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

Technical Report 68-12-CM

(SEMIANNUAL REPORT NO. 5)

by

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

June 1967

Contract No. DA19-129-AMC-487(N)

U. S. ARMY NATICK LABORATORIES
NATICK, MASSACHUSETTS

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UNITED STATES RUBBER COMPANY
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for the period
December 1, 1966 - May 31, 1967

Contract No. DA19-129-AMC-487(N)
Project No. 1K024401A113

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FOREWORD

This report describes work accomplished under Contract No. DA-19-129-AMC-487(N) between the United States Rubber Company (now UNIROYAL, Inc.) and the U. S. Army Natick Laboratories. Mr. C. B. Griffis is the Project Officer. This is the fifth Semiannual Report under this contract and covers the period December 1, 1966 through May 31, 1967.

During the six-month period covered by this report, the following manhours were expended on this project:

Senior Research Scientist	338
Research Scientists	1177
Technician (Sub-professional)	1470
Total direct labor	2985 manhours

The technical effort for the past six months exceeded that required by the contract and brought the manhours total to 11940. This figure is 5% over the prorated contract requirement. We plan a 2200 manhour effort during the next six months.

SUMMARY

1. Rhodium trichloride in aqueous emulsion initiates the homopolymerization of 1,1,2-trifluorobutadiene (1) and 1,1,2-trifluoro-3-chlorobutadiene (2). Monomers 1 and 2 are also readily copolymerized with each other or individually with butadiene (4) to give rubbery polymers. The 51:49 1-4 copolymer has a Tg of -48°C. A sample has been furnished to U. S. Army Natick Laboratories for evaluation.

2. Preliminary experiments with iridium compounds indicate they are also active catalysts for polymerization of fluorinated dienes. Both rhodium and iridium are much less active with olefins and non-conjugated dienes.

3. Other new catalyst-monomer combinations have been explored. Among those which appear promising is a cobalt octoate-initiated copolymer of 2-(trifluoromethyl)butadiene and butadiene.

4. Monomers synthesized for use during this report period include 1, 2, 3,3,3-trifluoropropene, 2,3-bis(trifluoromethyl)butadiene, 5,5,5-trifluoro-4-trifluoromethyl-1,3-pentadiene, and 1,1,2,2-tetrafluoro-3-vinylcyclobutane.

5. Adducts of sulfenyl chlorides and *cis*-polybutadiene have been prepared with the following characteristics (sulfenyl chloride addend, % saturation in adduct, and Tg): CF_3SCl, 15%, -84°; CF_3SCl, 30%,-44°; C_6F_5SCl, 20%,-66°; C_6F_5SCl, 25%, -52°; and C_6Cl_5SCl, 15%, -50°. Samples of these adducts have been furnished to U. S. Army Natick Laboratories for evaluation.

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INTRODUCTION

This is the fifth semiannual report of research on the polymerization of fluoroinated monomers to form random or stereospecific high polymers. This work, sponsored by the U. S. Army Natick Laboratories, has the objective of preparing new elastomeric materials which will be both oil- and chemical-resistant and have useful rubbery properties over a wide range of temperatures such as -65° to +300°C.

During the period coveredby this report we have explored the use of rhodium-containing catalysts as initiators of polymerization of fluorinated dienes and have continued to examine transition metal anionic coordination catalysts for both fluorinated olefins and fluorinated dienes. Additional samples of the adducts of sulfenyl chlorides to cis-polybutadiene have been prepared for continued evaluation at the U. S. Army Natick Laboratories.

DISCUSSION

1. Introduction

In our search for novel fluorine-containing polymers with extreme-temperature utility and oil- or chemical-resistance we have continued to explore combinations of polymerization catalysts and fluorine-containing monomers. During the period covered by this report the following types of polymerization systems have been studied:

Monomer	Catalyst	Reaction Medium
Fluorinated olefin, acetylene or diene	Rhodium salts	Emulsion
Fluorinated olefin, acetylene or diene	Iridium salt or complex	Emulsion
Fluorinated diene and/or olefin	Ziegler catalyst, e.g. $\text{TiI}_4 + \text{Al}\underline{i}\text{-Bu}_3$	Hydrocarbon

The principal studies have been made with diene monomers because of their greater reactivity relative to nonconjugated dienes or monomers containing only one double bond. The use of the noble metal catalysts, e.g. rhodium chloride, has led to the preparation of high molecular weight diene copolymers in good yield. Monomer syntheses where required and results of polymerization experiments are discussed below for each of the polymerization systems.

In addition, some further results are reported for the chemical modification of the readily available polymer *cis*-polybutadiene to provide elastomers having improved chemical and physical properties.

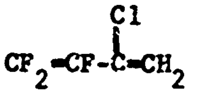
2. Rhodium Salt-initiated Emulsion Polymerization of Fluorine-containing Dienes

a. Polymerization

The UNIROYAL Corporate Research Center discovered the unique ability of rhodium salts to cause the stereospecific *trans* polymerization of butadiene[1,2]. We have now used rhodium chloride as catalyst to survey the reactivity of a range of fluorinated monomers in this type of controlled structure polymerization. Table I 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

$CF_2=CF-CH=CH_2$

1



$CF_2=CF-\overset{Cl}{C}=CH_2$

2

$CF_3-\overset{CF_3}{C}=CH-CH=CH_2$

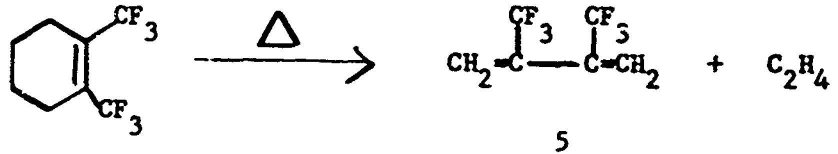
3

in aqueous emulsion. 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 I, are briefly summarized as follows:

Monomer	% Conversion to Polymer
3-Chloro-3,4,4-trifluoro-2-isopropenyl-cyclobutene-1	18
α,β,β-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

Monomer 5 is of interest because its free radical-initiated homopolymer has been reported to have good high-temperature stability[3]. It was prepared by pyrolysis of the precursor obtained as described in our last report[4].



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Copolymerizations of butadiene (4) or monomer 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. These polymerizations are described in detail in Table II. The most successful ones are summarized below.

Monomer Pair	Mole-% of First Monomer in Polymer	Tg, °C.
1-4	51.4	-48
2-4	55.1	-35
3-4	9.8	-20
5-4	31.9	-27
2-1	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 the butadiene portion[14] and n. m. r. to establish the presence or absence of unsaturation on certain carbon atoms of the fluorinated monomers. The results are suggestive of trans-1,4 polymerization but further study on polymers and model compounds needs to be done before unequivocal structure assignments can be made. For instance, it is puzzling that the 3-4 copolymer has a Tg as high as -20° when it is known that trans-polybutadiene has Tg = -80°. It is possible that a significant amount of vinyl monomer unit is present, but again a further study of spectra-structure correlation must be made to establish the answer.

The monomer pair 5 and 4 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% per hour in these preliminary 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.

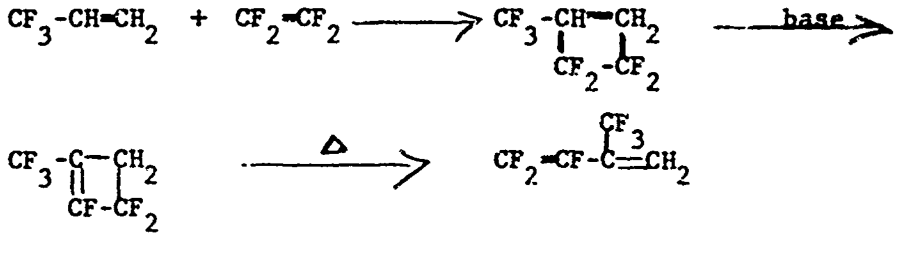
It has been reported that formic acid promotes the rhodium-initiated polymerization of butadiene[12], but we have found it to be deleterious in the case of copolymerization of 1 and 4. Methylene chloride in the organic phase of the emulsion has a slightly favorable effect. Other organic solvents will be examined as well.

From the viewpoint of low Tg, the most promising copolymer is that of 1 and 4, with its observed value of -48°. This is an encouraging result in that it confirms that the butadiene-fluorinated diene approach may lead to good low temperature properties. Since it is known that rhodium in emulsion furnishes trans-polybutadiene[2] and that the Tg of trans-polybutadiene is higher than the Tg of cis-polybutadiene by about 30°, the discovery of a suitable catalyst for cis copolymerization of 1 and 4 may be expected to provide a rubber with Tg of -60 to -70°.

A small sample of the 1-4 copolymer was furnished to the U. S. Army Natick Laboratories for evaluation and larger quantities will be made for further testing.

b. New Monomer Synthesis

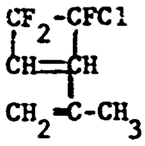
We are exploring the following cycloaddition route to the highly fluorinated monomer 1,1,2-trifluoro 3-(trifluoromethyl)butadiene which we consider to have potential in rhodium-initiated polymerization.



The initial attempts at the first step were unsuccessful. The cycloaddition reaction was carried out in solvent at pressures of 100 psig or less. This will be repeated without solvent at higher pressures since the literature reports this reaction to proceed under such conditions[7].

3. Iridium-initiated Polymerizations of Fluorine-containing Dienes

Other work in this Laboratory has shown the effectiveness of iridium catalysts in polymerizing norbornenes[11]. 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 catalystsin aqueous emulsion These experiments are summarized in Table III. 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. The iridium salt is comparable in activity to rhodium chloride with monomer 6, but much slower than rhodium chloride with monomer 3.



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4. Ziegler Catalyst-initiated Polymerizations of Fluorine-containing Dienes

As indicated in our previous report[4] the monomers which appear most reactive with Ziegler-type catalysts (e.g. Ti- or V- based catalysts) are conjugated dienes. We have examined these monomers further in both homopolymerizations and copolymerizations using catalysts which are known to be effective in forming cis-polybutadiene.

a. 2-(Trifluoromethyl)butadiene

This monomer was prepared as described previously[4] and used in a series of copolymerizations summarized below and described in detail in Table IV.

Comonomer	Catalyst Base	Conversion, %	Type of Polymer
4	Co octoate	52	High cis 1,4 content rubber, about 10% F monomer
4	$Ti(OBu)_4$	4	Fluid, viscous, mainly F monomer
4	TiI_4	<0.5	High trans resin, about 15% F monomer
Ethylene	$VOCl_3$	38	resin

The result with the cobalt-based catalyst is sufficiently interesting to warrant further study of this monomer when more is available.

In our version of the $Et_3Al_2Cl_3$-cobalt octoate system (115-1, Table VII) we have encountered crosslinking, as well as low cis content and high vinyl. Reduction of the cobalt concentration toward the Al/Co mole ratio of 500/1 used by Gippin at 5°[6], speeded up the polymerization and gave immediate improvement in cis content. The reaction mixture attained incipient gelation in five minutes. This type of recipe is supposed to be operable with benzene containing 5 weight % butadiene. We are confident that a more suitable balance for screening purposes can be found by adjusting the ratio of catalyst components, their total amount and the amount of solvent.

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

This monomer, which was prepared as described previously[4], was found to be unreactive toward the Ziegler-type catalysts as shown in Table V. It was shown in the same series of experiments that the cobalt-based catalyst was highly active in polymerizing butadiene. Thus there is a consistent picture of unreactivity of 3 with both the rhodium and Ziegler catalysts.

c. 2,3-Bis(trifluoromethyl)butadiene (5)

This diene appeared surprisingly unreactive in copolymerizations with ethylene or butadiene initiated by Ziegler catalysts (Table VI) in view of its ready copolymerization with butadiene initiated by rhodium (Table II). However, it is not uncommon that olefins with branching on the olefinic carbons are sluggish to polymerize with Ziegler catalysts.

d. 1,1,2-Trifluoro-3-chlorobutadiene (2)

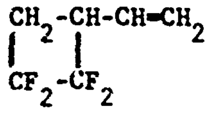
This compound was prepared by a method analogous to that used for 1,1,2-trifluorobutadiene[4,5]. Its reactivity in attempted homopolymerizations with Ziegler catalysts (Table VII) was also much less than that which might have been expected from its ready copolymerizations with either butadiene or 1,1,2-trifluorobutadiene by rhodium catalysis.

e. 1,1,2-Trifluorobutadiene (1)

This diene was examined in a series of copolymerizations with butadiene listed in Tables VIII and IX. Use of the sesquiethyl aluminum sesquichloride and cobalt octoate catalyst gave copolymers of promising Tg (-82 to -84°) but with halogen content that is lower than what is believed necessary for good oil resistance. The *cis*-polybutadiene catalysts (TiI_4 or cobalt octoate) performed well in control experiments with butadiene but were much less active with the mixtures of 1 and butadiene. This result suggested the presence of an impurity in the sample of 1. Although previously prepared samples of 1 were pure by v. p. c. criteria, examination of the present batch showed a trace of butanol. This contamination was apparently sufficient to prevent polymerization by all but the cobalt catalyst and further illustrates the advantage of the rhodium-based catalyst in being insensitive to most polar impurities in the monomers.

5. Ziegler Catalyst-initiated Polymerizations of Fluorine-containing Olefins

A small number of experiments of this type was carried out. They are described in Table X and include copolymerizations of monomer 7 with butadiene and of monomer 8 with ethylene.



$$\begin{array}{l} CH_2\text{-}CH\text{-}CH{=}CH_2 \\ | \quad\;\;\; | \\ CF_2\text{-}CF_2 \end{array}$$

7

$CF_3\text{-}CH{=}CH_2$

8

Monomer 7 did not homopolymerize with either the $Ti(OBu)_4$ or $TiCl_4$-based catalysts. In a TiI_4- or cobalt octoate-initiated copolymerizations with butadiene, high cis polymers containing only a little fluorine were obtained.

Monomer 8 was not commercially available at the time these polymerizations were carried out, therefore it was made by the following routes:

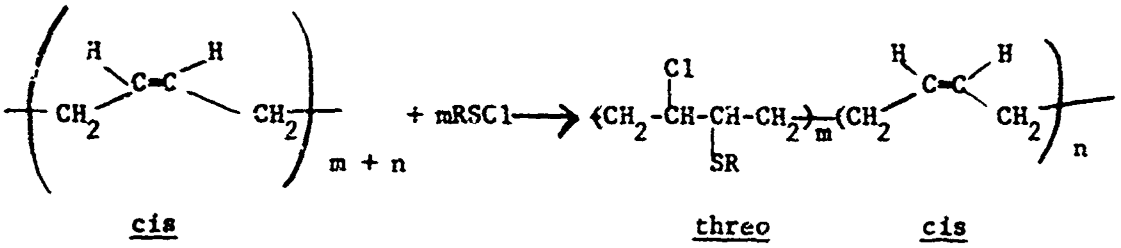
$$CCl_3CH_2CH_2Cl \xrightarrow[SbCl_5]{SbF_3} CF_3CH_2CH_2Cl \xrightarrow[EtOH]{KOH} 8$$

$$CF_3I + CH_2{=}CH_2 \xrightarrow{AIBN} CF_3CH_2CH_2I \xrightarrow[EtOH]{KOH} 8$$

Monomer 8 was only slightly reactive in a $VOCl_3 + Et_3Al_2Cl_3$-initiated copolymerization with ethylene. Analytical results for this copolymer are contradictory; microanalysis indicates 17% fluorine, whereas infrared spectroscopy suggests 1% or less. It is possible that the product is inhomogeneous and the polymerization will be rerun when more of monomer 8 is available.

6 Chemical Modification of cis-Polybutadiene

The very low glass transition temperature of 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. Our previous reports[4,9] have described the facile addition of several sulfenyl chlorides to cis-polybutadiene to form adducts according to the following equation:



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

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[13] 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 result is a disappearance in the adduct of the crystallization (-64°C.) and melting (-21°C.) phenomena characteristic of cis-polybutadiene. During the period covered by this report a new adduct containing 30% of the theoretical amount of trifluoromethanesulfenyl chloride and additional quantities of other less-saturated adducts have been prepared for evaluation at the U. S. Army Natick Laboratories. The Tg values for these adducts are summarized below:

Glass Transition Temperatures (°C.) for Adducts of cis-Polybutadiene and Sulfenyl Chlorides

	% Saturation				
Addend	10	15	20	25	30
CF_3SCl	-92	-84*	-75	-68	-44*
C_6F_5SCl	-90	-80**	-66*	-52*	-
CCl_3SCl	-85	-50	+28	-	-
C_6Cl_5SCl	-99	-50*	+18	-	-

* Submitted to Natick Laboratories for evaluation May 19, 1967.

** Previously evaluated at Natick Laboratories, see our previous report[4].

Inspection of the data above shows that the fluorinated sulfenyl chlorides have a less deleterious effect on Tg than do the chlorinated sulfenyl chlorides. For the same reason the aliphatic sulfenyl chlorides are preferable to the aromatic analogs. Work in our laboratory and at Natick has shown these adduct rubbers can be successfully sulfur cured; their utility in meeting the goals of this contract would appear to depend on having adequate oil resistance.

EXPERIMENTAL

1. Monomer Synthesis

a. Pyrolysis of 1,2-bis(Trifluoromethyl)cyclohexene to 2,3-bis(Trifluoromethyl)-1,3-butadiene

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% purity by VPC) 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, %
1	0.1		-	-	
2	2.4	52-58	1.3388	83.7	5.2
3	0.6	70-74	1.4040	31.7	
4	1.3	83-86	1.4058	-	
5	2.0	112-135	1.4010		
6	8.0	178-198	1.4972		
7	4.0	198-200	1.5557		
8	9.6	213	1.5680		
		Residue	1.5692		

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

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

In a one-liter 3-neck flask were placed 62.3 g. (0.865 m.) 90% 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 (Pierce Chemical, 96.7% purity) was carried out over 20 minutes and 63.6 g. of condensate was trapped with a dry-ice condenser (59A). Another 47.8 g. (0.185 m.) of the dichloro compound was added over 43 minutes to give 48.0 crude product. A second dry-ice trap used in both runs contained 11.4 g. (21.5%) 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%) of diene which was redistilled through a 12-inch long packed column at 184-188 mm. to give 17.2 g. (30%) of the diene of 92.8% purity. The major impurities were 4.8% of a low boiler and 0.5% of a high boiler believed to be n-butanol.

c. 3,3,3-Trifluoropropyl Chloride

In a 5-l 3-necked stainless steel flask were placed 500 g. (2.80 moles) of Peninsular ChemResearch 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%) of 3,3,3-trifluoropropyl chloride, b. p. 44-47°, n^{20} 1.3280-1.3282.

V. p. c. analysis of the product showed it to be 98.2% pure with 1.4% of a more volatile component.

d. 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 Peninsular ChemResearch 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% 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% 3,3,3-trifluoropropyl iodide by v. p. c. Distillation through a 12-in. packed column gave product, b. p. 88-89°, n_D^{25} 1.4170, 99.5% pure by v. p. c.

e. 3,3,3-Trifluoropropene

(1) 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% ethanol was treated with 30 ml. of 1.7 N ethanolic potassium hydroxide followed by another 90 ml. after twenty minutes. The solution was heated to 67° during ninety 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%) of 3,3,3-trifluoropropene, b. p. -22°.

A second reaction gave 11.4 g. (89%) of product, b. p. -22°.

(2) By dehydroiodination of 3,3,3-trifluoropropyl iodide

The method described above gave 78% yield of the olefin, b. p. -22°, when applied to the corresponding iodo compound.

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

The cycloaddition of butadiene and tetrafluoroethylene was carried out under conditions similar to those reported[8] except 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%) of adduct containing 3% of butadiene as determined by v. p. c.

2. Polymerizations

The rhodium- and iridium-initiated polymerizations were carried out by the aqueous emulsion technique described by Rinehart, Smith, Witt and Romeyn[1,2].

Polymerizations initiated by Ziegler-type catalysts were run by the vacuum line technique described in our earlier reports[4,9].

3. Chemical Modification of *cis*-Polybutadiene

a. Materials

Trifluoromethanesulfenyl chloride was obtained from Peninsular ChemResearch. Pentafluoro- and pentachloro-benzenesulfenyl chlorides were prepared by the method of Almasi and Gants[10].

b. Addition Reactions

These were carried out as described in an earlier report[9].

PROPOSED WORK

1. In the rhodium- and iridium-catalyzed emulsion polymerizations of fluorinated dienes, study the effect of feed ratio, temperature, solvent, etc. on microstructure and monomer combining ratio. Control of these two dependent variables will permit us to design polymers meeting the Contract objectives.

2. Follow up the lead on cobalt-catalyzed copolymerizations by screening other monomer pairs and studying effect of feed ratio, solvent, temperature, etc.

3. Prepare additional fluorinated diene copolymers for further evaluation.

4. Continue synthetic work to prepare 1,1,2-trifluoro-3-(trifluoromethyl)butadiene and other monomers as needed.

5. Prepare low-temperature rubbers by other chemical modifications of cis-polybutadiene. Prepare additional amounts of adducts as may be required for evaluation.

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TABLE I

SURVEY OF HOMOPOLYMERIZABILITY OF VARIOUS FLUORINATED MONOMERS IN EMULSION BY RHODIUM CHLORIDE

Experiment No.	96-1	97-1	97-2	97-3	97-4	103-1	103-2	103-3	103-6	119-1
Rhodium Chloride trihydrate, g.	.020	.020	.020	.020	.020	.020	.020	.020	.020	.020
Distilled Water, ml.	7	7	7	7	7	7	7	7	7	7
20% Nacconol NRSF, ml.	1	1	1	1	1	1	1	1	1	1
1,1,2-Trifluorobutadiene, mmoles	64.5	-	-	-	-	-	-	-	-	-
β,β,β-Trifluoroethyl vinyl ether, mmoles	-	25	-	-	-	-	-	-	-	-
α,β,β-Trifluorostyrene, mmoles	-	-	25	-	-	-	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-vinyl cyclobutane, mmoles	-	-	-	25	-	-	-	-	-	-
4,5,5-Trifluoro-1,4-pentadiene, mmoles	-	-	-	-	25	-	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-isopropenylcyclobut-3ene, mmoles	-	-	-	-	-	21.4	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, mmoles	-	-	-	-	-	-	20	-	-	-
1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene, mmoles	-	-	-	-	-	-	-	25	-	-
5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene, mmoles	-	-	-	-	-	-	-	-	25	-
1,1,2-Trifluoro-3-chlorobutadiene, mmoles (added as a solution 31% by weight in benzene)	-	-	-	-	-	-	-	-	-	20.8
Polymerization time at 50°C., hrs.	67	162	42	42	162	65	65	65	65	65
Yield, g.	6.915	0	.134	trace	0	.817	.051	0	4.00	3.059
Conversion, %	100	0	3	0	0	18	1+	0	84	100
X-ray crystallinity	slight	-	-	-	-	amorph.	slight	-	amorph.	-
Product Appearance	resin	-	resin	-	-	resin	resin	-	resin	rubber
$CHCl_3$ Solubility	partly	-	-	-	-	-	-	-	swells	soluble
Tg, °C.	-35	-	-	-	-	-	-	-	-	-17
Tm, °C.	56,79	-	-	-	-	-	-	-	112	-

Table II

Copolymerization of Fluroinated Dienes with Butadiene or Fluorinated Dienes in Emulsion with Rhodium Catalysts

Experiment No.	99-1	99-2	99-3	99-4	104-3	103-4	108-2	104-1	108-1	114-1	119-2	103-5	104-2	119-3
Rhodium chloride trihydrate, g.	.020	.020	020	.020	-	.020	.020	-	-	.020	.020	.020	-	.020
Bis(1,4-cyclohexadiene chlororhodium), g.	-	-	-	-	.05	-	-	.05	.05	-	-	-	.05	-
Distilled water, ml	7	7	7	-	13	7	7	13	13	7	7	7	13	7
20% Nacconol NRSF, ml.	1	1	1	-	2.5	1	1	2.5	2.5	1	1	1	2.5	1
Formic acid, ml.	-	.25	-	-	5	-	-	5	5	-	-	-	5	-
Methylene chloride, ml.	-	-	5	15	5	-	-	5	-	5	-	-	5	-
5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene, mmoles	-	-	-	-	-	25	18	25	18	-	-	25	25	-
2,3-Bis(trifluoromethyl) butadiene, mmoles	-	-	-	-	-	-	-	-	-	11.7	-	-	-	-
1,1,2-Trifluoro-3-chloro-butadiene, mmoles	-	-	-	-	-	-	-	-	-	-	20.8	-	-	20.8
1,1,2-Trifluorobutadiene, mmoles	21.5	21.5	21.5	21.5	21.5	-	-	-	-	-	-	21.5	21.5	21.5
Butadiene, mmoles	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	-	-	-
Polymerization time at 50°C., hrs.	17	17	17	143	65	65	115	64	283	18	65	65	65	65
Yield, g.	1.498	.455	2.068	0	.628	.70+	1.695	1.343	1.5±	.490	2.548	6.44	2.508	5.126
Conversion, %	43	13	59	0	18	7	37	28	32+	14.5	60	91	42	97
Product	(brown rubbers) tough nervy	soft	tough nervy	-	rubber logey	rubber 2 kinds I.R.'s alike	rubber leathery	dark resin + syrup	resin leathery	nervy rubber	nervy rubber	rubber white tough	tough rubber	tough rubber sl. sticky
Solubility in $CHCl_3$	swells		swells				swells					swells	swells	
% Fluorine	32.9	32.3	35.8		35.03		16.63	-	-	37.3	19.0[a]	56.5	55.3	14.5[a]
Mole % F monomer	45.4	44.1	51.4		49.7		9.8	-	-	31.9	55.1	90.5	87.1	51.4
T_g, °C.	-47	-	-48		-48		-20		-	-27	-35	-17	+2	-26
T_g, °C.	+58	-	+58		+55		+55		+69	-	-	+103	108	-

a. % Chlorine

Table III

Homopolymerization of Various Types of Fluorinated Monomers in Emulsion with Iridium Catalysts - All polymerizations run 240 hrs. at 50°C.

Experiment No.	106-1	106-2	106-3	106-4	106-5	106-6	106-7	106-8	106-9	106-10
Ammonium iridium chloride, g.	.075	.075	.075	.075	.075	.075	.075	.075	.075	-
Bis(1,4-cyclohexadiene chloroiridium), g.	-	-	-	-	-	-	-	-	-	.055
Distilled water, ml.	8	8	8	8	8	8	8	8	8	8
20% Novulphor C, ml.	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
20% Aquarex ME, ml.	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
40% Formaldehyde, ml.	.5	.5	.5	.5	.5	.5	.5	.5	.5	.5
3-Chloro-3,3,4-trifluoro-2-isopropenyl cyclobutene-1, mmoles	25	-	-	-	-	-	-	-	-	25
1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, mmoles	-	25	-	-	-	-	-	-	-	-
1,2-Bis(trifluoromethyl)-4-methyl-1,4-cyclohexadiene, mmoles	-	-	25	-	-	-	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-methyl-3-(3,3,4-trifluoro-4-chlorocyclobutenyl)cyclobutene, mmoles	-	-	-	25	-	-	-	-	-	-
α,β,β-Trifluorostyrene, mmoles	-	-	-	-	25	-	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-vinyl cyclobutane, mmoles	-	-	-	-	-	25	-	-	-	-
1,1,2-Trifluoro-2-chloro-3-methyl-3-vinylcyclobutane, mmoles	-	-	-	-	-	-	25	-	-	-
2,2,2-Trifluoroethyl vinyl ether, mmoles	-	-	-	-	-	-	-	25	-	-
5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene, mmoles	-	-	-	-	-	-	-	-	25	-
Yield, g.	2.83	.008	.007	-	-	-	-	-	.560	.727
Conversion, %	77	<1	<1	-	-	-	-	-	12	20
Product appearance	white resin	white resin	gray resin	- -	- -	- -	- -	- -	white resin	white resin

Table IV

Polymerizations of 2-(Trifluoromethyl)butadiene with Ziegler Catalysts

Experiment No.	91-3	91-4	91-5	91-6	91-7	91-9
Dry benzene, ml.	12.2	12.2	16	10	-	-
Dry heptane, ml.	-	-	-	-	15	15
1.25 M $Al(i\text{-}bu)_3$ in benzene, ml.	.4	.4	-	-	-	-
0.06 M Cobalt Octoate in benzene, ml.	-	-	1	-	-	-
0.55 M $Al(i\text{-}bu)_3$ in benzene, ml.	-	-	-	.55	-	-
0.05 M $VOCl_3$ in heptane, ml.	-	-	-	-	10	10
Freeze in	< dry ice >				< liquid N_2 >	
Butadiene from vac. line, mmoles	43	43	21.5	-	-	-
2-Trifluoromethyl butadiene, mmoles	-	9.7	9.7	7.3	9.7	-
Ethylene from vac. line, mmoles	-	-	-	-	10.8	21.8
Made homogeneous at °C.	25	25	25	25	78	no
0.017 M Dow TiI_4 in C_6H_6, ml.	5.6	5.6	-	-	-	-
0.30 M $Et_3Al_2Cl_3$ in heptane, ml.	-	-	1	-	4.2	4.2
0.25 M $Ti(OBu)_4$ in benzene, ml.	-	-	-	.4	-	-
Shake & stir in air bath, min.	15	15	15	15	instant	
Exotherm	+	-	-	-	polymer	
Color after assembly	dark brown	cherry red	blue green	clear yellow	purple	purple
Polymerization time at 25°: hrs.	68	68	67	67	17	17
Yield, g.	2.27	.018	1.21	.04	.56	.66
Conversion, %	98	<.5	52	4	38	100
Product	solid rubber	flaky soft resin	solid rubber (some gel)	viscous fluid	resin	resin
Composition						
% cis by infrared	73[a]	-	70[a]	-	-	-
% trans by infrared	23[a]	84	20[a]	-	-	-
% vinyl by infrared	4[a]	-	10[a]	-	-	-
% $C_5F_3H_5$ by infrared	-	16	13	(100)	34	-
888 cm^{-1} possible $-C(CF_3)=CH_2$	-	-	-	yes	-	-
840 cm^{-1} possible $-C=C(CF_3)-$	-	-	-	-	yes	-
% $C_5F_3H_5$ baxed on F	-	-	4.8	-	6.4	-
X-ray crystallinity %	-	-	-	-	37	-

a. Normalized to 100%.

Table V

Polymerizations of 5,5,5-Trifluoro-4-trifluoromethyl-1,3-pentadiene with Ziegler Catalysts

Experiment No.	92-2	92-3	92-6	92-7	92-8	94-5	94-6
Dry benzene, ml.	5	5	4	4	10	-	-
Dry heptane, ml.	-	-	-	-	-	15	23
1.25 M $Al(i\text{-}Bu)_3$, ml.	.4	.4	-	-	-	-	2
0.06 M CoOctoate, ml.	-	-	1	1	1	-	-
0.05 M $VOCl_3$, ml.	-	-	-	-	-	10	-
$CH_2=CH\text{-}CH\text{-}C(CF_3)_2$, mmoles	11.6	11.6	11.6	11.6	-	25	25
Seal							
Freeze in	-	-	-	-	CO_2	N_2	N_2
Butadiene, mmoles	-	-	-	-	21.5	-	-
Ethylene, mmoles	-	-	-	-	-	11.2	11.2
Condition to 25°C.	yes	yes	yes	yes	yes	-	-
Condition to 5°C.	-	-	-	-	-	yes	yes
0.25 M Ti $(OBu)_4$, ml.	.4	.4	-	-	-	-	-
0.30 M $Et_3Al_2Cl_2$, ml.	-	-	1	1	1	4.2	-
0.25 M $VO(OBu)_3$, ml.	-	-	-	-	-	-	2
Stir 15' at 25°, run at 25°	-	yes	-	yes	yes	yes	yes
Shake & run at 60°	yes	-	yes	-	-	-	-
Exotherm	-	-	-	-	+	-	-
Catalyst color	< yellow brown>		gray green	bluish green	greenish	purple	yellow
Time, hrs.	19	19	19	19	19	16	16
Yield, g.	(.016 gm. combined)		.010	0	1.10	.25	.26
Conversion, %	<1	<1	<1	0	95	5	5
X-ray crystallinity	-	-	-	-	-	(like polyethylene)	
% F	-	-	-	-	-	3.61	1.36
Mole-% $C_6H_4F_6$ in polymer	-	-	-	-	-	6.02	2.27

Table VI

Copolymerizations of 2,3-Bis(trifluoromethyl)butadiene with Ziegler Catalysts

Expt. No.	94-1	94-2	94-3	94-4
Dry benzene, ml.	12.2	16	-	-
Dry heptane, ml.	-	-	15	23
1.25 M $Al(\underline{i}\text{-}bu)_3$, ml.	.4	-	-	-
.06 M Co octoate, ml.	-	1	-	-
.05 M $VOCl_3$ in heptane, ml.	-	-	10	-
$CH_2{=}C(CF_3)\text{-}C(CF_3){=}CH_2$, mmoles	20	20	20	20
Seal & freeze				
Butadiene, mmoles	21.8	21.8	-	-
Ethylene, mmoles	-	-	11.5	11.5
Condition to	25°	25°	5°	5°
.018 M TiI_4, ml.	5.6	-	-	-
.30 M $Et_3Al_2Cl_3$, ml.	-	1	4.2	-
.25 M $VO(OBu)_3$, ml.	-	-	-	2
Polymerize at 25°, hrs.	46	46	16	16
Yield, gms.	.004	.63	.293	.281
Conversion, %	<1	13	7	7
	brown oily scum	sticky rubber	brown-white resin	brown-white resin
X-ray crystallinity	-	-	(resemble polyethylene except 4.50Å line is weaker)	
Infrared			(polyethylene & faint F at 1130 cm^{-1}	
% F Schwarzkopf	-	5.72	1.91	1.71
% $CH_2{=}C(CF_3)\text{-}C(CF_3){=}CH_2$	-	9.54	3.18	2.85
Butadiene portion				
% cis	-	79	-	-
% vinyl	-	13	-	-
% trans	-	8	-	-

Table VII

Polymerizations of 1,1,2-Trifluoro-3-chlorobutadiene with Ziegler Catalysts

Expt. No.	119-4	119-5
Apparatus		
250 ml. stainless steel bomb	+	
100 ml. pyrex reaction tube		+
Reagents		
Dry heptane, ml.	13.3	8.3
Dry benzene, ml.	-	-
0.05 M $VOCl_3$, ml.	10	10
1,1,2-Trifluoro-3-chlorobutadiene, mmoles[a]	4.1	10.5
0.30 M $Et_3Al_2Cl_3$, ml.	4.2	4.2
Shake behind safety screen	yes	yes
Polymerization time at 25°C., hrs.	66	66
Yield, g.	.069	.355
Conversion, %	12	24
Product	lt. brown resin	lt brown resin
X-ray crystalinity	-	amorphous

a. Added as a solution 31% by weight in benzene

Table VIII

Attempted Copolymerization of Butadiene and 1,1,2-Trifluorobutadiene

Comparison of Benzene and Methylene Chloride Using a Cobalt Catalyst

Experiment No.	102-1	102-2	102-3	102-4	102-6	102-5
Dry benzene, ml.	20	20	20	-	-	-
Dry methylene chloride, ml.	-	-	-	20	20	20
0.06 M CoOctoate, ml.	2	2	2	2	2	2
Seal, freeze in dry ice						
Butadiene, mmoles	22	33	11	22	33	11
1,1,2-Trifluorobutadiene, mmoles	22	11	33	22	11	33
Pressurize 4 psi N_2						
Condition to 25°C.						
0.30 M $Et_3Al_2Cl_3$, ml.	2					→
Shake and stir at 25°						
Polymerization time at 25°, hrs.	16					→
Exotherm	+	+	+	0	0	0
Vixcosity of reaction mixture	medium	highest some gel	low	low some gel	lowest	low
Yield, g.	1.16	1.720	.726	1.060	1.539	.579
Intrinsic viscosity in $CHCl_3$	.73	-	-	.82	-	-
Properties	<		all slightly sticky rubbers with poor cobalt cleanup			>
Conversion, %	33	59	18	30	53	14
Tg/Tm	-84 +57	-82 +50				
Composition from Infrared [a]						
% cis	45	42	24	9	13	7
% trans	11	12	20	20	22	25
% vinyl	44	46	56	71	65	70
% trifluorobutadiene	31	22	44	34	34	60

a. Sum of % cis + % trans + % vinyl is normalized to 100%.

Table IX

Attempted Copolymerization of Butadiene and 1,1,2-Trifluorobutadiene with Some Cis-Polybutadiene Catalysts

Experiment No.	116-3	116-4	116-7	116-8
Dry benzene, ml.	16.2	8.3	16.2	8.3
Dry heptane, ml.	-	8.3	-	8.3
0.55 M $Al(\underline{i}\text{-bu})_3$, ml.	.37	-	.37	-
0.06 M Cobalt octoate, ml.	-	.2	-	.2
Butadiene, mmoles	32.25	32.25	32.25	32.25
1,1,2-Trifluorobutadiene, mmoles	-	-	21.5	21.5
0.017 M TiI_4, ml.	2.25	-	2.25	-
0.30 M $Et_3Al_2Cl_3$, ml.	-	1	-	1
Exotherm	+	+	-	+
Appearance	thick dark brown	light blue	red	yellow
Color	normal	normal	no	
Yield, g.	1.534	1.833	-	1.723
Infrared analysis[a]				
% cis	80.9	73.3	-	87.3
% trans	15.3	18.9	-	8.2
% vinyl	3.8	7.9	-	4.5
F	-	-	-	0

a. Sum of % *cis* + % *trans* + % vinyl is normalized to 100%.

Table X

Polymerization of Fluorinated Non-Dienes with Ziegler Catalysts

Experiment No.	112-5	112-6	112-7	112-4	112-9	111-1	105-1
Dry benzene, ml.	10	10	12.2	10	16	-	-
Dry heptane, ml.	-	-	-	-	-	15	15
0.125 M Al(i-bu)$_3$, ml.	.4	.4	.4	-	-	-	-
0.06 M Cobalt octoate, ml.	-	-	-	1	1	-	-
0.05 M VOCl$_3$ in heptane, ml.	-	-	-	-	-	10	10
1,1,2,2-Tetrafluoro-3-vinyl cyclobutane, mmoles	25	25	25	-	25	50	-
Seal, freeze in	-	-	CO$_2$	CO$_2$	CO$_2$	N$_2$	N$_2$
Butadiene, mmoles	-	-	43	21.5	43	-	-
3,3,3-Trifluoropropene, mmoles	-	-	-	-	-	-	5.38
Ethylene, mmoles	-	-	-	-	-	11.25	11.25
Pressurize 4 psi dry N$_2$							
Condition to °C.	25	25	25	25	25	5	5
0.25 M Ti(OBu)$_4$ in C$_6$H$_6$, ml.	.4	-	-	-	-	-	-
0.5 M TiCl$_4$ in C$_6$H$_6$, ml.	-	.2	-	-	-	-	-
0.017 M TiI$_4$, ml.	-	-	5.6	-	-	-	-
0.30 M Et$_3$Al$_2$Cl$_3$, ml.	-	-	-	1	1	4.2	4.2
Catalyst color	yellow brown	black	dark brown	blue-green	blue-green	purple initially	purple initially
Exotherm	0	0	+++	+	+	-	-
Polymerization time at 25°, hrs.	64	64	43	65	43	18	64
Yield, g.	0	0	2.163	1.088	2.546	.330	.162
Conversion, %	0	0	32	94	37	4	20
Product	-	-	soupy rubber	soft rubber	soft rubber	brown white resin	white resin
X-ray crystallinity	-	-	-	-	-	(resemble P.E.)	
% F	-	-	0	-	0	-	16.92[a]
% C$_3$H$_3$F$_3$	-	-	-	-	-	-	10.5
Infrared[a]	-	-	-	-	-	88% P.E. + minor amt.F polymer	
cis	-	-	75	67	60	-	
trans	-	-	22	7	18	-	-
vinyl	-	-	4	26	22	-	-
F	-	-	v.minor	-	minor	-	-
Solubility in CHCl$_3$	-	-	-	-	yes	-	-
Tg, °C.	-	-	-105		-97	-	-

a. Sum of % *cis* + % *trans* + % vinyl is normalized to 100%.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) UniRoyal U. S. Rubber Company Research Center 1361 Alps Road, Wayne, New Jersey 07470	2a REPORT SECURITY CLASSIFICATION Unclassified 2b GROUP

3 REPORT TITLE
Polymerization Studies Leading to High-Strength Chemical-Resistant Elastomers Serviceable at Temperature Extremes

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)
Semiannual Report December 1, 1966 - May 31, 1967

5 AUTHOR(S) (Last name, first name, initial)
Relyea, Douglas I.
Smith, Homer P.
Johnson, Arnold N.

6 REPORT DATE June 1967	7a TOTAL NO OF PAGES 27	7b NO OF REFS 14

8a. CONTRACT OR GRANT NO. DA19-129-AMC-487(N)	9a ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 1K024401A113	
c	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	68-12-CM

10 AVAILABILITY/LIMITATION NOTICES
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11. SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY U. S. Army Natick Laboratories Natick, Massachusetts 01760

13 ABSTRACT

Rhodium compounds were found to give good conversions of fluorinated dienes to polymers in aqueous emulsion systems. For example, a 51:49 copolymer (Tg -48°) of 1,1,2-trifluorobutadiene and butadiene was prepared in this way in 59% conversion in 17 hours at 50°C. Several of the copolymers are formed with monomer ratios approaching the feed ratios. Microstructure of these polymers has been examined in a preliminary way by means of infrared and n. m. r measurements. Other catalyst and fluorinated-monomer combinations were screened for activity in homopolymerization and copolymerization. A number of fluorinated sulfenyl chloride-modified *cis*-polybutadienes and one rhodium initiated copolymer were prepared on a scale large enough for preliminary evaluation at the U. S. Army Natick Laboratories.

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
POLYMERIZATION						
FLUORO-OLEFINS						
COPOLYMERIZATION						
TRANSITION METALS						
NOBLE METALS						
CATALYSIS						

INSTRUCTIONS

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