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FMC CORPORATION

CHEMICAL RESEARCH AND DEVELOPMENT CENTER

CENTRAL RESEARCH DEPARTMENT

Princeton, New Jersey

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Report No. PCR 337
Project No. B-132

(6) QM ELASTOMER CONTRACT .

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I. SUMMARY

The reaction of tetrafluoroethylene with fluoro-olefinic silanes has been shown to occur at elevated temperatures to form products containing a perfluorinated cyclobutane ring. Although conversions were low, the reaction provides a basis for further studies involving difunctional moieties which can lead to novel block copolymer systems comprised of siloxane units and fluorocarbon units in alternating sequences.

I. INTRODUCTION

A. Objectives

The objectives of this program are the development of high strength chemical resistant rubbers serviceable at low temperatures (down to -65°F.) and chemical resistant rubbers that have high strength and rubber-like properties at high temperatures (600°F. and above) through the investigation of fluorine-containing polymer systems.

B. Program

In order to achieve the above objectives a broad program was planned embracing (a) the development of block copolymers composed of fluorocarbon units alternating with fluoroalkyl siloxane units and (b) the synthesis of fluorocarbon polymers containing a nitrogen sulfur or oxygen heteroatom in the backbone of the macromolecule.

Full implementation of the program will depend on the rate at which suitable monomers and other reagents can be acquired from commercial suppliers or prepared by the academic contractors to the Army Natick Laboratories.

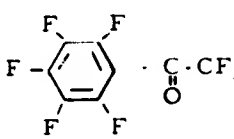
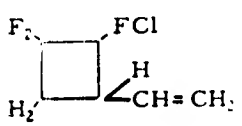
C. Statement of Costs

Approximately 14% of the authorized funds have been expended during this quarter. Since much of this expenditure has been incurred in the acquisition of materials and special equipment required for the project plus the development of suitable reaction conditions, only about 5% of the projected work has been completed. It is believed, however, that the funds allocated will be sufficient to permit completion of the proposed work.

III. DISCUSSION OF RESULTS

A. Monomer Procurement

The following monomers and successors were obtained during the period of this report:

Monomer	Amount	Source
$CF_2=CFCl$	4 lbs.	General Chemical Division, Allied Chemical Corp.
$CF_2=CH_2$	4 lbs.	General Chemical Division Allied Chemical Corp.
$CF_2\overset{O}{\overset{\|}{C}}CF_2$	2 lbs.	General Chemical Division Allied Chemical Corp.
CF_2BrCF_2Br	17 lbs.	Freon Products Division E. I. duPont de Nemours and Co.
$CF_2=CFCH_2CH_2Si(CH_3)_3$	15 g.	P. Tarrant, University of Florida
$CF_2=CFSi(CH_3)_3$	15 g.	P. Tarrant, University of Florida
$CF_2=CFCH_2CH_2\overset{CH_3}{\overset{\|}{Si}}-O-\overset{CH_3}{\overset{\|}{Si}}CH_2CH_2CF=CF_2$ (CH$_3$ and CH$_2$)	10 g.	P. Tarrant, University of Florida
	10 g.	P. Tarrant, University of Florida
$[CF_2CF_2CH_2CH_2\overset{CH_3}{\overset{\|}{Si}}O]_x$	110 g.	E. C. Stump, Peninsular Chemical Research, Inc.
$[CF_2CH_2CH_2CH_2\overset{CH_3}{\overset{\|}{Si}}O]_x$	75 g.	E. C. Stump, Peninsular Chemical Research, Inc.
	56 g.	J. D. Park, University of Colorado

B. Polymerization Research

The initial investigations conducted under this contract were concerned with a reaction suggested by Prof. Paul Tarrant (University of Florida) in which a fluoro-olefin is reacted with a fluoro-olefinic silane to form a product containing a four membered ring, i.e. a perfluorinated cyclobutane derivative:

$$CF_2=CF-CF=CFCH_2CH_2Si(CH_3)_3 \xrightarrow{\Delta} \begin{matrix} CF_2CFCH_2CH_2Si(CH_3)_3 \\ | \quad\quad | \\ CF_2CF_2 \end{matrix}$$

Moreover it was envisaged that a novel block copolymer would be formed by the co-reaction of an alpha, omega divinyl fluoro-olefinic monomer with a difunctional fluoro-olefinic siloxane prepolymer in which chain propagation would be effected by the cycloaddition reaction mentioned above. The initial experimental studies were concerned with the exploration of this reaction with the aid of two model compounds supplied by Prof. Tarrant viz. $CF_2=CFCH_2CH_2Si(CH_3)_3$ and $CF_2=CFSi(CH_3)_3$. The co-reactant selected for use with the above mentioned compounds was tetrafluoroethylene, $CF_2=CF_2$, a monomer known to participate in similar cycloadditions with a variety of unsaturated compounds (1). The formation of cyclobutane rings from the co-reaction of the respective starting materials is potentially complicated by the self dimerization of each of the starting materials and an effort was made to allow the favored reaction product to form with a minimum of side reactions occurring.

Equimolar quantities of the fluoro-olefinic silanes and tetrafluoroethylene were charged into a bomb and allowed to react at elevated temperatures for ca. 17 hours and the liquid products were removed from the bomb and subjected to a simple distillation to estimate the degree of conversion to the expected product. Table I. lists the experimental details. An inspection of the table reveals that the reaction of tetrafluoroethylene with the fluoro-olefinic silanes occurred at 150° C. but that somewhat higher conversions were obtained at 200° C. The identity of the product of the reaction between $CF_2=CF_2$ and $CF_2=CFCH_2CH_2Si(CH_3)_3$ i.e. $\begin{matrix} CF_2CFCH_2CH_2Si(CH_3)_3 \\ | \quad\quad | \\ CF_2CF_2 \end{matrix}$ was shown by the absence of unsaturation in the infrared spectra and by the carbon and hydrogen analyses which agreed with the theoretical calculated percentages.

As a consequence of the small quantities of monomer made available (ca. 10 grams) only a limited number of experiments could be performed, in some cases using recovered materials, and no attempt was made to determine exact yields of product. The availability of larger quantities of monomers is essential for a thorough examination of the various polymer-forming reactions set forth in the FMC contract proposal (2).

IV EXPERIMENTAL

Preparation of $CF_2=CF_2$

D-871-64-A A 50 ml. [illegible] was equipped with a mechanical stirrer, a dropping funnel, a nitrogen inlet tube, a thermometer and a dry ice condenser. The upper exit of the condenser was connected to another dry ice condenser set downward into a graduated tube (for immersion in a cooling bath) containing a side arm for connection to a vacuum pump and gas storage cylinder.

The above assembly was charged with 7.8g. of (0.11g. atom) zinc dust in 25g. of tetrahydrofuran and agitated for ca. 30 minutes to effect dispersion of the metal. Then 26.0g. (0.091 mole) of CF_2BrCF_2Br (Freon 114B2) was cautiously added from the dropping funnel and an exotherm was noted and the addition was continued to maintain a temperature of 50-60°C. The $CF_2=CF_2$ liberated was measured volumetrically in the graduated tube (ca. 70% yield) and collected for storage in an evacuated stainless steel cylinder which had been previously charged with 0.05g. of $(C_4H_9)_4N$ polymerization inhibitor.

Reaction of $CF_2=CF_2$ with $CF_2=CFCH_2CH_2Si(CH_3)_3$

D-871-64-B A 75 ml. stainless steel cylinder was charged with 10.0g. of $CF_2=CFCH_2CH_2Si(CH_3)_3$ and 0.03g. of $(C_4H_9)_4N$. The bomb was then fitted with a Hoke needle valve, cooled with liquid nitrogen, evacuated and charged with 5.5g. of $CF_2=CF_2$ from a gas transfer system. The sealed bomb was then allowed to remain at 150°C. for 17 hours in a barricaded Aminco rocker. Upon completion of the reaction, the bomb was cooled in liquid nitrogen, the unreacted $CF_2=CF_2$ allowed to escape and the liquid mixture remaining decanted from the bomb and placed in an apparatus for simple distillation. 4.4g. distilled at 116-120°C. and a fraction (0.4g.) was collected at 130-142°C. Infrared analyses indicated that both fractions were almost identical.

D-871-66 8.86g. of $CF_2=CFCH_2CH_2Si(CH_3)_3$, 0.05g. of $(C_4H_9)_4N$ and 4.8g. of $CF_2=CF_2$ were charged to a 75 ml. bomb using the procedure described above and the reaction mixture was allowed to remain at 200°C. for 17 hours. Upon distillation, 4.93g. was collected with a F.P. range of 118-138°C. and 1.6g. was

collected at 130-138° C. The second fraction exhibited less unsaturation than the starting material according to the infrared spectra.

D-871-68 6.78g. of $CF_2=CFCH_2CH_2Si(CH_3)_3$ (recovered from experiment D-871-66) 0.04g. $(C_2H_5)_3N$ and 3.7g. $CF_2=CF_2$ were charged to a 75 ml. bomb using the aforementioned procedure and the bomb contents were allowed to remain at 150° C. for 17 hours. Upon distillation 4.74g. was collected with a B.P. range of 124-136° C. Two major components were shown to be present by V.P.C. (vapor phase chromatographic) analysis. component I amounting to 25 wt. % and component II, 75 wt. %.

D-871-70 4.0g. of $CF_2=CFCH_2CH_2Si(CH_3)_3$ (recovered from experiment D-871-68) and 2.2g. of $CF_2=CF_2$ were charged to a 75 ml. bomb using the procedure described above and the reaction mixture was allowed to remain at 200° C. for 17 hours. Upon distillation 3.22g. was collected with a B.P. range of 129-135° C. Two major components were shown to be present by V.P.C. analysis, component I amounting to 16 wt. % and component II, 83 wt. %. A portion of the product was distilled through a 3" Vigreux column and a high boiling residue was separated from the main distillate. The former was shown to be essentially 100% pure by V.P.C. analysis and infrared analysis showed no unsaturation. Analyses for carbon (38.90%) and hydrogen (4.84%) were in good agreement with the calculated values (38.30% C and 4.61% H) for the desired product, $CF_2CFCH_2CH_2Si(CH_3)_3$.
CF_2CF_2

Reaction of $CF_2=CF_2$ with $CF_2=CFSi(CH_3)_3$

D-871-69 7.5g. of $CF_2=CFSi(CH_3)_3$, 0.04g. Dipentene No. 122 and 4.8g. of $CF_2=CF_2$ were charged to 75 ml. bomb using the procedure described above and the reaction mixture was allowed to remain at 200° C. for 17 hours. Upon distillation, 5.3g. was collected with a B.P. range of 70-86° C. and 0.4g. was collected at 94-98° C. V.P.C. analysis showed two major peaks, component I amounting to 87 wt. % in the first fraction and only 5% in the second fraction while component II was 7% in the first fraction and 87% in the second fraction. The identity of the higher boiling component has not yet been established but probably is the desired product, $CF_2CFSi(CH_3)_3$.
CF_2CF_2

Materials

Tributylamine (polymerization inhibitor) was a Matheson, Coleman and Bell product which was distilled before use.

Dipentene No. 122 (polymerization inhibitor) was used as received (Hercules Powder Company).

Analytical

Vapor phase chromatographic examinations were performed with an 8' by 1/4" O. D. column containing 33% Dow Corning Silicone fluid 550 on hexamethyldisilazane treated Chromosorb W (60 to 80 mesh).

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REFERENCES

(1) Organic Reactions 12 1 1962. Chapter 1 "Cyclobutane Derivatives from Thermal Cycloaddition Reactions."

(2) FMC Proposal 63-6 "Development of High Strength Chemically Resistant Rubbers" May 1 1963.

TABLE I

THERMAL CYCLOADDITION REACTIONS OF TETRAFLUOROETHYLENE WITH FLUORO OLEFINIC SILANES

Exp. No.	Co-reactants (1:1 mole ratio)	Temp. C.	Time hrs.	Composition of Distilled Reaction Mixtures[a]
D-871-64-B	10.0g. CF_2 $CFCH_2CH_2Si(CH_3)_3$ 5.5g. CF_2 CF_2 0.03g. $(C_4H_9)_3N$	150	17	4.4g. BP116-120 C. 0.4g. BP130-149 C. Both fractions appeared to be almost identical.
D-871-66	8.86g. CF_2 $CFCH_2CH_2Si(CH_3)_3$ 4.8g. CF_2 CF_2 0.05g. $(C_4H_9)_3N$	200	17	4.93g. BP118-128 C. 1.6g. BP130-135 C. Second fraction exhibited less unsaturation than starting material
				Composition of Distilled Reaction Mixtures[b]
D-871-68	6.78g. $CF_2CFCH_2CH_2Si(CH_3)_3$[c] 3.7g. CF_2 CF_2 0.04g. $(C_4H_9)_3N$	150	17	4.74g. BP124-136 C. (some material losses in transfer) Component I - 25% by weight Component II - 75% by weight
D-871-70	4.0g. CF_2 $CFCH_2CH_2Si(CH_3)_3$[d] 2.2g. CF_2 CF_2	200	17	3.22g. BP129-135° C. Component I - 16% Component II - 84% Distilled through a 3" Vigreux column {Component I - 19% Component II - 81%} main distillate Component II - 100%[e] residue

TABLE I - Continued

Exp. No.	Co-reactants (1:1 mole ratio)	Temp. C.	Time hrs.	Composition of Distilled Reaction Mixtures[b]
D-871-69	7.5g. CF CFSi(CH$_3$)$_3$ 4.8g. CF$_2$ CF$_2$ 0.04g. Dipentene No. 122[f]	200	17	5.3g. BP70-86 C. Component I - 87% Component II - 7%[g] 0.4g. BP94 98 C. Component I - 5% Component II - 87%[g]

a. Determined by infrared spectral analysis after simple distillation.
b. Determined by vapor phase chromatography after simple distillation.
c. Recovered monomer from D-871-66. V. P. C. data not available.
d. Recovered monomer from D-871-68.
e. Identified as: $CF_2CFCH_2CH_2Si(CH_3)_3$ (with CF_2CF_2). Identical to "Component II" in experiments D 871-68 and 70.

Analytical Data:
No unsaturation in the infrared spectra.
% C (Theo.) = 38.30 % H (Theo.) = 4.61
% C (Actual) 38.90 % H (Actual) = 4.84

f. Complex mixture of terpenes.
g. Identity undetermined.

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