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CHEMICAL RESEARCH & DEVELOPMENT CENTER

FMC CORPORATION

PRINCETON, NEW JERSEY

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U. S. ARMY CONTRACT DA19-129-AMC-147(N)

PROGRESS REPORT II

Period Covered

September 27, 1963 - December 26, 1963

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FMC CORPORATION

CHEMICAL RESEARCH AND DEVELOPMENT CENTER

CENTRAL RESEARCH DEPARTMENT

Princeton, New Jersey

January 9, 1964

Report No. PCR 349
Project No. B-132

QM ELASTOMER CONTRACT

SUPERVISION: B. F. Landrum and W. L. Riedeman

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I. SUMMARY

A

Reaction of dimethylchlorosilane with 3, 4, 4 Trifluoro-4-bromo-3 chlorobutene-1 on a 0. 5 mol scale at 75° C. in the presence of chloroplatinic acid catalyst provided a 44% conversion to the adduct, $Cl\text{-}Si(CH_3)_2CH_2CH_2CFClCF_2Br$.

Repetition of the reaction on a 5 mol scale was started and the product obtained will be hydrolyzed and dehalogenated to form the desired disiloxane monomer, $(CF_2{=}CFCH_2CH_2Si(CH_3)_2)_2\text{-}O\text{-}$.

II. 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.

Progress in polymerization research has been severely impeded by the lack of monomers in quantities sufficient to perform meaningful experimentation. Desired monomers have either been unavailable entirely or available in 10-20 gram quantities from the universities cooperating in the program.

In a move to alleviate this condition, the scope of the FMC contract was modified to include the following: (a) preparation of monomers in large quantities from established synthetic procedures available from the cooperating university laboratories or from the chemical literature and (b) purchase of fluorinated aromatic compounds in large amounts and the execution of research studies on the preparation of monomeric materials and polymerization of these monomeric materials in a variety of polymer systems.

Additional funds have been provided to facilitate this aspect of the program.

Scale-up of monomer preparations from established synthetic procedures is dependent upon obtaining suitable starting materials from commercial suppliers. This is being vigorously pursued and ample stocks should be on hand in the near future.

Meanwhile, sufficient quantities of certain chemicals have already been obtained. The program is rapidly expanding with additional manpower being made available to exploit the modified scope.

C. Statement of Costs

Approximately 17% (includes supplemental funds) of the authorized funds have been expended to date. Since much of this expenditure has been incurred in the acquisition of materials and special equipment required for the project, only about 7% of the projected work has been completed. The rate of expenditure will be increased sharply during the coming quarter. It is believed 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 precursors were obtained during the period of this report:

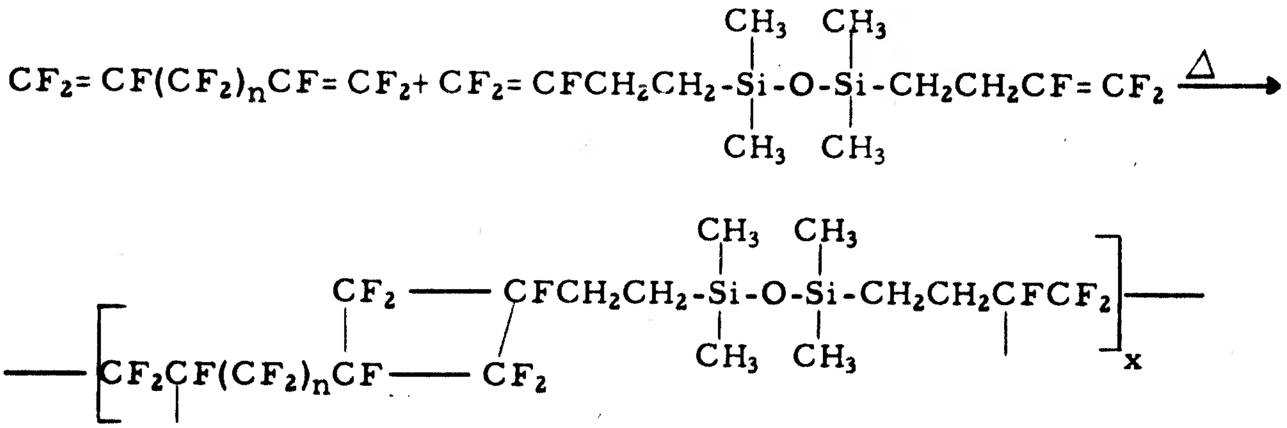
Monomer	Amount	Source
$CF_3CF=CF_2$	1 lbs.	Peninsular Chem Research, Inc.
$CF_3CH=CH_2$	113 g.	J. D. Park, University of Colorado
$CF_2BrCFClCH=CH_2$	1900 g.	Peninsular Chem Research, Inc.
$H\text{-}Si(CH_3)_2Cl$	2 lbs.	Dow Corning Corp.
$(C_4F_9)_3N$	8 lbs.	3-M Company
Kel-F Acid No. 8114	2 lbs.	Peninsular Chem Research, Inc.
$CF_2ClCFCl\ I$	200 g.	Peninsular Chem Research, Inc.
CF_2Br_2	4 kgs.	Columbia Organic Chemicals, Inc.

The following monomers and precursors have been ordered from Imperial Smelting Corp. (London, England):

pentafluorobenzene	2 kg.
hexafluorobenzene	1 kg.
pentafluoroaniline	300 g.
pentafluorothiophenol	1 kg.
pentafluorophenyl hydrazine	250 g.
4, 4' diaminooctafluorobiphenyl	100 g.
pentafluorophenol	1 kg.

B. Polymerization Research

Investigations were concerned with the eventual preparation of novel block copolymers via reaction of an alpha, omega divinyl fluoroolefinic monomer with a difunctional fluoroolefinic siloxane prepolymer as follows:



$$CF_2{=}CF(CF_2)_nCF{=}CF_2 + CF_2{=}CFCH_2CH_2\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_2CH_2CF{=}CF_2 \xrightarrow{\Delta}$$

Chain propagation is thus effected by a thermal cycloaddition reaction of the terminal fluoroolefinic groups of both reactants, forming a block copolymer composed of fluorocarbon and siloxane moieties.

In order to examine thoroughly the aforementioned polymer-forming reaction, it was deemed essential to obtain larger quantities of monomers than has been possible for the university laboratories to supply.

Accordingly, it was decided to use the facilities at FMC to scale-up known preparative procedures and thus implement the program effectively. To this end, the synthesis of the disiloxane $CF_2{=}CFCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CF{=}CF_2$ was initiated after acquisition of the necessary starting materials. The procedure followed was that supplied by Professor Tarrant (1) (University of Florida).

The synthesis consists of the following steps:

(a) $HSi(CH_3)_2Cl + CH_2{=}CHCFClCF_2Br \xrightarrow{H_2PtCl_6}$
$ClSi(CH_3)_2CH_2CH_2CFClCF_2Br$

(b) $ClSi(CH_3)_2CH_2CH_2CFClCF_2Br \xrightarrow{H_2O}$
$CF_2BrCFClCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CFClCF_2Br$

(c) $CF_2BrCFClCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CFClCF_2Br \xrightarrow[\text{alcohol}]{Zn}$
$CF_2{=}CFCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2CF{=}CF_2$

Two initial runs of step (a) were made on a 0. 5 mole scale to explore the reaction before scale-up.

The addition of dimethyl chlorosilane to 3, 4, 4 trifluoro-4-bromo-3 chloro-butene-1 in the presence of chloroplatinic acid catalyst proceeded to form the adduct, $ClSi(CH_3)_2CH_2CH_2CFClCF_2Br$. A 44% conversion was realized by conducting the reaction in an agitated bomb at 75° C. for 11 hours. Another run conducted under identical conditions produced a smaller conversion to product but loss of volatile dimethyl chlorosilane by the inadvertent purging of the bomb undoubtedly accounted for the discrepancy.

The product was isolated by distillation of the reaction mixtures and, in the first run, excellent recovery of the unreacted portion of the starting materials was also obtained, thus permitting future recycle of the silane and the butene after separation.

Preparation of the adduct, $ClSi(CH_3)_2CH_2CH_2CFClCF_2Br$, on a 5 mole scale was started and will be reported in detail in the next report. Gas formation was noted in all three preparations and a sample of the gas formed in this side-reaction was taken at the conclusion of the 5 mole run. The sample was identified by mass spectrometry as hydrogen, probably arising from alcoholysis of the dimethyl chlorosilane:

$$\text{——}\mathrm{SiH} + \mathrm{HOR} \longrightarrow \text{——}\mathrm{SiOR} + \mathrm{H_2}$$

Future efforts will be concerned with monomer preparations on a large scale followed by exploratory polymer research on the synthesized materials.

IV. EXPERIMENTAL

Reaction of $H\text{-}Si(CH_3)_2Cl$ with $CH_2{=}CHCFClCF_2Br$

D-871-104 A 300 ml. Aminco bomb was charged with 49.52 g. (0.52 mole) of $H\text{-}Si(CH_3)_2Cl$, 115.25 g. (0.51 mole) of $CH_2{=}CHCFClCF_2Br$ and 1.5 cc of 0.1M H_2PtCl_6 in isopropanol. The bomb contents were then rocked at 75° C. for 11 hours. At the conclusion of the heating period, the bomb was cooled and vented, releasing gaseous pressure that had been generated (side-reaction), and the bomb contents were then decanted into a dry container for distillation. Distillation of the reaction mixture was performed at atmospheric pressure through a 14'' insulated Vigreux column. Two fractions were collected, the first fraction (fraction I) distilling at 65-85° C. (uncorrected) and weighing 82 g. and the second fraction (fraction II) distilling at 180-185° C. (uncorrected) and weighing 71 g. (44% conversion). The latter represents the desired adduct, $Cl\text{-}Si(CH_3)_2CH_2CH_2CFClCF_2Br$ reported by Tarrant (1):

Calculated	Found
% C = 22.65	% C = 23.62
% H = 3.16	% H = 3.42
% F = 17.91	% F = 17.30

Recovery of product and unchanged starting materials was 93%.

D-871-101 A 300 ml. Aminco bomb was charged with 45.65 g. (0.48 mole) of $H\text{-}Si(CH_3)_2Cl$, 107.6 g. (0.48 mole) of $CH_2{=}CHCFClCF_2Br$ and 1 cc of 0.1M H_2PtCl_6 in isopropanol and the bomb was purged with nitrogen before sealing the contents. The bomb contents were then rocked at 75° C. for 11 hours. At the conclusion of the heating period, the bomb was cooled and vented, releasing gaseous pressure that had been generated (side-reaction) and the bomb contents were then decanted into a dry container for distillation. Distillation of the reaction mixture was performed at atmospheric pressure through a 14'' insulated Vigreux column. Two fractions were collected, the first fraction (fraction I) distilling at 63-70° C. (uncorrected) and weighing 58 g. and the second fraction (fraction II) distilling at 180-185° C. and weighing 40.2 g. (26% conversion to the desired adduct). The low conversion to product and the relatively poor recoveries of starting materials (64% over-all) are undoubtedly a consequence of the nitrogen purge employed initially, inadvertently venting the volatile dimethyl chlorosilane charged into the reactor.

D-871-108 A 2.7 liter Aminco bomb was charged with 473. g. (5 moles) of $H\text{-}Si(CH_3)_2Cl$, 1117.5 g. (5 moles) of $CH_2{=}CHCFClCF_2Br$ and 10 cc of 0.1M H_2PtCl_6 in isopropanol. The bomb contents were then rocked at 75° C. for 11 hours. At the conclusion of the heating period the bomb was cooled and a sample of the gaseous mixture generated in a side-reaction was collected in a 50 cc stainless steel storage cyclinder. Mass spectral analysis identified the sample as ca. 99% hydrogen gas. After venting of the bomb was complete, the contents were decanted into a dry container for distillation. Results of the distillation are incomplete and will be discussed in the next report.

Materials

Dimethylchlorosilane was obtained from the Dow Corning Corp. 3, 4, 4 Trifluoro-4-Bromo-3 Chloro-butene-1 was obtained from Peninsular Chem Research, Inc.

Chloroplatinic acid was obtained from Matheson, Coleman and Bell Company.

REFERENCES

(1) Semi-Annual Report 1, Contract DA19-129-AMC-79(N) Research on Synthesis of Unsaturated Fluorocarbon Compounds", P. Tarrant, April 1 - September 20, 1963.

TABLE I

REACTION OF $H\text{-}Si(CH_3)_2Cl$ WITH $CH_2{=}CHCFClCF_2Br$ at 75° C.

Reaction Time = 11 hours

Exp. No.	Co-reactants (1:1 mole ratio)	Conversion, %[a]
D-871-104	49.52 g. $H\text{-}Si(CH_3)_2Cl$ 115.25 g. $CH_2{=}CHCFClCF_2Br$ 1.5 cc 0.1M H_2PtCl_6 in isopropanol	44
D-871-101	45.65 g. $H\text{-}Si(CH_3)_2Cl$ 107.6 g. $CH_2{=}CHCFPlCF_2Br$ 1 cc 0.1M H_2PtCl_6 in isopropanol	26[b]
D-871-108	473 g. $H\text{-}Si(CH_3)_2Cl$ 1117.5 g. $CH_2{=}CHCFClCF_2Br$ 10 cc 0.1M H_2PtCl_6 in isopropanol	-[c]

Note:

a $Cl\text{-}Si(CH_3)_2CH_2CH_2CFClCF_2Br$.

b Reactor inadvertently purged with nitrogen initially, causing loss of dimethyl chlorosilane.

c Incomplete data.