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

SEMIANNUAL REPORT NO. 2

by

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

December 15, 1965

U. S. Army Natick Laboratories
Natick, Massachusetts

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

UNITED STATES RUBBER COMPANY
RESEARCH CENTER
WAYNE, NEW JERSEY 07470

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FOREWORD

This report was prepared by the United Stated States Rubber Company under Contract No. DA-19-129-AMC-487(N) for the U. S. Army Natick Laboratories with Mr. C. B. Griffis as Project Officer. This is the second Semiannual Report under this contract and covers the period June 1, 1965 through November 30, 1965.

During this period the following manhours were expended on this project:

Senior Research Scientist	203
Research Scientists	1056
Technician (Sub-professional)	872
Total direct labor	2131 manhours

The technical effort planned for the next six months period will require a greater expenditure of manhours than shown above. We expect that the planned effort will require 2600 manhours.

CONTENTS

INTRODUCTION

This is the second semiannual report on research on polymerization of fluorinated monomers to form random or stereospecific high polymers under the sponsorship of the U. S. Army Natick Laboratories. The objective of this work is the preparation of elastomeric materials which will have both oil and chemical resistance and useful rubbery properties over a wide range of temperature, for example -65° to +300°C.

Our approach has been to polymerize a number of easily procurable fluorinated monomers with a variety of catalysts differing in olefin complexing power. Exploratory work in copolymerization has been started. The list of monomers has been extended to include fluorinated acetylenes and cyclic fluoroolefins which might undergo ring-opening polymerizations. The monomers studied include hexafluoropropene, vinylidene fluoride, 1,1,2-trifluorobutadiene, perfluorocyclobutene, hexafluoro-1,2-dichlorocyclopentene, 1,1,2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane, vinyl fluoride and hexafluoro-2-butyne, as well as ethylene and butadiene.

DISCUSSION

1. Attempted Homopolymerizations of Fluorinated Olefins

One point of departure for obtaining an oil- and freeze-resistant rubber is the polyethylene chain, glass temperature -70° to -110°C.[1] 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 α-olefin or by copolymerization of ethylene with a fluorinated α-olefin.

Our previous report[2] described preliminary experiments in the polymerization of fluorinated olefins with transition metal catalysts of the general type used by us and others for the polymerization of ethylene, propylene and related olefins. We now report additional results in the attempted polymerization of fluorinated monoolefins. Polymerization with typical Ziegler catalysts requires anionic polymerization of monomers having electron-poor double bonds. It can be inferred from the literature that this approach has been commercially unsuccessful with vinyl chloride[3]. Therefore, we have examined several electron-rich catalysts for the polymerization of vinylidene fluoride and hexafluoropropene. The first of these catalysts to be examined was tetrakis(diethylamino)titanium in attempted polymerizations of hexafluoropropene (Table I) and vinylidene fluoride (Table II). Neither monomer was initiated by this titanium compound alone or in combination with aluminum triisobutyl, or by a typical anionic initiator such as triphenyl phosphine.

Table I

Polymerizations of 23.5 Mmoles of Hexafluoropropene in 10 ml. Benzene

Reactions run 360 hrs.

Expt. No.	Catalyst	Temp. °C.	Final Pressure psig	Product Recovered
16-1	1 Mm.triphenyl phosphine	25	0*	buff material like 16-2
16-2	1 Mm. " "	4	45	.181 gm.resinous material mostly triphenyl phosphine
16-3	1 Mm. $(Net_2)_4$ Ti	4	40	trace brown fluid
16-4	1 Mm. $(Net_2)_4$ Ti	25	44	trace brown fluid
16-5	1 Mm. $(Net_2)_4$ Ti 2.5 Mm. $Al(i\text{-}bu)_3$	25	44	trace red brown powder
16-6	1 Mm. $(Net_2)_4$ Ti 6.25 Mm.$Al(i\text{-}bu)_3$	25	50	.267 gm. grayish resinous catalyst residue

*After an initial pressure measurement of 60 psig, this tube leaked monomer.

Table II

Polymerizations of 23.5 Mm. of Vinylidene Fluoride in 10 ml. Benzene

Reactions run in 50 ml. tubes for 400 hrs.

Expt. No.	Catalyst	Temp. °C.	Final Pressure psig	Product Recovered
17-1	1 Mm.triphenyl phosphine	25	31*	trace white resin
17-2	1 Mm.triphenyl phosphine	4	72 (cold)	.204 gm. resinous material mostly triphenyl phosphine
17-3	1 Mm. $(Net_2)_4$ Ti	4	76 (cold)	.093 gm. white product insoluble in isopropanol
17-4	1 Mm. $(Net_2)_4$ Ti	25	**	trace
17-5	1 Mm. $(Net_2)_4$ Ti 2.5 Mm. $Al(i\text{-}bu)_3$	25	**	trace only white material insoluble in HCl
17-6	1 Mm. $(Net_2)_4$ Ti 6.25 Mm. $Al(i\text{-}bu)_3$	25	46	.445 solid catalyst residue recovered

* After an initial pressure measurement of 75 psig at 0°, this tube leaked monomer.

** Butyl gasket material swelled from the absorption of vinyl fluoride and lifted the cap.

Since there is a growing patent literature on the use of chlorinated solvents with Ziegler catalysts[4], mixtures of heptane with methylene chloride, carbon tetrachloride or Freon 113 were tested as possible solvents for fluoroolefin polymerizations. The results are summarized in Table III. The chlorinated solvents appeared to promote the degradative attack of aluminum triisobutyl-tetrabutyl titanate catalyst on monomer, as the products were all highly colored.

Table III

Polymerizations of 23.5 Mm. of Hexafluoropropene in 20 ml. Mixed Heptane-Halocarbon Solvent

Catalyst 12.5 Mm. Al(i-bu)$_3$ - .5 Mm. Ti(OBu)$_4$ stirred in the presence of monomer 15 minutes at 25°. Polymerizations run 320 hrs. at 25° (18-3, 18-4 only 15 hrs.)

Expt. No.	Solvent	Final Pressure psig	Product Recovered
18-1	50 Heptane - 50 CH_2Cl_2	36	red brown powder
18-2	50 Heptane - 50 CH_2Cl_2	1	trace black powder
18-3	50 Heptane - 50 CCl_4	41	black solid
18-4	50 Heptane - 50 CCl_4	41	black solid
18-5	50 Heptane - 50 Freon 113	25	trace buff and black solid
18-6	50 Heptane - 50 Freon 113	24	brown powder
18-7	92 Heptane - 8 CH_2Cl_2	10	small amount red brown resin
18-8	92 Heptane - 8 CH_2Cl_2	1	small amount dark powder

A series of experiments was run to compare the above halogenated solvents (in mixtures with heptane) with heptane alone or benzene-heptane. With the decyl magnesium iodide catalyst, the yield was much higher with the hydrocarbon solvents. From this point on we have used only heptane or benzene as solvent.

Table IV

Polymerizations of 23.5 Mm. Hexafluoropropene in Mixed Heptane-Halocarbon Solvent

Catalyst 1.67 or .83 Mm. decyl magnesium iodide - .5 Mm. $Ti(OBu)_4$ stirred in the presence of monomer 15 minutes at 25°. Polymerizations run 268 hrs. at 25°. Similar pairs combined in work-up.

				Product	
Expt. No.	Decyl MgI Mm.	Solvent	Final Pressure psig	X-ray Cryst.	Yield
19-1	1.67	Heptane	40	amorphous	.123 gm. buff resin
19-2	.83	Heptane	40		
19-3	1.67	72 Benzene-28 Heptane	34*	amorphous	.145 gm. buff resin
19-4	.83	83 Benzene-17 Heptane	40*		
19-5	1.67	72 CH_2Cl_2-28 Heptane	40	amorphous	.037 gm. buff resin
19-6	.83	83 CH_2Cl_2-17 Heptane	44		
19-7	1.67	72 CCl_4-28 Heptane	0	amorphous	.042 gm. buff resin
19-8	.83	83 CCl_4-17 Heptane	0		
19-9	1.67	72 Freon 113-28 Heptane	25	amorphous some TiO_2	.056 gm. buff resin
19-10	.83	83 Freon 113-17 Heptane	25		

*Catalyst completely soluble.

Since poly(vinylidene fluoride) has probably the lowest glass temperature of any fluorinated homopolymer[5], we made several attempts to find the best catalyst system for it. In Table V we show results obtained with electron-rich catalysts prepared in situ by the addition of compounds containing N, O, P or S atoms to a tetrabutyl titanate-diphenyl magnesium catalyst. Only small yields of low molecular weight products resulted.

Table V

Polymerization of 23.5 Mmoles Vinylidene Fluoride at 25°C.

Electron donors added to a catalyst of .5 Mmole tetrabutyl titanate and 1.9 Mmoles diphenyl magnesium. Reaction time 64 hrs. Catalyst prepared by stirring at room temperature for 15 minutes. Solvent 22 ml. benzene.

Expt. No.	Additive	Final Pressure psig	Product Solid	Product Oil
33-1	.25 Mmole Anisole	60	0	.2 ml.
33-2	.25 Mmole Diphenyl Ether	0 leaked	43 mg.	-
33-3	.25 Mmole Triphenyl Phosphine	51	0	.1 ml.
33-4	.25 Mmole Tributyl Phosphite	53	0	.25 ml.
33-5	.25 Mmole Thiophene	51	0	.2 ml.
33-6	.25 Mmole Ethyl Sulfide	46	0	.13 ml.
33-7	.25 Mmole Triethyl Amine	51	0	.45 ml.
33-8	.25 Mmole Hexamethyl Phosphoric Triamide	50	0	.40 ml.
33-9	None	50	0	.17 ml.

Table VI shows results in a set of experiments in which nucleophilic reagents were reacted <u>in situ</u> with titanium tetrachloride catalyst. It was noted that $TiCl_4$-benzene reacted with monomer vapor in the polymerization tube of experiments 34-1 and 34-2.

Table VI

Polymerization of 23.5 Mmoles Vinylidene Fluoride at 25° with Electron Donors Added

Catalyst of .5 Mmole titanium tetrachloride and 1.9 mmole diphenyl magnesium. Catalyst prepared by stirring 15 minutes at room temperature. Solvent 27 ml. benzene. Run for 160 hours.

Expt. No.	Additive	Final Pressure psig	Product Solid	Product Oil
34-1	.25 Mmole Anisole	1*	0	0
34-2	.25 Mmole Diphenyl ether	0*	10 mg. solid amorphous ring	0 by X-ray
34-3	.25 Mmole Triphenyl Phosphine	25	0	0
34-4	.25 Mmole Tributyl Phosphite	22	0	0

*Caps had lifted and leaked. In Expts. 27, 31, 33, 34, and 36 a Paracril gasket was used for backing the Teflon liner when the monomer was vinylidene chloride, because of swelling of the gasket by this monomer in Expt. 17. This gasket shows a greater tendency to leak monomer and was abandoned.

In this experiment $TiCl_4$ in benzene solution was added last to the reaction tube containing monomer frozen on top of the frozen solution of diphenyl magnesium in benzene. As the $TiCl_4$ ran down the side of the tube it made black streaks by immediate reaction with the monomer vapor, before the tubes could be warmed with shaking and stirred.

Another experiment was run with a titanium tetrachloride catalyst, in this case premixed before the addition of monomer. The same set of O, P, S and N donor compounds was used. Brown liquid products again resulted.

Table VII

Polymerization of 23.5 Mmoles of Vinylidene Fluoride at 25° with Electron Donors Added

Catalyst .5 Mmole of titanium tetrachloride and 1.9 Mmoles of diphenylmagnesium. Catalyst premixed in absence of monomer 15 mins. at R. T. Solvent 27 ml. benzene. Run for 140 hours.

Expt. No.	Additive	Final Pressure psig	Product Solid mg.	Product Liquid mg.
36-1	.25 Mmole Anisole	0	7	201
36-2	.25 Mmole Diphenyl ether	1	5	114
36-3	.25 Mmole Triphenyl Phosphine	0	0	135
36-4	.25 Mmole Tributyl Phosphite	1	0	133
36-5	.25 Mmole Thiophene	0	0	84
36-6	.25 Mmole Ethyl Sulfide	55	0	72
36-7	.25 Mmole Triethylamine	1	0	84
36-8	.25 Mmole Hexamethyl Phosphoric Triamide	0	0	177
36-9	None	47	0	88

Run with Paracril gasket.

X-ray pattern of 36-1 is an amorphous ring centered at 4.5 to 5.0. X-ray pattern of 36-2 is the ring centered at 4.5 to 5.0 plus a faint line at 4 (evidence of slight crystallinity).

A series of experiments was carried out in which it was attempted to modify the reactivity of titanium tetrachloride and tetrabutyl titanate catalysts by the addition of low levels of water. The titanium compound was added first and frozen in the solvent. Only low molecular weight oils were obtained (Table VIII).

Table VIII

Polymerization of 23.5 Mmoles of Vinylidene Fluoride at 25° with Water Added

Catalysts of .5 mmole of either tetrabutyl titanate or titanium tetrachloride with 1.9 mmoles of diphenyl magnesium. Catalyst prepared by stirring 15 minutes at R. T. Solvent 32 ml. benzene. Run 112 hours.

Expt. No.	Catalyst	Water Mm.	Final Pressure psig	Product Oil mg.	
35-1	$Ti(OBu)_4$	.115	35	14.7	
35-2	$Ti(OBu)_4$	.173	45	11.7	
35-3	$Ti(OBu)_4$	.233	48	9.8	
35-4	$Ti(OBu)_4$	.338	45	7.9	semi-solid
35-5	$TiCl_4$	.115	42	21.3	
35-6	$TiCl_4$	.173	48	20.4	
35-7	$TiCl_4$	.233	36	19.6	
35-8	$TiCl_4$	.338	45	19.0	

In this experiment a softer Paracril gasket (57 Duro) was tested with better seating behavior than the previous Paracril gasket (65 Duro).

The Ti compound was added first and frozen in the solvent before the monomer was added. There was slight but visible reaction between monomer and $TiCl_4$ at the surface of the frozen mixture.

Tables IX and X show a series of amines (primary, secondary, and tertiary), butyl alcohol and diphenyl ether used as catalyst modifiers in attempted polymerizations of vinylidene fluoride with the tetrabutyl titanate-aluminum triisobutyl catalyst. There were some further variations in technique, noted in the tables. However, none of these experiments gave a significant yield of polymer.

Table IX

Polymerization of 23.5 Mmoles Vinylidene Fluoride in the Presence of Amines

Catalyst .5 Mm. tetrabutyl titanate - 1.5 mmole aluminum triisobutyl prepared by stirring in the presence of monomer at room temperature. Solvent 28 ml. heptane. Run 160 hrs. at room temperature.

Expt. No.	Additive	Final Pressure psig	Product
37-1	.25 Mmole n-butylamine	40	0
37-2	.25 Mmole diethylamine	27*	trace black scum
37-3	.25 Mmole pyridine	33*	trace black scum
37-4	.25 Mmole n-butyl alcohol	0*	-
37-5	.25 Mmole diphenyl ether	8*	trace black scum
37-6	none	15	trace black scum

Dummy, monomer and solvent only, gave an initial pressure of 44 psig.

*In this experiment the solvent, titanate and additive were put in the reaction tube initially. It was sealed, frozen with liquid nitrogen, evacuated, loaded with monomer from the vacuum line, and pressurized with dry nitrogen in the usual manner. A procedure was tried of letting the tube stand seal down in dry ice while the heptane melted preparatory to adding the aluminum triisobutyl. It was found by this procedure the heptane did not swell the cold gasket and make a seal. 37-2, 37-3 and 37-5 lost some solvent, 37-4 lost all. We returned to the use of a butyl gasket. The second catalyst component is added to the frozen tube immediately after loading with monomer and pressurizing. The tube is then warmed with continuous shaking and the catalyst developed by stirring at room temperature. Where the gasket may become swollen by monomer, we now use more solvent to reduce the vapor pressure of monomer.

Table X

Polymerization of 23.5 Mmoles Vinylidene Fluoride in the Presence of Amines

Catalyst .5 mmole tetrabutyl titanate - 1.5 mmole aluminum triisobutyl formed by stirring 15 minutes in the presence of monomer at room temperature. Solvent 28 ml. heptane. Polymerizations run 138 hours at room temperature.

Expt. No.	Additive	Final Pressure psig	Product
38-1	.25 Mmole n-butylamine	38	1 mg. black solid
38-2	.25 Mmole diethylamine	45	0
38-3	.25 Mmole pyridine	47	trace black smear
38-4	.25 Mmole n-butyl alcohol	53	trace black smear
38-5	.25 Mmole diphenyl ether	50	1 mg. black smear
38-6	None	40*	1 mg. black smear

*Leaked slightly after first puncture.

Butyl gasket, remainder of catalyst immediately after monomer loading and pressurizing, immediate shaking and warming to room temperature before stirring to develop catalyst. Average final pressure is 45 psi, compared with 44 psi, for the dummy tube in Expt. 37. We are satisfied leakage is not important.

2. Homopolymerization of 1,1,2-Trifluorobutadiene

A second approach to an oil- and freeze-resistant rubber is *via* the *cis*-polybutadiene chain, glass temperature -110°C.[6] 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 since *trans* or vinyl polymerization is detrimental (glass temperatures -83°C. and -9°C., respectively[7,8]). 1,1,2-Trifluorobutadiene was chosen as the monomer because of its ready availability.

Table XI shows that attempted homopolymerizations of 1,1,2-trifluorobutadiene with the cis-polybutadiene catalysts titanium tetraiodide/diphenyl magnesium or titanium tetraiodide/aluminum triisobutyl gave very low conversions. However, the use of the more nucleophilic catalyst tetrabutyl titanate activated with either diphenyl magnesium, decyl magnesium iodide or aluminum triisobutyl led to significant conversion to polymer (Table XII). 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 the monomer 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 are compared in Table XIII. The results indicate that the titanium-initiated polymerization is ten to twenty 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 Mr. C. B. Griffis of the U. S. Army Natick Laboratories. Details of this polymerization are given in Table XIV.

Table XI

Polymerization of 23.5 Mmoles 1,1,2-Trifluorobutadiene
Catalyst 0.5 Mmole Titanium Tetraiodide Plus $Al(i\text{-}bu)_3$
or Diphenyl Magnesium in Benzene

Catalyst prepared by stirring 15 mins. in presence of monomer. Run 64 hours at 25°C.

Expt. No.	Vol. C_6H_6	Activator	Final Pressure psig	Product
22-1	18	.75 Mm. Diphenyl Mg.	33	.003 gm.white resin
22-2	20	.9 Mm. Diphenyl Mg.	45	.001 gm.white resin
22-3	11	1.25 Mm. $Al(i\text{-}bu)_3$	9	.01 gm.white polymer
22-4	12	2.50 Mm. $Al(i\text{-}bu)_3$	10	.21 gm.brown powder amorphous

Table XII

Polymerization of 23.5 Mmoles 1,1,2-Trifluorobutadiene
in 12 ml. Benzene

Catalyst .5 Mm. tetrabutyl titanate plus diphenyl magnesium, decyl magnesium iodide or aluminum triisobutyl. Catalyst prepared by stirring 15 mins. in presence of monomer. Run for 160 hours.

Expt. No.	Activator	Final Pressure psig	Product Yield gm.	Product Conversion %	
23-1	.55 Mm. Diphenyl Magnesium	0	.545	21	gray resin
23-2	.75 Mm. Diphenyl Magnesium	0	.350	14	gray resin
23-3	.834 Mm.Decyl MgI	0	trace	<1	-
23-4	1.67 Mm.Decyl MgI	8	.401	16	gray resin
23-5	1.25 Mm.$Al(i\text{-}bu)_3$	0	1.32	52	gray resin
23-6	2.5 Mm.$Al(i\text{-}bu)_3$	0	1.02	40	brown resin

All products (except 23-3, not tested) were crystalline by X-ray, showing a very strong line at 4.45, a strong line at 4.0 and a weak line at 2.35. Additional weak lines were shown as follows: at 1.7 (23-2, 23-4, 23-6), at 2.2 (23-2, 23-4, and 3.4 (23-4, 23-6).

Table XIII

Comparison of Rate of Thermal Polymerization with Rate of Initiated Polymerization for 1,1,2-Trifluorobutadiene at Room Temperature

Catalyst stirred 15 minutes in the presence of 23.5 Mm. monomer at room temperature.

Expt. No.	Solvent	Catalyst	Time hrs.	Yield gm.	Conv. %	Rate of Conv. %/hr.
28-1	5 ml. C_6H_6	none	208	.255	10	.048
28-2	5 ml. Heptane	none	208	.187	7.4	.036
23-5	12 ml. C_6H_6	.5 Mm.$Ti(OBu)_4$-1.25 Mm.$Al(i\text{-}bu)_3$	160	1.32	52	.325
32-1	10 ml. C_6H_6	same as above	23	.242	9.5	.41
32-2*	10 ml. C_6H_6	same as above	89	1.556	61.5	.69
27-4**	10 ml. Heptane	.25 Mm.$Ti(OBu)_4$-.625 Mm.$Al(i\text{-}bu)_3$	112	.836	7.05	.063

* This sample gave a low value of unsaturation with our usual determination of iodine number using mercuric acetate catalyst. A method for unsaturation using bromine is being tried.

** .11 mole monomer.

Table XIV

Polymerization of 83 Mmoles of 1,1,2-Trifluorobutadiene in 22 ml. Benzene

Catalyst prepared by stirring 15' in presence of monomer. Polymerization run at 25°.

Expt. No.	Catalyst	Time hrs.	Yield gm.	Conv. %	Conv. hr.
25-1	1.25 Mm.$Al(i\text{-}bu)_3$-.5 Mm. $Ti(OBu)_4$	16	2.83	31.5	1.85 %/hr.

3. Copolymerization of 1,1,2-Trifluorobutadiene and of Butadiene

Two series of copolymerizations were carried out. Table XV shows that the tetrabutyl titanate-aluminum triisobutyl catalyst promotes the copolymerization of the fluorinated butadiene with either hexafluoropropylene or vinylidene fluoride. Infrared spectra of these polymers indicate qualitatively that both vinylidene fluoride or hexafluoropropene were copolymerized with trifluorobutadiene. The copolymer of vinylidene fluoride and hexafluoropropene was not formed under these conditions. The blank (27-4) was run with reduced catalyst. All three products are highly crystalline.

Table XV

Copolymerizations of the Three Combinations of 1,1,2-Trifluorobutadiene, Hexafluoropropene and Vinylidene Fluoride

Catalyst 1 Mm. Ti(OBu)$_4$ - 2.5 Mm. Al(i-bu)$_3$ prepared by stirring at room temperature in presence of monomer in heptane.

Expt. No.	Monomers	Solvent ml.	Time hrs.	Residual Pressure psig	Product	Conversion
27-1	.11 mole $C_4F_3H_3$ .110 ± .002 mole C_3F_6	40	88	55	5.2 gm. white resin	34
27-2	.11 mole $C_4F_3H_3$ .13 mole $C_2H_2F_2$	40	88	120	3.7 gm. white resin	29
27-3	.11 mole C_3F_6 .125 ± .005 mole $C_2H_2F_2$	40	406	144	0	0
27-4	.11 mole $C_4F_3H_3$ and catalyst 25% of that given above	10	112	10	.84 gm. white resin	11

The experiments listed in Table XVI were planned to determine the possibility of copolymerizing butadiene and 1,1,2-trifluorobutadiene by means of either the cis polybutadiene catalyst (titanium tetraiodide) or the best fluoroolefin catalyst found to date (tetrabutyl titanate). The tetrabutyl titanate-aluminum triisobutyl catalyst gives only a small conversion of butadiene to polybutadiene (expt. 24-3), but the copolymerization (expts. 24-4 and 24-5) proceeds in higher yield. The titanate catalyst makes high vinyl polybutadiene homopolymer[9] and the same structure is anticipated in the copolymer. The titanium tetraiodide-aluminum triisobutyl catalyst gives copolymers in higher yield and higher butadiene/fluorinated diene ratio than the titanate catalyst. We are not able to completely interpret the structure of the butadiene part of the copolymer from the infrared spectra at this time.

Table XVI

Polymerizations in Benzene with Titanate and Tetraiodide Catalysts and Various Monomers

Monomer amounts at 23.5 Mm. Catalyst developed by stirring 15 mins. in presence of monomer.

Expt. No.	C_6H_6 ml	Catalyst	Monomer	Time hrs.	Final Pressure psig	Product
20-1	22	1.9 Mm.$Mg(Ph)_2$-.5Mm.$Ti(OBu)_4$	C_3F_6	18	37	.256 gm. amorphous light brown resin
24-1	22	1.9 Mm.$Mg(Ph)_2$-.5Mm.$Ti(OBu)_4$	$C_4F_3H_3$	160	0	.203 gm. buff resin crystalline
24-3	3	.63 Mm.$Al(i\text{-}bu)_3$-.25Mm.$Ti(OBu)_4$	C_4H_6	240	10	.080 gm. sticky gray rubber
24-4	6	1.25 Mm.$Al(i\text{-}bu)_3$-.5Mm.$Ti(OBu)_4$	C_4H_6 $C_4F_3H_3$	240	23	.374 gm. gray semi-solid
24-5	6	1.88 Mm.$Al(i\text{-}bu)_3$-.5Mm.$Ti(OBu)_4$	C_4H_6 $C_4F_3H_3$	240	23	.628 gm. gray semi-solid
24-6	6.5	1.88 Mm.$Al(i\text{-}bu)_3$-.5Mm.TiI_4	C_4H_6 $C_4F_3H_3$	160	0	.473 gm. orange resin amorphous
24-7	7	2.5 Mm.$Al(i\text{-}bu)_3$-.5Mm.TiI_4	C_4H_6 $C_4F_3H_3$	240	11	1.02 gm. black resin amorphous

20-1 infrared spectrum has no resemblance to polyhexafluoropropene. A black resin is left after treatment with conc. HCl. Infrared spectrum of 24-3 shows a 60% vinyl, 26% trans and 14% cis structures in the polybutadiene. A comparison of spectra of 24-4 and 24-7 shows relatively more fluorine and less butadiene in 24-4 than in 24-7. We are waiting for F analyses. X-ray spectrum of 24-1 is similar to that of 23-4.

4. Attempted Ring-opening Polymerizations

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[10,11], cyclopentene[12] and norbornene[13]. The application of this polymerization technique to cyclic fluorocarbon olefins could lead to novel fluorinated polymers. However, our attempts to date, summarized in Tables XVII-XX, were negative.

Table XVII

Attempted Polymerization of 23.5 Mmoles Perfluorocyclobutene with Typical Ziegler Catalysts Prepared by Stirring 15 mins. in Presence of Monomer

Expt. No.	Solvent	Catalyst	Temp. °C.	Time hrs.	Final Pressure psig	Product
26-1	6 ml. heptane	.25 Mm. $VOCl_3$- .625 Mm. $Et_3Al_2Cl_3$	25	306	0	0
26-2	6 ml. heptane	same as above	50	306	leaked	2 mg. black polymer
26-3	4.5 ml. heptane 1.1 ml. C_6H_6	.25 Mm. $TiCl_4$- .75 Mm.$Al(i\text{-}bu)_3$	25	306	18	0
26-4	same	same	50	306	13	14 mg. black polymer
26-5	2.5 ml.ethylbenzene 3.25 ml. C_6H_6	.25 Mm.TiI_4- .94 Mm.$Al(i\text{-}bu)_3$	25	306	0	3 mg. brown powder
26-6	same	same	50	306	20	5 mg. brown powder
26-7	6 ml. benzene	.25 Mm.$Ti(OBu)_4$- .625 Mm.$Al(i\text{-}bu)_3$	25	306	21	0
26-8	6 ml. benzene	same	50	306	15	3 mg. brown solid

Infrared spectra of 26-2 and 26-4 are almost identical - bands at 2950, 1468, 1390, 1370, 1235, 1160, 1020 cm^{-1}. The background absorption decreases from 3500 to a window at 830 cm^{-1}. and rises up to 600 cm^{-1}.

Table XVIII

Exploratory Polymerizations in 6 ml. Heptane of 23.5 Mmoles of Perfluorocyclobutene at Room Temperature

Catalyst prepared by stirring with monomer at room temperature for 15 minutes. Time 281 hours.

Expt. No.	Catalyst	Final Pressure psig	Product Recovered mg.
31-1	.4 Mmole Vanadium III acetyl acetonate- 1.5 Mmoles $Al(i\text{-}bu)_3$	18	0
31-2	.5 Mmole $MoCl_5$- 1.5 Mmoles $Al(i\text{-}bu)_3$	28	0
31-3	.5 Mmole WCl_6- 1.5 Mmoles $Al(i\text{-}bu)_3$	27	0
31-4	.5 Mmole Chromium III acetyl acetonate 1.5 Mmoles $Al(i\text{-}bu)_3$	4	0
31-5	.5 Mmole $CrCl_3 \cdot 3THF$ 1.5 Mmoles $Al(i\text{-}bu)_3$	23	0
31-6	1 Mgmatom Iodine	23	11 red powder amorphous X-ray pattern v.v.faint line at 3.5
31-7	.5 Mmole Butyl Vanadate 1.5 Mmoles $Al(i\text{-}bu)_3$	27	0

Table XIX

Ring-opening Polymerizations of 14.5 Mmoles Hexafluoro-1,2-dichlorocyclopentene-1 with 1 ml. Benzene at Room Temperature

Catalyst prepared by stirring in presence of monomers 15 mins. at room temperature.

Expt. No.	Catalyst	Time hrs.	Product
29-1	.5 Mm. $MoCl_5$- 1.5 Mm. $Al(i\text{-}bu)_3$	287	20 mg. brown powder X-ray powder pattern shows amorphous ring 6-6.5
29-2	.5 Mm. WCl_6- 1.5 Mm. $Al(i\text{-}bu)_3$	287	10 mg. brown powder X-ray sample lost
29-3	.5 Mm. $TiCl_4$- 1.5 Mm. $Al(i\text{-}bu)_3$	287	12 mg. brown powder amorphous ring plus faint line at 5 in X-ray pattern

Table XX

Emulsion and Solution Polymerizations of 19.5 Mmoles of Hexafluoro-1,2-dichlorocyclopentene-1 or 31 Mmoles of Perfluorocyclobutene with Noble Metal Catalysts at 50°C.

Code		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
Hexafluoro dicyclopentene	Mmoles	19.5	-	19.5	-	19.5	-
Nitrogen flush & seal							
Perfluorocyclobutene	Mmoles	-	31	-	31	-	31
Polymerization Temp. °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 .

5. Polymerizations of 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane

This monomer was chosen as a representative of the acetylene class. It is also of interest as a compound in which the fluorine substituents are farther removed from the site of polymerization than in the previously studied monomers. Results from polymerizations with a series of catalysts are given in Table XXI.

Table XXI

Polymerization of 25 Mmoles 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane with Various Catalysts for 64 hrs. at Room Temperature

Catalyst prepared by stirring in the presence of monomer for 15 minutes.

Expt. No.	Solvent	Catalyst	Product gm. from C_3H_7OH	Product gm. from H_2O
39-1	12 ml. Heptane	.5 Mmole $VOCl_3$- 1.5 Mm.$Et_3Al_2Cl_3$	.065	.235
39-2	12 ml. Heptane	.5 Mmole Butyl Vanadate- 1.5 Mm. $Al(i\text{-}bu)_3$	.013	.116
39-3	12 ml. Heptane	.5 Mmole $Ti(OBu)_4$- 1.5 Mm. $Al(i\text{-}bu)_3$	.009	.075
39-4	12 ml. Heptane	.5 Mmole $TiCl_4$- 1.5 Mm. $Al(i\text{-}bu)_3$	-	2.903
39-5	13 ml. Benzene	.5 Mmole $Zr(acac)_4$ 1.5 Mm. $Al(i\text{-}bu)_3$	-	0
39-6	Polymer recovered from still residue on purification of monomer.			

The infrared spectrum of the monomer shows strong -C≡H absorption at 3305 cm^{-1}., also lines 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 weaker lines at 992 and 975.

39-4 polymer has only a trace of absorption at 3310. It has the strong bands at 1310, 1232 and 1105 but the band at 1140 is gone. Bands are present at 1,000, 984, 975 (shoulder) and 942 cm^{-1}.

Titanium tetrachloride-aluminum triisobutyl (expt. 39-4) gave an exotherm of 20°C. or so and a conversion of 63%. The polymerization was probably over in ten minutes or so. This is an interesting result because a monomer polymerizable with a $TiCl_4$ catalyst has a chance of copolymerizing with either ethylene or butadiene.

6. Copolymerizations of Fluorinated Monomers with Ethylene

Attempts were made to copolymerize ethylene with all of the fluorinated monomers at hand using a variety of catalysts. Tables XXII and XXIII permit comparison of the attempted homopolymerizations of the fluoromonomers and the attempted copolymerizations with ethylene. Table XXII (homopolymerizations) shows our results were very good with ethylene and the standard $VOCl_3$ catalyst. Ethylene did not polymerize with the tetrabutyl titanate-aluminum triisobutyl catalyst. We had poor results with various potential ring-opening catalysts on 2,3-bis(trifluoromethyl)norbornadiene (Experiments 41-2, 41-3, and 41-5). The $TiCl_4$ catalyst gave low molecular weight polymer in Expt. 41-1, while the titanate catalyst gave low yield (Expt. 41-5). We had more poor results with vinylidene fluoride, and with vinyl fluoride. Hexafluoro-2-butyne polymerized only with a tetrabutyl titanate catalyst.

In Table XXIII are shown the yields and products in copolymerizing ethylene with other monomers. Further tests are in process on many of these materials. With vinylidene, fluoride copolymerization was obtained only in small amount with a rather inactive catalyst. With the ethynyl cyclobutane , copolymerization occurred, but the proportion of ethylene was too high in the product. A different monomer feed ratio should rectify this. In the case of hexafluoropropene, conditions for copolymerization have not yet been found. Vinyl fluoride gave evidence of trace copolymerization with degradation. The hexafluoro-2-butyne formed copolymer in the presence of a titanate catalyst. Although the 1,1,2-trifluorobutadiene copolymerized in the presence of three different catalysts in fairly generous amount, there is also evidence of degradation. The single trial with 2,3-bis(trifluoromethyl) norbornadiene also was successful. The products of copolymerization were mostly resins.

Table XXII

Homopolymers of Fluorinated Monomers of Interest as Comonomers with Ethylene

Polymerization run at room temperature with
catalyst prepared by stirring in the presence
of monomer at room temperature

Monomer Expt. No.	Solvent	Catalyst	Final Pressure psig	Time hrs.	Product
C_2H_2	ethylene				*
40-1	30 ml. Heptane	.5 Mmole $VOCl_3$-1.25 Mm. $Et_3Al_2Cl_3$	1	16	.625 gm. 95% conv.
42-6	30 ml. Benzene	.5 Mm. Zr $(acac)_4$-2.5 MM. $Al(i\text{-}bu)_3$	30	148	.246 gm.
45-3	30 ml. Heptane	.5 Mm. $Ti(OBu)_4$-2.5 Mm. $Al(i\text{-}bu)_3$	1	210	trace
2,3-bis(trifluoromethyl)norbornadiene					
41-1	8 ml. Benzene	.5 Mm. $TiCl_4$-1.25 Mm. $Al(i\text{-}bu)_3$	-	187	3.892 gm. viscous oil
41-2	8 ml. Benzene	above + 2Mm. alpha picoline	-	187	.22 gm. brownish resin
41-3	8 ml. Benzene	.5 Mm. $TiCl_4$-1.25 Mm. $LiAl(bu)_4$- 2 Mm. alphapicoline	-	187	0
41-4	8 ml. Benzene	.5 Mm. $Ti(OBu)_4$-1.25 Mm. $Al(i\text{-}bu)_3$	-	187	.279 gm. brownish resin
41-5	8 ml. Benzene	above + 2 Mm. alphapicoline	-	187	.060 gm. brownish resin
$CH_2{=}CF_2$ vinylidene fluoride					
42-8	30 ml. Benzene	.5 Mm. Zr $(acac)_4$-2.5 Mm. $Al(i\text{-}bu)_3$	45	148	0
$CH_2{=}CHF$ vinyl fluoride					
43-5	30 ml. Heptane	.5 Mm. $VOCl_3$-1.5 Mm. $Et_3Al_2Cl_3$	38	89	.025 black semi-solid
43-6	30 ml. Heptane	.5 Mm. Butyl Vanadate-1.25 Mm. $Al(i\text{-}bu)_3$	43	89	0
43-7	30 ml. Heptane	.5 Mm. $Ti(OBu)_4$-1.25 Mm. $Al(i\text{-}bu)_3$	38	89	0
43-8	30 ml. Benzene	.5 Mm. $Ti(OBu)_4$-1.9 Mm. $Mg(phenyl)_2$	7	89	0
43-9	30 ml. Benzene	.5 Mm. Zr $(acac)_4$-1.25 Mm. $Al(i\text{-}bu)_3$	36	89	0

Table XXII (cont.)

Monomer Expt.No.	Solvent	Catalyst	Final Pressure psig	Time hrs.	Product
$CF_3C{\equiv}CCF_3$ hexafluoro-2-butyne					
44-5	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	40	64	0
44-6	30 ml. Heptane	.5 Mm.$VO(OBu)_3$-2.5 Mm. $Al(i\text{-}bu)_3$	37	64	0
44-8	30 ml. Heptane	.5 Mm.$Ti(OBu)_4$-1.5 Mm. $Al(i\text{-}bu)_3$	33	64	0
44-10	30 ml. Benzene	.5 Mm.$Ti(OBu)_4$-1.9 Mm. $Mg(phenyl)_2$	43	64	.219 gm.light brown resin**

*Polymer formed while the tube was being warmed to room temperature, before the catalyst had been stirred. A blank for this experiment with no catalyst gave a starting pressure of 48 psig. The polymer produced gave the usual polyethylene infrared spectrum and highly crystalline X-ray powder pattern.

**The infrared spectrum of the product coded 44-10 shows four peaks in the neighborhood of 1625 cm.$^{-1}$, also a weaker doublet at 1695 cm.$^{-1}$. Strong bands are located at 1180, 1205, 1270, and 1280 cm.$^{-1}$ There are also bands at 710, 770 and 875 cm.$^{-1}$

Table XXIII

Attempted Copolymerizations of Fluorinated Monomers with Ethylene at Room Temperature

Catalyst prepared by stirring in the presence of monomer at room temperature.

Monomer Expt. No.	Ratio Monomer C_2H_4	Solvent	Catalyst	Time hrs.	Final Pressure psig	Product
$CH_2=CF_2$ vinylidene fluoride						
40-2	23.5/11	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	16	56	.242 gm.white resin
40-3	same	30 ml. Heptane	.5 Mm.$VO(OBu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	16	45	.195 gm.white resin
40-4	same	30 ml. Heptane	.5 Mm.$Ti(OBu)_4$-2.5 Mm.$Al(i\text{-}bu)_3$	16	60	.001 gm.
42-7	same	30 ml. Benzene	.5 Mm.Zirc$(acac)_4$-2.5 Mm. $Al(i\text{-}bu)_3$	148	27	.010 gm.white resin
$C_8H_6F_3Cl$ 1,1,2-trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane						
40-5	24/24	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	16	28	.692 gm.yellow resin
40-6	24/24	30 ml. Heptane	.5 Mm.$VO(OBu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	16	25	.540 gm.white resin
40-7	24/24	30 ml. Heptane	.5 Mm.$Ti(OBu)_4$-2.5 Mm.$Al(i\text{-}bu)_3$	16	48	.005 gm.white resin
$CF_3-CF=CF_2$ hexafluoropropene						
42-1	24/12	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	16	43	.294 gm.creamy resin
42-2	same	same	.5 Mm.$VO(OBu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	16	39	.117 gm.white resin
42-3	same	same	.5 Mm.$Ti(OBu)_4$-2.5 Mm.$Al(i\text{-}bu)_3$	148	30	trace oil
42-4	24 + 24/12*	same	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	16	33	.265 gm.creamy resin
*termonomer is $C_8H_6F_3Cl$						
42-5	same	30 ml. Benzene	.5 Mm.$Ti(OBu)_4$-1.9 Mm.$Mg(phenyl)_2$	16	37	.065 gm.grayish white resin
$CH_2=CHF$ vinyl fluoride						
43-1	23.5/11	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	89	37	.283 brown resin
43-2	same	same	.5 Mm.$VO(OBu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	89	52	.131 white resin

Table XXIII (cont.)

Monomer Expt. No.	Ratio Monomer C_2H_4	Solvent	Catalyst	Time hrs.	Final Pressure psig	Product, gms.
$CH_2=CHF$ vinyl fluoride (cont.)						
43-3	23.5/11	30 ml. Heptane	.5 Mm.$Ti(OBu)_4$-2.5 Mm.$Al(i\text{-}bu)_3$	89	46	.006 white resin
43-4	same	30 ml. Benzene	.5 Mm.$Ti(OBu)_4$-1.9 Mm.$Mg(phenyl)_2$	89	50	.087 greasy fluid
$CF_3C\equiv CCF_3$ hexafluoro-2-butyne						
44-1	23.5/11	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	64	47	.286 white resin
44-2	same	same	.5 Mm.$VO(Bu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	64	42	.234 white resin
44-3	same	same	.5 Mm.$TiCl_4$-1.5 Mm.$Al(i\text{-}bu)_3$	64	35	.247 buff resin
44-4	same	same	.5 Mm.$Ti(OBu)_4$-1.5 Mm.$Al(i\text{-}bu)_3$	64	38	0
44-9	same	30 ml. Benzene	.5 Mm.$Ti(OBu)_4$-1.9 Mm.$Mg(phenyl)_2$	64	57	.590 light brown resin
$CF_2=CF-CH=CH_2$ 1,1,2-trifluorobutadiene						
45-1	19/11	30 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	18	25	1.830 orange resin
45-2	19/11	same	.5 Mm.$VO(OBu)_3$-2.5 Mm.$Al(i\text{-}bu)_3$	18	7	.712 light brown resin
45-4	7/21	same	.5 Mm.$TiCl_4$-2.5 Mm.$Al(i\text{-}bu)_3$	18	3	.513 light brown resin
45-5	15/11	30 ml. Benzene	.5 Mm.$Ti(OBu)_4$-1.9 Mm.$Mg(phenyl)$	210	22	.416 gm. white skins plus brown grease

Table XXIII (cont.)

Monomer Expt. No.	Ratio Monomer C_2H_4	Solvent	Catalyst	Time hrs.	Final Pressure psig	Product
$C_9H_6F_6$	2,3-bis(trifluoromethyl)norbornadiene					
41-6	22/23.5	26 ml. Heptane	.5 Mm.$VOCl_3$-1.25 Mm.$Et_3Al_2Cl_3$	187	10	.502 buff resin

Analytical Data

Code	X-ray Powder Pattern	Infrared Spectrum
40-2	Polyethylene	Polyethylene
40-3	Polyethylene	Polyethylene
42-7	Not complete	$CH_2=CF_2$ is a minor component. New bands at 1235, 1100 (broad) and 1390 cm.$^{-1}$ occur which are not in polyethylene, while the band at 1365 is strengthened, that at 1300 weakened.
40-5	Polyethylene pattern	Bands at 1311, 1258, 1232, 1140, 1112, 1000, 984, and 935 cm.$^{-1}$ indicate perhaps 20% of the cyclobutane monomer present.
40-6	Faint P. E. pattern	Bands at 1311, 1258 (pip) 1232, 1140 (pip), 1000, 978, 935 cm.$^{-1}$, indicate perhaps 15% of the cyclobutane monomer present.
40-7	Amorphous	-
42-1	-	Polyethylene
42-2	-	Polyethylene
42-4	-	Copolymer almost identical with 40-6 in detail.
42-5	-	Polyethylene
43-1	-	Polyethylene plus additional pip at 950 cm.$^{-1}$.
43-2	-	Polyethylene plus weak 990 and 911 cm.$^{-1}$ bands. Vinyl from dehalogenation?
43-3	P.E. + 3.38 line and without 4.55 line	-
44-1	-	P.E. spectrum plus very weak 1145, 1180 cm.$^{-1}$.
44-2	-	P.E. plus a minor component with 1175, 1195, 1240 cm.$^{-1}$ bands.
44-3	-	P.E. spectrum plus weak 1145, 1230 cm.$^{-1}$ bands.
44-9	-	Butyne appears to be a major constituent. Very strong bands at 1255, 1250, 1190, 1170, 1135 as well as bands at 877, 770, 1692, 1710 and 1600 cm.$^{-1}$ are superimposed on the P.E. spectrum.
45-1	-	75% C_2H_4 - 25% $C_4F_3H_3$ - a guess.
45-2	-	30% C_2H_4 - 70% $C_4F_3H_3$ - a guess.
45-4	-	90% C_2H_4 - 10% $C_4F_3H_3$ - a guess.
41-6	-	The norbornadiene a moderate constituent. Unsaturation at 1750 & 1785 cm.$^{-1}$. 1140, 1170 cm.$^{-1}$ bands are very strong. 1210, 1245, 1270, 1290 bands are also present.

EXPERIMENTAL

1. Apparatus

The vacuum line described in the previous report[2] was used for the distillation and storage of monomers and for filling polymerization tubes. Additional monomer storage traps were added. The lines were modified to pump out directly the residual gas in the connecting tubing next to the mercury cut-offs leading to gas measuring bulbs. Bumping of mercury by inflow of residual gas to an empty bulb when a mercury reservoir is lowered can now be avoided.

2. Monomers

a. Analysis

New monomers were tested by purity by vapor phase chromatography. The results are shown in Table XXIV.

b. Purification of 1,1,2-Trifluoro-2-chloro-3-methyl-3-ethynylcyclobutane

Approximately 125 gms. of material DNM IV-92 was received from Dr. D. N. Matthews. It had a yellow color. In vacuum distillation, after a 5.5 gm. forerun, a 105.3 gm. fraction was collected at a pot temperature of 45.5-51.0, vapor temperature 41-43°, at 36 mm. pressure. The main fraction had $n_D^{21.3}$ of 1.4035 (lit. n_D^{25} 1.4039, b. p. 44-49 at 35.3-36 mm.). Some polymer was recovered from the pot residue. A rough density measurement (weight of 1 ml. at room temperature) gave a value of 1.22.

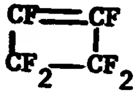
c. Preparation of 2,3-Bis(trifluoromethyl)norbornadiene

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 Peninsular ChemResearch 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%) of crude 2,3-bis(trifluoromethyl)norbornadiene, n_D^{21} 1.3695.

Two fractional distillations gave 47.1 g. (59%) 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%; one component amounted to 0.6%.

Table XXIV

Vapor Phase Chromatography of Fluorinated Monomers

Compound	Source	Purity %	Res.Cen. VPC No.	Stationary Phase[a]	Temp.[b] °C.	Ret. Time mins.	Impurities Ret.Time	Impurities %
CF_2=CFCl	Matheson	99.9	5130	Q	60I	1.0	2.6	-
			5131	Q	34	1.2	4.7	-
			5132	U	34	1.4	5.8	.07
			5133	G	I23 mins., then P_2	30.6	-	-
CH_2=CHF	Matheson	99.5	5257	G	60P_2	7.3	.9 36	.2 air .3 ?
			5258	Q	29I	1.1	-	-
Argon	Matheson	99.9	5148	G	60I	.9	-	-
			5149	G	30I	1.0	-	-
			5150	M	75P_3	1.8	3.1	.1%
CF_2=CF-CH=CH_2	USRCo.	99.4	5160	G	24I	35.9		
			after 30 mins. started heating - no program					
	Peninsular Chem.Research	98.2	5161	GP_2	60I	16.0	.9	.6% air
			5158	Q	24I	1.2	1.0	1.7% air
			5159	G	60P_2	14.6	.9 4.0	1.8% air .08% ?
CH_2=CH_2	Phillips Res.Grade	96.6	5208	G	50P_1	6.1	1.0	3.4% air and/or CH_4
CH_3CH=CH_2	Phillips		5209	G	60P_1	16.3	.9	.3% air and/or CH_4
CH_2=C-C=CH_2	used recently not tested by VPC							

a G = 4 ft. silica gel; Q = 2-meter squalene; U = 6 ft.Ucon LB550; M = 6 meter 5A molecular sieve

b I = isothermal; P_1 = programmed at 2.9°C./min., P_2 = programmed at 7.9°C./min. P_3 = programmed at 15°C./min.

d. Preparation of 1,1,2-Trifluorobutadiene

This material, b. p. 7.8-9°, was prepared from Peninsular ChemResearch 4-bromo-3-chloro-3,4,4-trifluorobutene-1 in 81-86% yield by the zinc-promoted dehalogenation method of Tarrant and Lilyquist.[14]

3. Preparation of Catalyst Components

a. 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 gm. (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 of 268 gms. (1 mole) of 1-iododecane were added over 3/4 hr. while the flask was chilled with some 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 oz. 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.

b. 5% Suspension of TiI_4 in Diethylbenzene

As our TiI_4 procured from McKay turned out to be oxidized to I_2+ TiO_2, a preparation of a 0.1 M TiI_4 suspension in inert solvent was made according to the directions of Dr. Walter Nudenberg.

c. Dehydration of Zirconium Acetyl Acetonate[15]

Zirconium $(acac)_4 \cdot 10H_2O$ (K. & K.) was dehydrated by pumping at room temperature on 59 grams of starting material at 2×10^{-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.

d. Preparation of Tetrakis (diethylamino)titanium

The method of Bradley and Thomas[16] 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% yield.

4. Polymerizations

Polymerizations were carried out essentially as described in the first report[2] with the exception that the general practice has been to form the catalyst (i.e. mix the two components) in the presence of monomer. The reasons are to obtain an active catalyst and a catalyst which makes amorphous polymer with certain monomers.

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, we returned to butyl gaskets.

One of the catalyst components is the last ingredient in loading a tube. This is added immediately after the cold tube has been loaded with monomer and pressurized with dry nitrogen. The tube is warmed at once with continuous shaking to room temperature and then stirred fifteen minutes at room temperature for catalyst development.

5. Polymer Isolation Technique

The simplest way of recovering polymer has been to pour the reaction mixture into 5 parts isopropanol - 1 part concentrated HCl. After soaking it is given a water soak, isopropanol soak (with PBNA if unsaturation is present in the polymer), and vacuum dried at room temperature. Decantation and/or centrifuging are used to recover small amounts of material.

Beginning with Experiment 27 the gas blanket for all purposes has been high purity nitrogen deoxygenated over active copper and dried with 5A molecular sieve. Up until then the gas blanket was argon. We had trouble pumping argon out of reaction tubes frozen with liquid nitrogen but avoided this with the use of a nitrogen gas blanket.

SUMMARY

1. The survey of transition metal catalysts for the polymerization and copolymerization of fluorinated olefins and dienes has been continued.

2. The tetrabutyl titanate-aluminum triisobutyl and titanium tetraiodide-aluminum triisobutyl catalysts are the best found so far for the homo- and copolymerization of 1,1,2-trifluorobutadiene. In preliminary experiments, the polymerization proceeded to 52-62% conversion with rates of 0.3-0.7%/hour using tetrabutyl titanate-aluminum triisobutyl catalyst.

3. 1,1,2-Trifluoro-2-chloro-3-ethynylcyclobutane is polymerized in 67% conversion (with a good initial exotherm) with titanium tetrachloride-aluminum triisobutyl catalyst.

4. Hydrocarbon solvents (benzene, heptane) are preferable to halocarbon solvents (carbon tetrachloride, methylene chloride, Freon 113) as polymerization media.

5. Little success has been had to date in homopolymerizations of vinylidene fluoride or hexafluoropropane with a catalyst based on tetrakis(diethylamino) titanium or with Ziegler catalysts modified by the addition of electron donors such as amines, alcohols, water or ethers.

6. Copolymerization of ethylene and fluorocarbons proceeds best with comonomers in which halogen is not on the carbon-carbon double bond or adjacent to it.

7. Ring-opening polymerization of fluorinated cyclic olefins has not yet been achieved with catalysts based on vanadium, titanium, molybdenum, tungsten, chromium, rhodium or ruthenium.

PROPOSED WORK

1. Further study of copolymerizations of fluorinated dienes with butadiene using titanium tetraiodide and soluble cobalt catalysts. 2-Fluorobutadiene-1,3, 2-(trifluoromethyl)butadiene 1,3, 1,1-difluoro-3-(trifluoromethyl) butadiene 1,3, and 1,1,3-trifluorobutadiene are of particular interest.

2. Test several fluorinated styrenes as comonomers with butadiene.

3. Continue further explorations of copolymerizing ethylene (containing an electron rich double bond) with fluorinated substituted acetylenes (containing an electron-poor triple bond), where the halogen is not close to the unsaturation.

4. Examine other monomers in which the fluorine atoms are slightly removed from the vinyl unsaturation, such as fluoroalkyl vinyl ethers or fluoroalkyl vinyl sulfides.

5. A limited study of the possibility of upgrading cis-polybutadiene to meet the objectives of this contract by chemical modification with fluorinated reagents such as pentafluorothiophenol.

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Elastomers	2		2			
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