm.), 128-1 (.37 gm.) and 128.2 (5.0 gm.) and containing 2 parts PBNA was sampled after blending and adding stearic acid in the recipe below. Microanalysis indicated 36.24% F. Correcting for 3 parts of additives, this becomes 37.33% F, or 70.8% $C_4H_3F_3$ by wt. and 54.8 mole %.

This rubber was mixed in the following recipe: rubber 100, Philblack O 15, XX zinc oxide 1, stearic acid 1, mercaptobenzothiazole disulfide 1.5, tetramethylthiuram disulfide .5, sulfur 1. It was given a 15' break on a tight 5" mill and mixed in about 45 minutes.

Density determinations in mixtures of ethylene dichloride and $CCl_2Br\text{-}CHBr_2$ indicated the density of the mixed stock is about 1.335, and that of the polymer was calculated to be about 1.28.

The stock was cured 30 and 60 minutes at 300°F. in 1-3/4" x 1-3/4" x .1" mold.

Table XIV (Cont'd.)

Physical Properties	127-128 Blend		[illegible]
	30' cure	60' cure	30' cure
Modulus at 100	125 psi	115 psi	
200	235	225	
300	425	435	
400	735	760	
500	1150	1210	
Autographic Tensile	1610 psi	1485 psi	
Elongation	585%	555%	
Modified Gehman Test .			
T2	-17	-18	-6
T5	-37.5	-38	-30
T10	-42	-43.5	-37
T100	-52.5	-52.2	-42.5
DTA (cured)	-46	-46	
Swelling Test - 24 hr. exposure, based on ASTM - D471-59T:			
70 isooctane/30 toluene	128	133	72
50 isooctane/50 toluene	239	263	180

TGA Decomposition Temperatures in N_2

Raw Rubber	Decomposition Temp. [illegible]
Code 121 Butadiene-Trifluorobutadiene Copolymer about 26% F	250
Neoprene	200
Phillips cis-4	355
Synpol 1500 (butadiene-styrene)	350

*Sample 7 (copolymer of monomer 1 and 4) in letter of Angus Wilson to D. [illegible] [illegible] 10, 1967.

Table XV

COMPOSITION OF POLYMERIZATION CATALYSTS

Catalyst Code	mMoles of Reducing Agent	mMoles of Transition Metal Compound
1	1.25 $Et_3Al_2Cl_3$	.5 Vanadium Oxychloride $VOCl_3$
1A	.5	.5
1B	1.5	.5
1C	.625	.25
2	2.5 Aluminum Triisobutyl	.5 Butyl Vanadate $VO(OBu)_3$
2A	1.25	.5
2B	1.5	.5
2C	1.25	.25
2D	.75	.25
3	1.5 Aluminum Triisobutyl	.5 Tetrabutyl Titanate $Ti(OBu)_4$
3A	2.5	.5
3B	1.25	.5
3C	.76	.5
3D	1.90	.5
3E	1.00	.5
3F	1.25	.25
3G	.625	.125
3H	.5	.5
3I	.625	.25
3J	.3	.1
3K	12.5	.5
4	1.5 Magnesium Phenyl	.5 Tetrabutyl Titanate $Ti(OBu)_4$
4A	1.9	.5
4B	.63	.5
4C	.55	.5
4D	.75	.5
4E	3.8	.5
4F	.32	.5
5	1.5 Aluminum Triisobutyl	.5 Titanium Tetrachloride $TiCl_4$
5A	2.5	.5
5B	.75	.25
5C	1.25	.5
5D	1.2	1.0

Table XV (Cont'd.)

Catalyst Code	mMoles of Reducing Agent	mMoles of Transition Metal Compound
5E	.5 Aluminum Triisobutyl	.1 Titanium Tetrachloride TiCl$_4$
5F	.22	.2
5G	.275	.2
5H	.33	.2
6	1.25 Aluminum Triisobutyl	.5 Titanium Tetraiodide TiI$_4$
6A	2.50	.5
6B	.50	.15
6C	.50	.10
6D	1.0	.2
6E	.94	.25
6F	.675	.133
6G	.675	.146
6H	1.0	.15
6I	.75	.15
6J	1.88	.5
6K	.2	.04
6L	.60	.12
7	.3 $Et_3Al_2Cl_3$	.06 Cobalt Octoate
7A	.075	.015
7B	.25	.015
7C	.15	.03
7D	.60	.12
7E	.30	.012
7F	.15	.006
7G	.15	.0012
7H	.6	.0024
8	.3 Aluminum Triisobutyl	0.033 $Ti(OBu)_4$ + 0.067 TiI_4
8A	.6	0.067 $Ti(OBu)_4$ + 0.133 TiI_4
9	1.25 Aluminum Triisobutyl	.5 Zirconium (acetyl acetonate)$_4$
9A	2.5	.5
9B	1.5	.5
10	2.5 Aluminum Triisobutyl	.1 Tetrakis (diethylamino) titanium
10A	6.25	.1

Table XV (Cont'd.)

Catalyst Code	mMoles of [illegible] Agent	mMoles of Transition Metal Compound
11	1.25 $Et_3Al_2Cl_3$	.5 Vanadyl Acetylacetonate, $VO(C_5H_7O_2)_2$
11A	.5	.5
12	2.5 Aluminum Triisobutyl	.5 Vanadyl Acetylacetonate, $VO(C_5H_7O_2)_2$
12A	1.0	.5
13	1.25 $Et_3Al_2Cl_3$	.5 Tetrabutyl Titanate
13A	.5	.5
14	1.67 Decyl Magnesium Iodide	.5 Tetrabutyl Titanate
14A	.83	.5
15	1.9 Magnesium Phenyl	.5 Titanium Tetrachloride
15A	1.5	.5
16	1.25 Lithium Aluminum Tetraheptyl	.5 Titanium Tetrachloride
17	.75 Magnesium Phenyl	.5 Titanium Tetraiodide
17A	.9	.5
17B	.325	.16
17C	.27	.2
17D	.12	.04
17E	.3	.1
17F	.6	.2
18	1.5 Aluminum Triisobutyl	.4 Vanadium (acetyl acetonate)$_2$
19	1.5 Aluminum Triisobutyl	.5 Molybdenum Pentachloride
20	1.5 Aluminum Triisobutyl	.5 Tungsten Hexachloride
21	1.5 Aluminum Triisobutyl	.5 Chromium (acetyl acetonate)$_3$
22	1.5 Aluminum Triisobutyl	.5 $CrCl_3 \cdot 3$ Tetrahydrofuran
23	1 Milligram Atom Iodine	-
24	.37 Magnesium Phenyl	.067 $Ti(OBu)_4$ + .133 TiI_4
25	2.1 Aluminum Triisobutyl	.2 $VOCl_3$
26	.45 Decyl Magnesium Iodide	.15 TiI_4

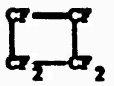
Catalyst is stirred 15 minutes in the presence of monomers except where otherwise stated. A preformed catalyst is stirred 15 minutes before monomer addition. Where reducing agent is added first, the catalyst code is followed by a small letter "r"; where transition metal compound is added first, the catalyst code is followed by a small letter "t". Where neither "r" nor "t" follow the catalyst code, the catalyst is preformed.

[illegible]

VAPOR [illegible] CHROMATOGRAPHY OF [illegible]

Compound	Source	Purity %	Res. Cen. VPC No.	Stationary Phase[a]	Temp. °C.[b]	Ret. Time mins.	Impurities Ret. Time	Impurities %
$CH_2=CF_2$	Peninsular ChemResearch, pink cylinder	99.2	5062	Q	23 I	0.9	9.6	0.03
			5078	G	60 P_2	4.3		0.8
$CH_2=CF_2$	Peninsular ChemResearch, blue cylinder	99.7	5066	Q	27 I	1.2	-	-
			5078	G	60 P_2	4.2	-	0.25
$CF_3CF=CF_2$	Peninsular ChemResearch	98.6	5065	Q	24 I	0.2	2.3	0.9
			5077	G	60 P_2	9.2	-	0.12
							2.9	0.07
							11.8	0.3
CF_2BrCF_2Br	Peninsular ChemResearch	99.9	5083	Q	75 I	3.5	0.5	0.002
							1.2	0.005
							1.7	0.003
							2.9	0.016
			5082	U	60 P_1	3.9	2.5	0.01
							3.2	0.01
$CF_2BrCFClC$[illegible]	Peninsular ChemResearch	93.8	5081	Q	75 I	17.7	11 cpds.	0.17 total
			5080	U	60 P_1	14.1	15.4	6
$(CF_2=CFCF_2)_2$	Prof.J.D.Park Univ. of Colo.	92.9	5085	Q	75 I	5.1	<5.1	7 cpds.
							>5.1	13 cpds.
			5084	U	60 P_1	4.1	<4.1	6 cpds.
							>4.1	13 cpds.
$(CF_2=CHCF_2)_2CH_2$	Prof. J. D. Park,	97.4	5087	Q	75 I	6.1	<6.1	7 cpds.
							>6.1	10 cpds.
			5086	U	60 P_1	9.4	<9.4	5 cpds.
							>9.4	5 cpds.
$CF_2=CFCl$	Matheson	99.9	5130	Q	60 I	1.0	2.6	-
			5131	Q	34	1.2	4.7	-
			5132	U	34	1.4	5.8	.07
			5133	G	123 mins., then P_2	30.6	-	-
$CH_2=CHF$	Matheson	99.5	5257	G	60 P_2	7.3	.9	.2 air
			5258	Q	29 I	1.1	36	.3 ?

[illegible]

Compound	Source	Purity %	[illegible]es. Cen. VPC No.	Stationa[illegible] Phase^a	[illegible]	[illegible] mins.	[illegible] Time	[illegible]
Argon	Matheson	99.9	5148	G	60 I	.9	-	-
			5149	G	30 I	1.0	-	-
			5150	M	75 P_3	1.8	3.1	.1
$CF_2=CF-CH=CH_2$	UNIROYAL, Inc.	99.4	5160	G	24 I	35.9	-	-
				after 30 mins. started heating - [illegible] program				
			5161	G P_2	60 I	16.0	.9	.6 [illegible]
	Peninsular ChemResearch		5158	Q	24 I	1.2	1.0	1.7 air
			5159	G	60 P_2	14.6	.9	1.8 air
							4.0	.08 ?
$CH_2=CH_2$	Phillips Res. Grade	96.6	5208	G	50 P_1	6.1	1.0	3.4 air and/or CH_4
$CH_3CH=CH_2$	Phillips		5209	G	60 P_1	16.3	.9	.3 and/or CH_4
1,1,2-trifluoro-3-vinylcyclobutene-2	Univ. of Utah, Dr. Park FC-303	91	5340	Q	75 I	2.6	6.3	7
							9.7	1
		88	5341	U	40 I	4.8	14.1	1
							10.2	10
							13.5	1
							22	1
1,1,2-tri-2-chloro-3-vinylcyclobutane	Univ. of Utah, Dr. Park FC-300	98.4	5338	Q	75 I	6.7;	.39 air,	-
						6.9	1.04;	-
							1.50,	-
							11.4,	-
							13.4,	-
							22.1	-
		52.7	5342	V	40 P	10.5;	[illegible]race air,	-
						11.1	2.8,	-
							2.95,	-
							3.5,	-
							4.8,	-
							8.1,	-
							13.9,	-
							23.3	-

[illegible]VI (C[illegible])

Compound	Source	Purity %	[illegible]es.Ce[illegible] VPC No.	Stationa[illegible] Phase[a]	[illegible]	[illegible] mins.	[illegible] Time	[illegible]
1,1,2-trifluoro-2-chloro-3-methyl 3-ethynylcyclobutane	UNIROYAL	-	5306	SE	75 P_4	3.0	>3.0 two broad lo[illegible] peaks	
		51	5335	V	40 I for 10 mins., then P_5	21.3		
		48				22.2		
		98.6	5333	C1	75 I	9.2	1.8	-
							2.9	-
							5.2	-
							13.1	-
							17.9	-
							19.6	-
							27.7	-
							31.6	-
$CH_3CF=CH_2$	Pierce Chemical Co.	92.9	5359	C1	60 I	1.1	.9	
							3.4	-
			5357	G	60 P_2	13.0	11.6	
							27.2	
							29.7	
							7.1	total
$CH_3C(CF_3)=CH_2$	Pierce Chemical Co.	98	5356	G	60 P_2	16.1	3.82	.4
							10.8	total
							plus air	
$CF_2=CF-CF=CF_2$	Pierce Chemical Co.		5269	Q	60 I	-	1.0, .9	-
		99.5	5358	G	60 P_6	13.9	3.9, 11.2	.5
							plus air	total
1,1,2-trifluorobutadiene vac. distilled	UNIROYAL	100	5506	G	60 P_2	15.6	-	0
Trifluoroethyl vinylether "Fluoromar"	Ohio Chemical & Surgical Equipment Co.	100	5474	U	60 I	3.4	-	0
			5481	U	60 I	3.6	-	0
			5482	X	60 I	9.9	-	0
α,β,β-Trifluorostyrene	Moleculon Research Corp.	-	5480	Y	60 P_6	19.7	5 more volatile plu[illegible]	
		98.5	5485	Y	75 I	13.5	3 less volatile tota[illegible] 1.5%	

TABLE XVI (Cont'd.)

Compound	Source	Purity %	Res.Cen. VPC No.	Stationary Phase[a]	Temp. °C[b]	Ret. Time mins.	Impurities Ret. Time	%
Perfluoro-1,5-hexadiene	Univ. of Utah, Dr. Park FC-305	98 93 min.	5617 5620	S Z	N.T.I. 60 I	14.5 16.7	6 more volatile plus 1 less volatile total 2 resolves additional minor constituent, conc 5% max.	
1,1,3,3,5,5,7,7-Octafluorohepta-1,6-diene	Dr. Harrison	99	5618	S	60 I for 10 min. then P	3.7	9 trace	-
	5195	90+	5619	Z	60 I for 10	3.7	20 trace total 1 1 not quant. det'd. may be as high as 10%	

a. Q = 2-meter squalene; U = 6 ft. Ucon B550; SE = 8 ft. SE 30; G = 4 ft. silica gel; s = 6' squalene GAW;

Z = 6 ft. squalene 10% HF; Y = 6' Ucon LB 550XC; X = ODPN; V - 150' Ucon LB 550Xber 80; M = 6 meter 5A molecular sieve.

b. I = isothermal. Programmed procedures: P_1 at 2.9°C/min., P_2 at 7.5°C/min., P_3 at 15°C/min., P_4 at 5.6°C/min., P_5 at 2°C/min., P_6 at 4°C.min.

[illegible]

SUMMARY OF FLUORINE ANALYSES

Code	% F	F Monomer	Weight %	Mole %	Comonomer	Weight %	Mole %
40-5	2.19M*	1,1,2-Trifluoro-2-chloro-3 methyl-3-ethynyl cyclobutane	7.07	1.15	Ethylene	92,93	98.9
40-6	1.75M	1,1,2-Trifluoro-2-chloro-3 methyl-3-ethynyl cyclobutane	5.65	.90	Ethylene	94.35	99.1
41-6	12.81M	2,3-Bis(trifluoromethyl) norbornadiene	25.26	4.1	Ethylene	74.38	96.0
44-9	46.33M	Hexafluoro-2-butyne	65.9	25.1	Ethylene	34.1	74.9
45-1	29.51M	1,1,2-Trifluorobutadiene	38.9	14.1	Ethylene	61.1	85.9
45-2	34.03M	1,1,2-Trifluorobutadiene	64.6	32.2	Ethylene	35.4	67.8
45-4	6.15M	1,1,2-Trifluorobutadiene	16.67	3.32	Ethylene	88.33	96.7
46-1	2.17M	1,1,2-Trifluoro-2-chloro-3-vinyl-cyclobutane	6.52	1.1	Ethylene	93.48	98.9
47-1	31.07M	1,1,2-Trifluoro-3-vinylcyclobutene-2	30.8	8.5	Ethylene	69.2	91.5
50-3	2.51M	Hexafluorobutadiene	3.13	.6	Ethylene	96.87	99.4
67-2	8.56M	1,1,2-Trifluoro-2-chloro-3-iso-propenyl cyclobutene	27.45	5.30	Ethylene	72.55	94.7
67-4	5.67M	1,1,2-Trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclo-butenyl) cyclobutane	14.88	1.61	Ethylene	85.12	98.4
67-7	1.52M	1,1,2-Trifluoro-2-chloro-3-vinyl-cyclobutane	2.89	.385	Ethylene	97.11	99.6
68-3	2.26M	1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynyl cyclobutane	7.29	1.19	Ethylene	92.71	98.8
68-7	12.26M	1,1,2-Trifluorobutadiene	23.64	6.74	Ethylene	76.36	93.2
91-7	3.35S	2-Trifluoromethylbutadiene	7.19	1.75	Ethylene	92.81	98.25
91-7	2.54S	2-Trifluoromethylbutadiene	5.66	1.36		94.34	98.64
94.3	1.91S	2,3-Bis(trifluoromethyl) butadiene	3.18	.49	Ethylene	96.82	99.51
94-4	1.71S	2,3-Bis(trifluoromethyl) butadiene	2.85	.43	Ethylene	97.15	99.57
94-5	3.61S	5,5,5-Trifluoro-4(trifluoromethyl)-1,3-pentadiene	6.02	.94	Ethylene	93.98	99.06
94-6	1.36S	5,5,5-Trifluoro-4(trifluoromethyl)-1,3-pentadiene	2.27	.34	Ethylene	97.73	99.66
105-1	16.96S	3,3,3-Trifluoropropene	28.6	10.5	Ethylene	71.4	89.5

Table [illegible] (Cont'd)

Code	% F	[illegible]	Weight %	Mole %	[illegible]	Weight %	Mole %
Copolymers with Butadiene							
24-4	40.09M	1,1,2-Trifluorobutadiene	76.3	61.6	C_4H_6	23.7	38.3
24-7	21.00M	1,1,2-Trifluorobutadiene	39.9	24.9	C_4H_6	60.1	75.1
47-3	4.04M	1,1,2-Trifluoro-3-vinylcyclobutene-2	9.52	4.1	C_4H_6	90.48	95.9
47-4	12.53M	1,1,2-Trifluoro-3-vinylcyclobutene-2	29.55	14.5	C_4H_6	70.45	85.5
48-9	2.43M	2-Fluoropropene	7.94	7.2	C_4H_6	92.06	92.8
50-11	16.13M	Hexafluorobutadiene	20.15	8.8	C_4H_6	79.85	91.2
57-3	1.40M	1,1,2-Trifluorobutadiene	2.66	1.35	C_4H_6	97.34	98.65
57-4	8.56M	1,1,2-Trifluorobutadiene	16.26	8.86	C_4H_6	83.74	91.14
57-5	15.02M	1,1,2-Trifluorobutadiene	28.55	16.7	C_4H_6	71.45	83.3
57-6	4.55M	1,1,2-Trifluorobutadiene	8.65	4.5	C_4H_6	91.35	95.5
73-3	2.64M	1,1,2-Trifluorobutadiene	5.01	2.56	C_4H_6	94.99	97.44
79-1	0.95M	1,1,2-Trifluorobutadiene			C_4H_6		
79-4	0.59M	1,1,2-Trifluorobutadiene			C_4H_6		
79-9	0.67M	1,1,2-Trifluorobutadiene			C_4H_6		
81-1	41.14M	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	68.7	38.4	C_4H_6	31.3	61.6
81-2	38.50M	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	64.3	33.9	C_4H_6	35.7	66.1
91-5	2.26S	2-Trifluoromethylbutadiene	4.84	2.20	C_4H_6	95.16	97.8
94-2	5.72	2,3-Bis(trifluoromethyl)butadiene	9.54	2.9	C_4H_6	90.46	97.1
99-1	32.92M	1,1,2-Trifluorobutadiene	62.6	45.5	C_4H_6	37.4	54.5
99-2	32.29M	1,1,2-Trifluorobutadiene	61.4	44.3	C_4H_6	38.6	55.7
99-3	35.81M	1,1,2-Trifluorobutadiene	68.1	51.6	C_4H_6	31.9	48.4
104-3	35.03S	1,1,2-Trifluorobutadiene	66.5	49.8	C_4H_6	33.5	50.2
108-2	16.63S	5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene	27.78	9.9	C_4H_6	72.25	90.1

[illegible]

Code	% F	F Monomer	Weight %	Mole %	[illegible]	Weight %	Mole %
Copolymers with Butadiene (cont'd.)							
114-1	37.27S	2,3-Bis(trifluoromethyl)-1,3-butadiene	62.1	31.8	C_4H_6	37.9	68.2
118-2	3[illegible].82S	1,1,2-Trifluorobutadiene	60.5	43.4	C_4H_6	39.5	56.6
118-3	18.74S	1,1,2-Trifluorobutadiene	35.6	21.7	C_4H_6	64.4	78.3
112-7	0S	1,1,2,2-Tetrafluoro-3-vinyl cyclobutane	0	0	C_4H_6	100	100
112-9	0S	1,1,2,2-Tetrafluoro-3-vinyl cyclobutane	0	0	C_4H_6	100	100
127-128 Blend	36.24M 37.33	1,1,2-Trifluorobutadiene (corrected)	70.8	54.8	C_4H_6	29.2	45.2

[illegible]le [illegible] ([illegible])

Code	[illegible]	M_1	Weigh. % M_1	Mol. % M_1	[illegible]	Weight % M_2	Mole % M_2
Other [illegible]olymers of Fluorina[illegible] [illegible]							
27-4	52.56M	1,1,2-Trifluorobutad[illegible] This blank gave the theoretical content	100	100			
27-1	51.53M	1,1,2-Trifluorobutadiene			[illegible]$_3$CF=C[illegible] [illegible]		
27-2	50.09M	1,1,2-Trifluorobutadiene Analysis in 27-1 and 27 [illegible] [illegible]ow for any significance.			$CH_2=CF_2$ [illegible]4.4%[illegible]		
73-4	4.12M	1,1,2-Trifluorobutadiene	7.83	4.21	Isobutylene	92.17	95.79
73-5	4.23M	1,1,2-Trifluorobutadiene	8.03	4.33	Isobutylene	91.97	95.67
73-6	3.22M	1,1,2-Trifluorobutadiene	6.11	3.94	Isoprene	93.89	96.1
73-7	1.65M	1,1,2-Trifluorobutadiene	3.13	2.00	Isoprene	96.87	98.0
73-8	12.87M	1,1,2-Trifluorobutadiene	24.4	14.8	Methyl vinyl ether	75.6	85.2
103-5	56.61S	1,1,2-Trifluorobutadiene	46.1	60.1	$(CF_3)_2C=CH-CH=C$[illegible]	53.9	39.9
104-2	55.29S	1,1,2-Trifluorobutadiene	64.1	75.8	$(CF_3)_2C=CH-CH=CH_2$	35.9	24.2

* M = analysis by Microanalysis, Inc.

S = analysis by Schwarzkopf Microanalytical Laboratory

TABLE XVIII

DESIRED PHYSICAL PROPERTIES OF RUBBERS FOR LOW TEMPERATURE, OIL-RESISTANT SERVICE

Tensile Strength	2500 psi minimum
Ultimate Elongation	250% minimum
Hardness Shore A - 5 sec.	60 ± 10
Gehman Torsional Modulus, T_5	-65°F. maximum
U. S. Retraction, TR-50	-65°F. maximum
Volume Swell, test Fluid III (30% toluene, 70% isooctane)	20% maximum
Building Tack	Good
Calendering Quality	Good
Extrusion Quality	Good
Permeability of Fluid III, 0.075 ± .010 inch thick sample oz./sq.yd./24 hrs.	2 maximum
Ozone resistance, 6 hours in 50 pphm ozone (R. T.)	No crack

13. ABSTRACT (Cont'd)

It was observed that the fluorinated monomers were generally much less reactive than their hydrocarbon homologs. The most reactive monomers were seen to be the conjugated dienes. Rhodium-initiated polymerization of the conjugated fluorinated dienes was most satisfactory from the viewpoints of rate of conversion to polymer, yield of polymer, ease of copolymerization with hydrocarbon olefins and insensitivity to water or other polar contaminants. Several fluorinated butadienes are quantitatively converted to polymer by the rhodium catalyst in less than a day at 50°C. The 1;1 copolymer of 1,1,2-trifluorobutadiene and butadiene has Tg of -48°C., is sulfur-vulcanizable and shows 180% swell in ASTM fuel C. At the other end of the monomer-catalyst reactivity range is the combination hexafluoro-propene-sesquiethyl-aluminum sesquichloride-vanadium oxychloride which gives less than 4% conversion to polymer in 280 hours.

A minor effort was directed toward chemically modifying a stereospecific polymer such as high cis polybutadiene as an approach to forming stereospecific polymers of improved oil-resistance and low-temperature properties. Thus the reaction of pentafluorobenzenesulfenyl chloride with 20% of the unsaturation of cis-polybutadiene yields a sulfur-curable rubber of improved oil resistance having Tg of -66° and no melting or crystallization phenomena above that temperature.

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13. ABSTRACT

The findings of a three-year program of research on the polymerization of fluorinated monomers to form high polymers having random or stereospecific microstructure are described. The objective of this program was the preparation of new elastomeric materials which might be both oil-and chemical-resistant and which might have useful rubbery properties over a wide range of temperatures such as -65° to +300°C.

The initial approach was to apply to several easily-procurable fluorinated olefins some of the stereospecific catalyst systems previously developed for hydrocarbon olefins. Apparatus was constructed for handling the volatile monomers and screening potential polymerization catalyst. The monomers tested included olefins and acetylenes which might undergo 1,2-polymerization, cyclobutenes and norbornenes which might participate in ring-opening polymerization, and conjugated dienes for which several potential polymerization processes are possible. In addition to monomer type, a number of other polymerization variables were explored including (a) the catalyst type, whether cationic, anionic coordination or free radical, (b) the transition metal of the catalyst, (c) the olefin complexing power of the catalyst, (d) solvent, (e) temperature, and (f) monomer ratio in copolymerizations.

(cont'd)

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymerization	8					
Fluorochemicals	9					
Monomers	9					
Oil-resistant	0					
Chemical resistant	0					
Elastomers	4					