T-17986

Quarterly Letter Report No. 2

March 15, 1967

to

National Aeronautics and Space Administration

Contract NSR-10-005-047

Synthesis of Elastomers for Use with Liquid Fluorine

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Submitted by

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N67-85098
(ACCESSION NUMBER)
9
(PAGES)
CR-86523
(NASA CR OR TMX OR AD NUMBER)
(THRU)
(CODE)
(CATEGORY)
FACILITY FORM 602

TABLE OF CONTENTS

		Page No.
I	INTRODUCTION	2
II	DISCUSSION	2
	A. Preparation of Hexafluorobutyne-2	2
	B. Homopolymerization of Hexafluorobutyne-2	3
	C. Attempted Copolymerization of Hexafluorobutyne-2 and Trifluoronitrosomethane	4
	D. Attempted Terpolymerization of Hexafluorobutyne-2, Trifluoronitrosomethane and Tetrafluoroethylene	6
III	CONCLUSIONS	7
IV	FUTURE WORK	7
V	MAN-HOURS; EXPENDITURES AND COMMITMENTS	8

I. INTRODUCTION

The objective of this research is the synthesis of elastomeric polymers that will be resistant to the action of elemental fluorine.

During the present quarter much of the project effort has been devoted to seeking conditions for the copolymerization of hexafluorobutyne -2 and trifluoronitrosomethane.

Anomalous results were obtained in the initial copolymerization attempts and in subsequent homopolymerizations of hexafluorobutyne -2. It is apparent that impurities in the monomer have a distinct effect on the results obtained.

Copolymerization of hexafluorobutyne and trifluoronitrosomethane has been attempted under a variety of conditions and with samples of monomer prepared or purified by various procedures. Although a viscous liquid was obtained in one experiment (probably with impure hexafluorobutyne), the remaining experiments have given no copolymer.

Terpolymerizations with hexafluorobutyne -2, trifluoronitrosomethane and tetrafluoroethylene have been attempted.

II. DISCUSSION

A. Preparation of Hexafluorobutyne -2

It has been found that the exact conditions, and particularly the absence of moisture, influence markedly the amount of other materials produced in the preparation of hexafluorobutyne -2 by the dehalogenation of 2,2,3,3, tetrachlorohexafluorobutane. This reaction is quite slow, requiring several

days at the reflux temperature of the solvent used. Product from the dehalogenation is conducted through a water-cooled condenser, through an ice-cooled trap and collected in a dry-ice-cooled trap. Under careful control and with precautions to exclude moisture from all reactants, very little liquid is collected in the ice-cooled trap. With these conditions, about 62% of the theoretical yield of hexafluorobutyne -2 containing 5 to 7% of higher boiling impurities was produced. Fractionation in a glass helices-packed column reduced impurities to less than 1%. The amount of impurities may go as high as 15% with less careful preparation of reactants, and the increase is accompanied by a decrease in yield of hexafluorobutyne -2 to 30-35%.

Gas chromatographic analysis of the hexafluorobutyne -2 showed four impurity peaks. Possible compounds which may be present are <u>cis</u> and <u>trans</u> $CF_3CH{=}CClCF_3$ and <u>cis</u> and <u>trans</u> $CF_3CCl{=}CClCF_3$; the possibility of the further reduced isomers, $CF_3CH{=}CHCF_3$ has not been eliminated.

It may be necessary to positively identify these impurities since there is an apparent effect from their presence on the polymerization reactions of hexafluorobutyne under irradiation.

B. <u>Homopolymerization of Hexafluorobutyne -2</u>

The previous report described the homopolymerization of hexfluorobutyne -2 by ultraviolet irradiation and by Co^{60} γ radiation. It is now apparent that impurities present in the butyne sample were responsible for this behavior. After further purification of hexafluorobutyne -2, ultraviolet radiation for 72 hours produced only about 4% polymer; Co^{60} γ radiation at a dose rate of 2000 r/min. gave a yield of only 14% polymer after 85 hours. However, a sample of hexafluorobutyne -2 which had been exposed previously to ultraviolet radiation and to the lower dose rate Co^{60} γ radiation, could be

almost completely polymerized by exposure to a different Co^{60} source with a higher dose rate(25,000 r/min.-localized, 10,000 r/min. average) for 45 hours. The residual gas from this polymerization shows no infrared absorption at 5.85μ (probably characteristic of C=C unsaturation) though it may still be present in very small quantities.

The polymer obtained by the γ-ray polymerization appears by both chemical and physical tests to be the same as reported in the literature (Brown and Gewanter, J. Org. Chem. 25 2071 (1960)).

Attempts were made to homopolymerize hexafluorobutyne -2 by more conventional techniques, since information is not available in the literature concerning their possible effectiveness. The use of benzoyl peroxide in toluene at 60-70° at approximately atmospheric pressure and of potassium persulfate in aqueous media under three atmospheres pressure failed to produce polymer.

C. Attempted Copolymerization of Hexafluorobutyne -2 and Trifluoronitrosomethane.

Several attempts have been made to copolymerize hexafluorobutyne with trifluoronitrosomethane. The results described below are typical and indicate the behavior that may be expected from this system.

The initial copolymerization reaction was carried out with hexafluorobutyne -2 prepared as described in A above and not fractionally distilled. Hexafluorobutyne -2 and trifluoronitrosomethane in a 1.0 to 1.0 molar ratio were sealed in a glass ampule at 10 atmospheres pressure and exposed to Co^{60} γ radiation (2000 r/min.) for 75 hours. The product from this reaction was a viscous yellow liquid, soluble in tetrahydrofuran. Yield was approximately 80%.

The infrared spectra of the residual gas from the reaction tube showed the absence of CF_3NO; absorption was found at 3.35 and 9.65μ. The infrared spectra of the hexafluorobutyne sample used in this reaction was taken and showed definite absorption at 5.8 and 3.35μ ; the residual gas showed no absorption at 5.8 μ .

The infrared absorption spectra of the viscous product from this initial reaction showed absorption at 3.0-3.4 μ (possible C-H stretch), 5.55μ (possible C=C stretch), much C-F absorption between 7 and 9μ and small peaks at 10.0 and 10.25μ .

Attempts were then made to copolymerize a sample of hexafluorobutyne-2 that was purchased, and presumably had been purified, with trifluoronitrosomethane by sealing the gases (mole ratio, butyne /CF_3NO, 2.0-1.0) in a glass tube and exposing the mixture to γ-radiation (2000 r/min.) for 75 hours. No polymer was formed; examination of the gases from the reaction tube by volume determination, molecular weight and infrared absorption spectra indicated that no reaction had taken place. This gas mixture was then exposed to ultraviolet radiation in a Vycor flask for 50 hours. Under these photolytic conditions the blue color of the trifluoronitrosomethane disappeared, the mixture became deep brown, the pressure increased,average molecular weight decreased, and a portion of the gas mixture, on examination was found to be non-condensable at liquid nitrogen temperature. The infrared spectra of the gas mixture indicated that only the CF_3NO had undergone reaction, probably to dimer and other products as has been reported.

A sample of purified (purchased) hexafluorobutyne (1.5 atm.) and trifluoronitrosomethane (1.0 atm.) was sealed in a glass tube and maintained

at - 78° for several days, then at 0° for an additional day. No change in color or evidence of polymerization was visible. This gas mixture was then slowly heated to 150° and kept at this temperature overnight, again without producing a visible change. The temperature was raised slowly to 300°C; white vapors appeared, then the inside of the tube became coated with a black deposit. It seems probable that, at the high temperature, hexafluorobutyne -2 trimerized to hexatrifluoromethyle benzene and the trifluoronitrosomethane decomposed. No indication of either starting material was found in the infrared spectra of the residual gas.

D. Attempted Terpolymerization of Hexafluorobutyne -2, trifluoronitrosomethane and Tetrafluoroethylene.

Since trifluoronitrosomethane and tetrafluoroethylene are readily polymerized, it was considered possible that tetrafluoroethylene, or the initial reaction product of this olefin with trifluoronitrosomethane, could function as an initiator for the copolymerization of hexafluorobutyne -2 with trifluoronitrosomethane or be incorporated in a terpolymer of the three possible monomers.

A mixture of trifluoronitrosomethane (3 atm.), hexafluorobutyne -2 (2 atm.) and tetrafluoroethylene (1 atm.) after each was passed through a silica gel column, was sealed in a glass tube and exposed to Co^{60} γ radiation (2000 r/min.) for 90 hours. No color change or polymer formation was evident.

Terpolymerization in suspension in aqueous media was attempted by placing CF_3NO (3.4 atm.), $CF_3C{\equiv}CCF_3$(2.7 atm.) and $CF_2{=}CF_2$(1.0 atm., passed through silica get to remove traces of inhibitor) in a glass tube containing 40 ml. of aqueous suspension of 1.15 g. of magnesium carbonate and 21.2 g. of lithium bromide. The sealed tube was maintained at -30 to -15 °C for 24 hours with periodic shaking. The liquid slurry was then removed from the tube, after

venting the residual gas, and treated with concentrated hydrochloric acid. A very small amount of translucent, rubber-like gel was obtained.

Another attempt at terpolymerization was made by sealing hexafluorobutyne -2,trifluoronitrosomethane and tetrafluoroethylene in a glass tube and holding the mixture at -25 to -5°C for 48 hours. A viscous transparent liquid product was formed. The total yield of polymer,the infrared spectra of the product and of the residual gas, the molecular weight and VPC analysis of the residual gas all indicate that little or no hexafluorobutyne -2 was incorporated in the polymer.

III CONCLUSIONS

It has been shown by many examples in the literature that CF_3NO, itself a stable biradical, can generate radical centers in many polyfluoro vinyl monomers and initiate polymerization, even at very low temperatures. The failure of trifluoronitrosomethane to do this with hexafluorobutyne -2 at any temperature may be attributed to the inertness of the triple bond in this compound to a biradical attack. Formation of polymer with the impure hexafluorobutyne -2 indicates that radicals from another source may aid in formation of radical centers in the butyne, which can then copolymerize with the trifluoronitrosomethane. The failure of hexafluorobutyne -2 to polymerize in the presence of CF_3NO or CF_3NO plus $CF_2{=}CF_2$, even under the influence of γ-radiation, can possibly be explained by assuming that CF_3NO acts as a radical scavenger rather than initiator or that the molecular complex or oxazetidine formed is unstable under these conditions.

IV FUTURE WORK

During the next quarter it is expected that the impurities formed in the preparation of hexafluorobutyne -2 will be isolated and identified

and their initiating properties investigated. Arrangements have been made for irradiation of hexafluorobutyne -2 and trifluoronitrosomethane at low temperatures and these experiements will be carried out with various initiators if so indicated. Exploratory work on the possible copolymerization of both $CF_2=CF_2$ and $CF_3C\equiv C\ CF_3$ with perfluoroalkyl nitriles and of hexafluoropropylene oxide with hexafluorobutyne and perfluoroalkyl nitriles will be started.

V MAN-HOURS; EXPENDITURES AND COMMITMENTS

Total effort during this quarter has been at the rate of 50 man-hours per week. Dr. Mukherjee has been working full time (40 hours) and Dr. Brown one-quarter time (10 hours).

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