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SYNTHESIS OF ELASTOMERS FOR USE WITH LIQUID FLUORINE

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SYNTHESIS OF ELASTOMERS FOR USE WITH LIQUID FLUORINE

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to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT No. NSR-10-005-047

Submitted by

Department of Chemical Engineering
Florida Engineering and Industrial Experiment Station

University of Florida
Gainesville, Florida

FOREWORD

This report has been prepared according to the provisions of Contract NSR-10-005-047, National Aeronautics and Space Administration, with the University of Florida and covers work performed during the period 1 September 1968 through 30 November 1968.

Personnel engaged in this work were Dr. Henry C. Brown, Principal Investigator, and Dr. A. R. Mukherjee.

TABLE OF CONTENTS

I. INTRODUCTION

The objective of this research is the synthesis of of elastomeric polymers that will be resistant to the strong oxidizing effect of fluorine, oxygen difluoride, nitrogen tetroxide and similar agents. In addition, the material should be flexible at cryogenic temperatures.

During the present quarter, attempts have been made to use some trialkyl or triaryl phosphines as initiators for ionic polymerization of hexafluorobutyne-2 and its copolymerization with some suitable comonomers. Being ionic in nature, the rate of homopolymerization was extremely fast even at very low temperature in some cases; in regard to copolymerization, little success has been achieved.

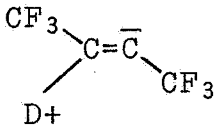
The reaction between hexafluorobutadiene and sulfur tetrafluoride in presence of cesium fluoride as a catalyst was further studied to examine the role of catalyst in the process.

Efforts have been made to characterize some of the reaction products of perfluoroalkyl isocyanate and ammonia.

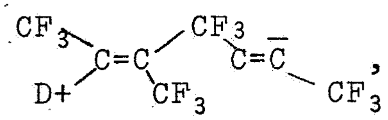
II. DISCUSSION

A. Use of Phosphines as Initiators of Polymerization of Hexafluorobutyne-2

While studying some reactions of hexafluorobutyne-2 with phosphines and amines, Cullen and Dawson noticed that triphenylphosphine causes the butyne to polymerize at -78°. A similar but slower reaction takes place with triethylamine Ref: W. R. Cullen and D. S. Dawson, Canad. J. Chem., 45, 2887 (1967). They also noticed that in a toluene solution of triphenyl phosphine, the polymerization reaction was smooth at temperatures as low as -78°C, and resulted in a white, solid, high melting polymer, but in absence of solvent the reaction can be violent at or above room temperature. The obvious mechanism is the formation of a 1,3-dipolar intermediate such as



in the initiation step and then propagation via addition of butyne-2 molecules as



, etc., D being the nucleophile such as triphenylphosphine.

To date, attempts have been to homo- or copolymerize hexafluorobutyne-2 in the presence of three phosphines:

Triphenyl phosphine, $(C_6H_5)_3P$.	Yellowish solid, m.p. 75-77°C
Tri-n-butyl phosphine $(C_4H_9)_3P$.	High boiling colorless liquid
Trioctyl phosphine $(C_8H_{17})_3P$	High boiling colorless liquid

Phosphines have been used both in the presence and the absence of solvents; solvents used in these experiments were toluene and tetrahydrofuran.

When toluene was used as a solvent, it was recovered almost in full after the experiment (Expt. M-1,3); thus the solvent did not take any part in the reaction.

1. Homopolymerization of Hexafluorobutyne-2

Homopolymerization of hexafluorobutyne-2 in the presence of triphenyl phosphine is almost instantaneous and yield is over 90% if sufficient initiator is present in the system (Expt -M-4). In the presence of toluene, the reaction takes place at a low temperature (-50°C to-60°C)with darkening of the whole mass and though the reaction is almost instantaneous, not much heat is generated in the process. Polymer is formed in flakes, film and powder and it is very difficult to remove all the phosphine even after repeated extraction with ether or chloroform. Toluene (solvent) perhaps becomes incorporated in films or flakes and comes out under vacuum and heat.

In one particular experiment (Expt M-13), an effort has been made to find the limiting concentration of initiator (triphenyl phosphine), using toluene as a solvent. It was noticed that little or no reaction took place when the initiator: monomer molar ratio was 1:120; (approx); on increasing the ratio to 1:30 (approx), about 75% of the monomer could be polymerized. Polymer in the final form was a yellowish white powder or flakes having an in frared spectra the same as that of typical polyhexafluorobutyne-2 (prepared by Co^{60} γ-radiation or under ultraviolet radiation) with an extra strong peak at 3.4μ, probably due to phosphine in some form incorporated in the polymer. The portion extracted with ether or chloroform is a dark solid with a melting range and might be a mixture of products of the phosphine. The polymer is insoluble and infusible and gives a brittle mold at 300° and 4200 lbs./sq. inch pressure. Molding under similar conditions in the presence of 10% sulfur, also gave a brittle mold.

Attempted homopolymerization of hexafluorobutyne-2 in the presence of tri-n-butyl phosphine in toluene as a solvent resulted in a mixture of products (Expt. M-1) and some reaction took place even when the tube was cooled in liquid air (as indicated by darkening of mass). The reaction is almost instantaneous at about -70° to -80°C and the product is a very dark liquid and some yellowish solid (polymer). Almost all the toluene could be pumped out and the dark, viscous liquid product was taken out by repeated extraction with ether. About 90% of the monomer was consumed but yield of polymer was about 45%. Perhaps the viscous dark mass was the addition product of phosphine and perfluorobutyne-2, or very low molecular weight polymer. Its infrared spectra showed a very strong peak at 3.4μ (C-H) and other peaks at 5.75μ (C=C), 6.8μ (CH_3), 7.2μ , 7.7-9μ (C-F, strong), etc.

Attempted homopolymerization of hexafluorobutyne-2 in the presence of either trioctyl phosphine or tributyl antimony and resulted in blackening of the initiator (temperature of reaction -70 to 100°C); but very little monomer was consumed in the process and no polymer was formed, (Expts. M-11, 12).

2. Attempted Copolymerization of Hexafluorobutyne-2.

Co-polymerization of hexafluorobutyne-2 with comonomers such as trifluoronitroso methane (CF_3NO), hexafluoroacetone (CF_3COCF_3), tetrafluoroethylene (C_2F_4), and hexafluorobutadiene (CF_2=CF=CF=CF_2), in the presence of either triphenyl phosphine or tri-n-butyl phosphine was tried without success (Expts. M-2,3,8, 9 and 10).

In presence of CF_3NO as a comonomer and toluene solution of $(C_6H_5)_3P$, no reaction (Expt M-2) took place at -70° to room temperature (overnight). An attempt was made to pump out CF_3NO under vacuum at low temperature, but both the monomers volatilized. However, during the process, some polyhexafluorobutyne-2 was formed (about 20% of the respective monomer), and no other type of polymer product. The remainder of the reaction product was soluble in ether (products from phosphine).

Attempted copolymerization with CF_3COCF_3 using either $(C_6H_5)_3P$ or $(C_4H_9)_3P$ as initiators in presence or absence of toluene (solvent) over a wide range of temperature, resulted only in darkening of the mass, but no polymer was formed (Expt M-3,10). The reaction product was almost completely soluble in ether, chloroform, etc. Thus hexafluoroacetone rather inhibited the polymerization of hexafluorobutyne-2 in this process. In one expt. (M-3), some colorless liquid product volatilized under vacuum (immiscible with and heavier than toluene), amd showed infrared absorption at 5.4µ, 5.7-6.3µ (broad), 7.5-9µ (C-F), 10.2µ, 10.5µ, etc.

In presence of the C_2F_4 as the comonomer and $(C_4H_9)_3P$ as initiator, almost 50% of the butyne-2 monomer could be polymerized as in Expt M-1 (Expt M-8) and some dark viscous material was also formed. In the presence of $CF_2=CF-CF=CF_2$ as comonomer, and $(C_6H_5)_3P$ as initiator, there was no reaction below room temperature. With time some polyhexafluorobutyne-2 (about 25-30% of the monomer was formed; no further reaction took place even when the mixture was heated to 100°C. In the presence of $(C_4H_9)_3P$ as initiator, only some dark colored, viscous material was formed. Perfluorobutadiene was almost fully recovered and thus there was probably no copolymerization (Expt M-9).

Perfluorobutadiene alone did not react with $(C_6H_5)_3P$.

Hexafluoroacetone or perfluorobutyronitrile also did not react with $(C_6H_5)_3P$ either in absence of solvent or in the presence of tetrahydrofuran as solvent. (Expt M-5,6).

B. Reaction between Perfluorobutadiene and Sulfur Tetrafluoride in the Presence of Cesium Fluoride:

As reported earlier, sulfur tetrafluoride and perfluorobutadiene react in presence of cesium fluoride at about 100-150°C to produce some higher boiling liquid product (B.P. 145-147°C (approx), as determined by microcapillary method), but no polymer was formed (Annual Report, 1968). The infrared spectra of the liquid shows only a small hump at 5.9-6.1μ and no other peak below 7.0μ. There are quite a few sharp peaks at higher wave length with strong C-F absorption and S was detected in the sample. It seems the liquid might be 1:1 or 1:2 addition products of hexafluorobutadiene and sulfur tetrafluoride. Some water insoluble grey solid has also been recovered from the CsF after reaction, but it did not melt up to 400°C and did not show any prominent C-F absorption in the infrared spectra. It seems that an excess of dehydrated CsF is needed for this reaction and reaction is not always reproducible.

C. Attempted Characterization of Isocyanate-ammonia Reaction Products

It was reported earlier that reaction between isocyanates such as CF_3NCO, C_2F_5NCO or C_3F_7NCO always result in a number of products; the expected product $R_FNH\ CONH_2$ (R_F being CF_3, C_2F or C_3F_7), a substituted urea, was probably not present in any of the mixtures. However, some ammonium salt, evidently NH_4F, was detected in all the product mixtures, indicating liberation of HF in the process; this was also indicated by etching of the glass vessel during reaction.

The reaction product of CF_3NCO and NH_5 was different from other two mixtures, as regards solubility, fusibility, infrared spectra, etc. It did not show any fusibility up to 300°C except some sublimation and was almost completely soluble only in caustic soda solution, and partially soluble in alcohol and water. It could only be sublimed partially under vacuum at high temperature (∼130°C) resulting in a poor separation. Infrared spectra of the overall mixture or of separate parts (obtained through sublimation or solubility difference) were not sharp enough to characterize any part, but there were absorptions at 3-3.5μ (broad, $\overset{+}{NH_4}$), 4.0μ, 4.5μ, 5.8-6.4μ, 6.8-7.0μ, etc.

The reaction products of C_2F_5NCO and C_3F_7NCO were a mixture consisting of viscous semisolid to white solid and the best way of separating NH_4F from the mixture was extraction with tetrahydrofuran. The tetrahydrofuran insoluble part was not completely NH_4F (as indicated by some C-F absorption and partial melting), though it was almost completely soluble in water. In the case of the C_3F_7NCO and NH_3 product, this part showed infrared absorption at 2.95μ, 3.05μ, 3.1-3.5μ ($\overset{+}{NH_4}$) 4.5μ, 5.0μ, 6.0μ, 6.25μ,6.7μ and some broad C-F absorption.

The tetrahydrofuran soluble part of the C F NCO and NH reaction product was a sticky white solid, soluble in ether also and was evidently a mixture (range of melting point and infrared pattern. It could be completely sublimed under vacuum and showed strong infrared absorption at 2.95µ, 3.0µ, 3.1µ, 5.8µ, 6.0µ, 6.2µ, 7.1µ, (7.5µ, 8.3µ, 8.5µ, 9µ- all due to C-F), 10.5µ, etc.

In the case of the C_3F_7NCO and NH_3 reaction product, the mixture was first extracted with ether; the ether solution (Fraction I) on being dried under vacuum overnight, gave a very viscous liquid which was soluble in water also. Some crystals separated out of this viscous mass on standing. The viscous mass on being heated at about 70-80°C for a long time gave a viscous semisolid having infrared absorption peaks at 2.9-3.5µ (broad), 5.8-6.3µ (broad), 6.6-7.1µ (broad), 7.5µ (C-F), 8-8.7µ, (C-F) and some other strong peaks at higher wave lengths. It could be sublimed, but further purification was not possible by that method. Perhaps the viscous mass had some other things solubilized in it. The crystals separating out were dried;their melting range and infrared pattern indicated it to be a mixture. It had very low solubility in ether and portions after repeated washing with ether showed infrared absorption at 2.9µ, 3.0µ, 5.9µ, 6.1-6.3µ, 6.8µ, etc. The residual mass was then extracted with tetrahydrofuran to give some white crystalline nonhygroscopic mass, soluble in other solvents such as CF_3COOH, acetone, alcohol, ethyl acetate, etc. but insoluble in water and sparingly soluble in ether (Fraction II). It remained unchanged on being treated with either CF_3COOH or NH_3. It was recrystalized from tetrahydrofuran and showed the following characteristics:

Sample A-252

a. % C = 23.26
% H = 1.16
% N = 13.50
% F = 50.56

M.P. 191-193°C

Infrared absorption:
2.9μ, 3.0μ, 3.1μ, 5.8μ, 6.2μ, 6.65μ, 7.2μ, 7.5μ, 7.8μ, 8.1μ, 8.25μ, 8.4μ, 8.6μ, 9.0μ - all due to C-F, 9.6μ, 10.5μ, 11.5μ, 12.5μ, 13.5μ, 14.1μ, etc.

b. Mol. Wt. (by V.P.O.) 200±5 (using tetrahydrofuran as solvent and $C_2F_5\,\overset{O}{\overset{/\!\!/}{C}}{-}NH_2$ as standard).

c. It could be sublimed completely under vacuum at about 90-100°C.

d. Ultraviolet absorption maxima at 213-215 mμ. $\log\varepsilon_{max}$ = 3.43 (approx) in methanol solution.

e. NMR spectra (in THF showed only the presence of CF_3 and CF_2 groupings.

The sample (5 g) was heated with P_2O_5 and some gaseous product (A252G) was collected (1.5 g) having mol. wt. of 142 (approx). It was found to be pure by gas chromatographic analysis (only one peak except air) and infrared spectra did show peaks at 4.45μ ($C\equiv N$), [7.45μ, 8μ, 8.3-8.4μ, 9.5μ- for C-F], a triplet at 12.3-12.5μ and no other peaks. 1 g of the gas was reacted with NH_3(excess) in 10 ml ether and a white, crystalline hygroscopic solid (A276) was obtained having m.p: 49-50°C and infrared peaks at 3.0μ, 3.2μ, 3.5μ (hump), 5.9μ, [7.5μ, 8-9μ broad for C-F], 9.6μ, 9.7μ, 12.5μ,etc.

NMR spectra of the gas (A252G) showed the presence of only CF_3 and CF_2groupings. A276 has been identified as perfluoropropamidine $\left(C_2F_5-\overset{/\!\!/NH}{C}-NH_2\right)$ and the gas (A252G) as $CF_3CF_2C\equiv N$.

III EXPERIMENTAL

A. Experimental Methods

Reactions using trisubstituted phosphines or tributyl antimony as initiators were carried out in pressure tubes made of glass (100 ml capacity) and having metal cap and valve fitted through rubber ' 0 ' ring. The initiators were handled in a nitrogen atmosphere and bath temperature was varied by adding Dry-Ice to acetone.

In the case of the reaction between hexafluorobutadiene SF_4 cesium fluoride used was dried by heating at 200-300°C under vacuum for a few hours. This reaction was also carried out in the pressure tubes mentioned above. SF_4 used might contain a HF as an impurity and efforts were made to remove the HF as much as possible by repeatedly exposing the condensed gas at Dry-Ice-acetone temperature to vacuum, and trapping the portion volatilized.

B. Tabular Summary of Results

Abbreviations: Hexafluorobutyne-2, HFB-2; Hexafluoroacetone, HFA; Perfluorobutadiene, PFBD; Perfluorobutyronitrile, PFBN; Tetrahydrofuran, THF.

TABLE I

Attempted Homo- or Copolymerization of HFB-2 in the Presence of Trisubstituted Phosphines or Tributylantimony as Initiators.

No. of Expt.	Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-1	$(C_4H_9)_3P$ 2 ml	4.79	-	Toluene -10 ml; -70 to -80°C bath - then room temp. overnight.	Residual gas: 10% Poly HFB-2: 45% (yellowish powder)-2.15 gm Ether soluble dark viscous mass. (Instantaneous reaction at low temp.)
M-4	$(C_6H_5)_3P$ 0.58 gms	2.7	-	Toluene -10ml; Tube kept at -70°C and slowly warmed	Residual gas : 5% Poly-HFB-2 (yellowish powder & flakes): 2.53 g. Reaction instantaneous at about -50°C; probably not exothermic. Ether soluble part: 0.5 g.
M-13 a.	$(C_6H_5)_3P$ 0.052 gm.	4	-	Toluene -10 ml; -70 to room temp.	No reaction
b.	0.2 gm	Monomer (a) recovered & used	-	Toluene -5 ml Bath Temp slowly raised from -70°C	Reaction instantaneous at -30 to -40°C, Residual monomer: 23% Poly-HFB-2: 3.08 g, yellowish powder and flakes, gave brittle mold at 300°C & 4200 lbs/sq.in. press. Ether soluble part: 0.2 g (approx).
M-12	$(C_8H_{17})_3P$ 0.4 ml. (approx)	2.7	-	No solvent; Temp. of bath raised from -70°C to 100°C.	Phosphine became dark colored and viscous. Residual gas: 85%; Very little reaction and no polymerization. Product soluble in ether.

Table I (Cont'd)

No. of Expt.	Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-11	$(C_4H_9)_3$ 0.5 ml (Approx)	2.07	-	No solvent; Temp of bath -70° to room temp. overnight.	Liquid turned dark; Monomer recovered: Almost 100%; little or no reaction.
M-5	$(C_6H_5)_3P$	-	PFBN 2.84	No Solvent	No reaction up to room temp.
				THF (10ml)	No reaction up to room tem; Kept overnight - rubber ' 0 ' ring disintegrated.
M-2	$(C_6H_5)_3P$ 1.32 gm	2.50	CF_3NO 1.25	Toluene: 10 ml Temp of bath: -80°C to 30°C overnight	Apparently no reaction
				Monomers slowly pumped out at low temp.	Some reaction takes place; Poly HFB-2 formed: 0.53 g; No reaction with CF_3NO
M-3	$(C_6H_5)_3P$ 1.85 gm	2.82	HFA 2.52	Toluene -10 ml Bath temp : -80°C to 30°C overnight.	No poly-HFB-2 formed. Product: dark mass soluble in ether (2.93 g). Res.gas: Mixture of both the monomers (2.65 g). Some colorless liquid (Immiscible with toluene) also came out under vacuum, and did show C-F absorption.
M-10 a.	$(C_6H_5)_3P$ 0.6 g	2.40	HFA 2.25	No solvent: Temp: 30-100°C (few hours)	Very little poly-HFB-2 formed; about 90% monomer recovered. Residual black mass mostly soluble in ether.
b.	$(C_4H_9)_3P$ 1 ml	Residual gas above expt.		Tube warmed up to 30°C.	Liquid in tube turned dark; no poly-HFB-2 formed. Residual gas: 75%

Table I (Cont'd)

No. of Expt.	Initiator, gms. or ml.	HFB-2 gms.	Other Co-monomer gms.	Conditions of Expt.	Results
M-9 a.	$(C_6H_5)_3P$ 0.5 gm	2.13	PFBD 2.1	Tube warmed up to 100°C. Some reaction at or above room temp., and no further reaction.	Product: Solid product (probably poly-HFB-2) -0.57 gm. and some ether soluble dark material. Residual gas: about 70% of monomer.
b.	$(C_4H_9)_3P$	Residual gas from room temp. 9(a)			Product: Dark colored viscous liquid soluble in ether. Residual gas: mostly PFBD and little HFB-2 (About 45% of Starting monomer, 9 a).
M-8	$(C_4H_9)_3P$	2.08	C_2F_4	Tube kept at -70 to -80°C, and then slowly heated after primary reaction.	Instantaneous reaction and then no further reaction on heating. Product: Slightly colored solid (probably HFB-2): 0.94 g Residual gas: 1.47 gm. (Mol.wt.: 108, mostly C_2F_4). Ether soluble dark mass: 0.8 gm.

TABLE II

Reaction between Perfluorobutadiene and Sulfur Tetrafluoride in the Presence of Cesium Fluoride

Powdered CsF (gms)	PFBD gms.	SF_4 gms	Condition of expt.	Remarks
0.32 (Heated, 200°C, Vac., 3 hrs.)	9.5	6.9	Pressure tube, 30-35 atm., room temp., 90 hrs.	No reaction; monomers recovered in full. Probably HF in SF_4 etched glass.
2.5 (Heated 200-260°C Vac. overnight)	Recovered gas mixture from above expt.		Tube heated up to 150°C and kept there for 65 hrs.	Some high boiling liquid product was formed. 75% of reactants recovered.
10 (new stock, heated, 250-300°C Vac. Overnight	Recovered gas mixture from above expt.		Tube kept at 100-150°C for few hrs. and at room temp. for a few days.	Very little reaction; no liquid product visible.
5 (old stock, heated 300-350°C, vac. 2 hrs.	Recovered gas mixture from above expt.		Tube kept at about 150°C, overnight	Some liquid product formed. Residual CsF on disolving in water gave some water insoluble grey solid. Residual gas: only about 15% of the starting material. It seems that a portion of the reactants was lost during one of the operations. (Product: Liquid: 2.5-3 g; solid: 2 g (approx.).