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WADC TECHNICAL REPORT 55-221

PART IV

ASTIA DOCUMENT No. 151009

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INVESTIGATION OF CONDENSATION TYPE ELASTOMERS

GEORGE C. SCHWEIKER
BURTON S. MARKS
CARL J. VERBANIC
BLAINE L. LUCAS
EDWARD V. GOUINLOCK

HOOKER ELECTROCHEMICAL COMPANY

FEBRUARY 1958

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FEBRUARY 1958

MATERIALS LABORATORY
CONTRACT No. AF 33(616)-2421
PROJECT No. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report was prepared by Hooker Electrochemical Company under USAF Contract No. AF 33(616)-2421. This contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers." The work was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Capt. C. H. Schmid as project engineer.

This report covers work conducted from 1 December 1956 to 1 November 1957.

The personnel of the Hooker Electrochemical Company who worked on the project were Dr. George C. Schweiker, Research Supervisor; Dr. Burton S. Marks, Dr. Carl J. Verbanic, Mr. Blaine L. Lucas, and Dr. Edward V. Gouinlock, Research Investigators; Mr. Rudolph N. Deleo, Mr. Mansfield B. Jordon, Mr. William E. Weber, and Mr. John J. Zedick, Technicians; with Mr. Paul Robitschek, Manager of Plastics Research acting as director.

ABSTRACT

The ultimate goal of the exploratory investigations described is the development of a rubber for special Air Force applications. Major requirements for such a material include good mechanical properties, high thermal stability (originally 350°F or higher), satisfactory performance at -65°F or lower, and resistance to aromatic fuels, synthetic ester-base oils, and hydraulic fluids.

To this end, fluorine-containing condensation polymers are being investigated in an effort to discover and develop suitable new elastomers.

This report describes the preparation, compounding, cross-linking, and properties of certain fluorine-containing polyester elastomers which appear to meet the goals outlined above. The report also describes the research performed on the synthesis of fluorine-containing difunctional starting materials, polyesters and nitrogen-substituted polyamides therefrom, and their characterization.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



R. T. Schwartz
Chief, Organic Materials Branch
Materials Laboratory

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I. INTRODUCTION

In June of 1954, research on new types of condensation elastomers containing fluorine was started at Hooker Electrochemical Company under USAF Contract No. AF 33(616)-2421 with Materials Laboratory, Wright Air Development Center. Three summary reports have been issued¹ which describe the research to December 1956 in detail. The present report covers the research performed from December 1956 to November 1957.

The ultimate goal of the work performed is the development of a rubber possessing a balance of properties superior to that presently found in available elastomers. Major requirements for such a material include good mechanical properties, thermal stability (originally 350°F or higher), satisfactory performance at -65°F or lower, and resistance to aromatic fuels, synthetic ester-base oils, hydraulic fluids, ozone, and weathering oxidation effects.

Presently available elastomers do not offer the combination of these desired properties. In the rubbers so far developed, one or more attributes have been attained only at the expense of some other important quality. A more detailed discussion, with references, of these points and of the reasons why certain fluorine-containing condensation elastomers were expected to exhibit a superior balance of properties has been given.¹ It has also been shown¹ that high molecular weight linear polyesters, which exhibit rubber-like properties, can be prepared from fluorine-containing diols and dicarboxylic acid chlorides, and that the polyesters can be cross-linked to give desirable elastomers.

Work during the current contract year, described in this report, has been concerned with the synthesis of new, and the preparation of known fluorine-containing intermediates considered desirable for polymerization; the synthesis of polyesters and N-substituted polyamides containing fluorine, and polymerization techniques; preliminary screening of properties; compounding and cross-linking of selected polyesters; and testing and evaluation of promising elastomers. At the same time, of course, more data have been collected for the fundamental purpose of further relating and correlating physical properties of the polymers with chemical constitution.

Research on the synthesis of certain novel or unusual fluorine-containing intermediates considered desirable for polymerization in this project was performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company. Details of the syntheses performed at Purdue during the contract year comprise Appendix I of this report.

1. Manuscript released by Authors, 15 January 1958, for publication as a WADC Technical Report.

II. SUMMARY AND CONCLUSIONS

The following fluorine-containing difunctional compounds have been prepared as intermediates or starting materials for use in polycondensation reactions.

1. Perfluoroglutaric Acid
2. Diethyl Perfluoroglutarate
3. 2,2,3,3,4,4-Hexafluoropentane-1,5-diol
4. Perfluoroadipic Acid
5. Diethyl Perfluoroadipate
6. 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol
7. Bis(N-methyl)perfluoroglutaramide
8. Bis(N-ethyl)perfluoroglutaramide
9. Bis(N-isopropyl)perfluoroglutaramide
10. Bis(N-n-butyl)perfluoroglutaramide
11. Bis(N-tert-butyl)perfluoroglutaramide
12. Bis(N-1,1-dihydroperfluorobutyl)perfluoroglutaramide
13. Bis(N-methyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
14. Bis(N-ethyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
15. Bis(N-isopropyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
16. Bis(N-n-butyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
17. Bis(N-tert-butyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
18. Bis(N-1,1-dihydroperfluorobutyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine

In addition to the above, research on the synthesis of other fluorine-containing difunctional compounds has been performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company, and the results of that work comprise Appendix I of this report.

Work on the preparation of new fluorine-containing polyesters and copolyesters utilizing 2,2,3,3,4,4-hexafluoropentane-1,5-diol and 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol has progressed, and the properties of the polymers are described in detail in the body of this report. It was found that copolyesters prepared from the reaction of adipyl and isophthalyl chlorides with hexafluoropentane-1,5-diol markedly reduced the tendency of the homopolyesters to crystallize at low temperatures.

Process conditions and purity of starting materials for the preparation of the fluorinated polyesters have been investigated and standardized.

Larger amounts of hexafluoropentylene adipate and a copolyester thereof containing 25 mol % isophthalate were prepared and submitted to Materials Laboratory for further evaluation, and several samples of special polymers were submitted to Materials Laboratory.

Other copolyesters containing unsaturated carbon-carbon linkages were prepared which permit the use of new compounding and vulcanization recipes to be developed to obtain optimum physical properties.

More precise values for rates of crystallization, melting and brittle temperatures have been determined dilatometrically for the fluorinated polyesters and are very close to those approximate values previously reported.¹ Intrinsic viscosity was related to number average molecular weight by the equation: $[\eta] = 3.20 \times 10^{-5} M_n$. Polyesters with number average molecular weights from 5,000 to 50,000 have been obtained. It was found that normal milling of the polyesters for 30-90 minutes reduced molecular weights to about 16,000 regardless of initial molecular weight.

In the evaluation and development of the fluoropolyester rubbers, many properties of the vulcanized product were improved by compounding changes. For example, gums compounded with a mixture of 50 parts SRF carbon black and 20 parts calcium carbonate when cross-linked with 19 parts dicumyl peroxide-carbonate mixture are resistant to air at 400°F and to diester oil at 350°F. These same vulcanizates are resistant to MIL-O-5606 hydraulic fluid at 316°F, and to aromatic fuels at 250°F. Typical original and aged properties of the rubbers, together with a recommended compounding recipe and cure, are given in the body of this report. Various vulcanizates were submitted to Materials Laboratory for evaluation.

Work in the fluorinated polyamide series, more recently initiated, has been concerned with the synthesis of the monomers listed above, and with techniques of polymerization to high molecular weights. Using bis-(N-alkyl)1,6-hexanediamine, reaction with perfluoroglutarate ester is very rapid and leads to moderate to high molecular weight fluorine-containing polyamides. Their isomers, bis(N-alkyl)2,2,3,3,4,4-hexafluoropentylene adipamides, are much more difficult to synthesize to high molecular weights, due to the reduced basicity of the amine group, caused by the strong inductive effect of the neighboring difluoromethylene moiety. Thus, it is necessary in the latter case to employ dicarboxylic acid chlorides for reaction with the fluorine-containing diamines.

A comparison of the two different types of fluorinated N-substituted polyamides, where the nitrogen substituent is methyl, shows the polymers to be very similar in most respects. They are unusually resistant to common solvents but have relatively high brittle temperatures, around 15-30°C. Where fluorine is contained on the carbon atom alpha to the carbonyl group, the polyamide is water soluble and is apparently hydrolyzed, as reported previously¹ for analogous polyesters. However, preliminary results described in the body of this report indicate that when the nitrogen substituent is ethyl, brittle temperatures is decreased; and when the nitrogen substituent is n-butyl, solubility (and hydrolysis) in water is not marked.

III. DISCUSSION

A. INTERMEDIATES

In keeping with the aims of the contract, and guided by past experimental work,¹ emphasis has been centered on preparing and using selected fluorine-containing difunctional compounds, together with more conventional difunctional compounds, as starting materials for condensation polymerizations. The more readily available compounds of this type have been made in the laboratories of Hooker Electrochemical Company, and some hydrocarbon materials have been bought, with particular care placed in their purity.

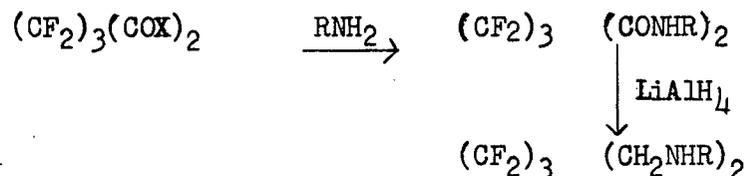
The following fluorine-containing difunctional compounds have been prepared in the Hooker laboratories during the period of time covered by this report.

1. Perfluoroglutaric Acid
2. Diethyl Perfluoroglutarate
3. 2,2,3,3,4,4-Hexafluoropentane-1,5-diol
4. Perfluoroadipic Acid
5. Diethyl Perfluoroadipate
6. 2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diol
7. Bis(N-methyl)perfluoroglutaramide
8. Bis(N-ethyl)perfluoroglutaramide
9. Bis(N-isopropyl)perfluoroglutaramide
10. Bis(N-n-butyl)perfluoroglutaramide
11. Bis(N-tert-butyl)perfluoroglutaramide
12. Bis(N-1,1-dihydroperfluorobutyl)perfluoroglutaramide
13. Bis(N-methyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
14. Bis(N-ethyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
15. Bis(N-isopropyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
16. Bis(N-n-butyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
17. Bis(N-tert-butyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine
18. Bis(N-1,1-dihydroperfluorobutyl)2,2,3,3,4,4-hexafluoropentane-1,5-diamine

In addition to these, research on the synthesis of other fluorine-containing difunctional compounds has been performed at Purdue Research Foundation under subcontract to Hooker Electrochemical Company, and the results of that work comprise Appendix I of this report.

Perfluoroglutaric acid was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene according to the method described by McBee, Wiseman and Bachmann.² Perfluoroadipic acid² was made similarly from 1,2-dichlorooctafluorocyclohexene. Esterification of the acids followed by reduction of the esters² with lithium aluminum hydride as described by McBee, Marzluff and Pierce³ gave 2,2,3,3,4,4-hexafluoropentane-1,5-diol and 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diol, respectively.

A series of N-substituted perfluoroglutaramides and N-substituted fluorine-containing diamines have been synthesized by the following general reaction scheme.



where: X = alkoxy or chlorine
 R = CH₃, C₂H₅, C₃H₇, C₄H₉, CH₂C₃F₇

In this reaction series, perfluoroglutarate esters have been used, giving good yields of the diamides, except when the bulky tert-butylamine was the co-reactant. In this special case, and where 1,1-dihydroperfluorobutylamine was used, perfluoroglutaryl chloride gave good yields of the diamides. Reduction of fluorine-containing amides with lithium aluminum hydride has been reported to lead to explosions.⁴ In the reactions described in this work using lithium aluminum hydride and fluorine-containing diamide, every safety precaution for possible explosive conditions was utilized and is recommended. However, no explosions or violent reactions were encountered during this work.

A series of bis (N-alkyl)adipamides, and their reduction products, bis(N-alkyl)hexamethylenediamines were also prepared by the general reaction scheme outlined above, where the alkyl groups are methyl, ethyl, isopropyl, n-butyl, and tert-butyl. In the case of bis(N-ethyl)hexamethylenediamine, an alternate synthesis was also performed, i.e., acetylation of hexamethylenediamine with acetic anhydride, followed by reduction of the product in the usual way with lithium aluminum hydride.

A variety of other hydrocarbon difunctional intermediates were prepared and/or purified including adipyl, fumaryl, itaconyl, isophthalyl, and terephthalyl chlorides. The preparation of other unsaturated dicarboxylic acid chlorides was also investigated, i.e., 3-hexenedicarboxylic acid chloride and the α, α' -dimethylene alkanedicarboxylic acids described by Marvel.⁵

B. LINEAR POLYESTERS CONTAINING FLUORINE

The investigations on the preparation and properties of linear polyesters containing fluorine, during this report period, have been directed toward the synthesis of new materials as well as to the solution of a number of problems. Of primary importance has been the development and standardization of the reaction conditions for polymerization of the fluorinated diol and dicarboxylic acid chlorides to give high molecular weight millable elastomer gums. Another problem, which is inherent in the nature of the polymer, was the elimination of the tendency of the vulcanized elastomer to cold harden, a phenomenon related to the tendency of the polymer to crystallize at low temperatures. This was overcome by the development of a copolyester of the fluorinated diol with adipic and isophthalic acids. Of great importance to the development of fluorinated elastomers is the ability to control the cross linking of the vulcanizates and to be able to accomplish cross linking by a number of vulcanization procedures. Both these objectives are more readily achieved if unsaturated segments are present in the elastomer gum. Polymerization conditions have been developed which permit the preparation of millable elastomer gums containing up to 10 mole % fumarate segments.

The polymerization of a number of new fluorine-containing dicarboxylic acid chlorides and the fluorinated diols was accomplished. The physical properties of most of these polymers verified previous conclusions concerning the effects of fluorine on polyesters.

A number of the physical properties of the fluorinated elastomers were determined more exactly. Methods have been established for determination of molecular weights by solution viscosity, and dilatometric measurements of first and second order transition temperatures as well as rates of crystallization, have been performed.

1. Polymerization Process Conditions

The preparation of high molecular weight elastomer gums (e.g. $\bar{M}_n > 15,000$) places severe requirements upon the polymerization conditions as well as the purities of the starting materials, solvents, and the environment of the reaction. Attainment of elastomer gums of number average molecular weights of 15,000 or greater requires degrees of polymerization of 100, and corresponding reaction of 99% or more of the functional groups. Combined sources of errors from impurities, weighings, transfers, entrainment, etc., therefore may not exceed 1%. Normal precautions eliminated the mechanical sources of error as much as possible. The purity of the fluorinated diol is good after two recrystallizations from benzene or mixed solvent, and complete removal of solvents. A suitable infrared standard has been established for adipyl chloride and a correlation of concentration of impurity to molecular weight of polymer produced has been obtained. Using adipyl chloride of high purity, polyesters of number average molecular weights greater than 15,000 are consistently obtained.

With regard to the polymerization reaction, it was found that the amount of solvent used was not critical since no significant differences in molecular weights were caused by changing this variable. Dichlorobenzene was preferred over trichlorobenzene because of its comparative ease of removal from the polymer under high vacuum.

The polymerization reaction consists of mixing the reagents at room temperature, heating at 35-40°C for 3-4 hours, then at 120-140°C for another 3-4 hours and then at 200-220°C for a like period of time, followed by removal of solvent at this temperature under high vacuum. In the case of adipate-isophthalate copolyesters the heating period at 200-220° is extended to 10-12 hours. This variation is needed because of the difference in reactivities between adipyl and isophthaloyl chlorides. The polymerizations proceeded satisfactorily on a fairly large scale, and quantities of both hexafluoropentylene adipate and hexafluoropentylene adipate-isophthalate were prepared and sent to Materials Laboratory.

2. Copolyesters

Although vulcanized hexafluoropentylene adipate has a brittle point of -98°F and a TR_{10} value of -62°F, its low temperature usefulness for extended periods is limited by its tendency to cold harden. This detrimental property is dependent upon the ability of the polymer to crystallize. Elimination of the tendency was sought by the preparation of copolyesters with the fluorinated diol, adipyl chloride and a second dibasic acid chloride as well as by the method of using a mixture of hexafluoropentane diol and octafluorohexane diol. Table I summarizes the data on the properties of the copolyesters, as well as data on new homopolyesters. The first column lists the reactants and the second column lists the melt viscosities $[\eta]$ of the polymers produced. The various functions of the melt viscosity; i.e., number average molecular weight (M_n), and degree of polymerization were calculated from Flory's equations used by him in the hydrocarbon polyester series using constants for hexafluoropentylene adipate determined previously during the course of this work.¹ These functions are subject to the limitations already discussed. The table also contains the approximate brittle and melting temperatures of the polyesters and some information on their solubilities in various liquids.

Some of the new copolyesters listed in Table I, exhibited significantly different properties with regard to crystallization tendencies. Table II lists the results of a preliminary survey in which samples of the polymers were placed in a cold room at -10°C and the times in days required for the samples to become completely opaque. This survey revealed that copolyesters incorporating 15 mole % isophthalate, or 25 mole % octafluorohexanediol crystallized very much slower than the other copolyesters and that a copolyester containing 25 mole % isophthalate did not even start to crystallize after 19 days at -10°C. A copolyester containing 20 mole % isophthalate remained clear for thirty days before some opaqueness was evident. The polymer, however, was still flexible.

Figure I represents the relative rates of crystallization at -10°C of polymers containing variable molar percentages of isophthalate segments and Figure 2 represents the number of days for 20% crystallization to occur in various isophthalate copolyesters. The elimination of the crystallization tendency in polymers containing isophthalate segments does not hold for polymers of 35 molar percentages or greater isophthalate content. These polymers crystallize in a few days at room temperature.

The results from these preliminary surveys indicates that polymers containing 20-25 molar percentages of isophthalate segments were promising as elastomers for low temperature uses for extended periods of time. Larger quantities of these hexafluoropentylene-adipate-isophthalate polymers were prepared for evaluation and substantial quantities were prepared and sent to Materials Laboratory, WADC. The results of elastomer evaluation of these polymers are given under the section on Cross-linking, Reinforcing and Properties of Vulcanizates.

Of great importance to the development of fluorinated elastomers is the ability to control the cross-linking of the vulcanizates and to be able to accomplish cross-linking by a number of vulcanization procedures. Both these objectives are more readily achieved if unsaturated segments are present in the elastomer gum. Previous attempts to prepare polyesters containing the fumarate segment gave low molecular weight polymer. It was suspected that the relatively volatile fumaryl chloride (b.p. 161°C) was being lost by entrainment thereby disturbing the stoichiometry of the reaction. These low molecular weight polymers, however, would have hydroxyl end groups and the chains could be extended by the addition of additional dibasic acid chloride. This approach was attempted and was found to give, with the addition of isophthaloyl chloride, higher molecular weight millable elastomer gums. Polyesters were thereby prepared containing up to 10 mole percent fumarate segments. These gums were compounded and molded and the molded vulcanizates tested and aged. Properties of vulcanizates are given in Section D of this report.

Attempts were also made to prepare polymers containing unsaturated segments using itaconyl chloride. However, in all cases, the polyesters gelled prematurely during their preparation even in cases in which the temperature of polymerization was held under 140°C . This is the first experience of premature cross-linking of any of the linear polyesters; it is evidence also for the high reactivity of the appended methylene double bond contained in itaconates. By contrast, the fumarate segment is remarkably resistant to cross-linking by thermal means alone since on no occasion did any polymer gell although temperatures of $200-220^{\circ}\text{C}$ were maintained for 10-12 hours.

Some elastomer applications, such as fuel tank sealants, do not require high molecular weight polymers. With this application in mind a number of samples of low molecular weight, hydroxy terminated homo and copolyester samples were prepared and submitted to Materials Laboratory. No new techniques were employed in the preparation of the low molecular weight polymers. Excess hydroxyl groups were obtained by adding 1 to 1.5 molar percent excess hexafluoropentanediol. The presence of hydroxyl groups was confirmed by examination of the infrared spectra of the polymers and by further reaction with added isophthaloyl chloride.

In addition, a number of low molecular weight polyesters terminating in hydroxy end groups and containing some unsaturation were prepared and submitted to Materials Laboratory.

3. New Polyesters

An important part of the research investigations has been the preparation of polyesters from the fluorinated diols and new dibasic acid chlorides, as these became available. A number of these monomers were prepared in these laboratories and others were prepared at Purdue University under subcontract to Hooker Electrochemical Company.

Homo and copolyesters were prepared with the fluorinated diols and diglycolyl chloride (3-oxaglutaryl chloride). The homopolyesters were of moderate molecular weight (9500) and parallel the results obtained with glutaryl chloride. Dicarboxylic acid chlorides which have a chain length of 5 atoms give lower degrees of polymerization (50-60) than higher chain length acid chlorides under the same conditions of polymerization. In addition, the 5 atom chain length monomers react noticeably slower than does adipyl chloride, which may be a factor in accounting for the observed lower degrees of polymerizations.

Polymers were prepared using perfluoroglutaryl chloride and the fluorine-containing diols (HFPD and OFHD). In both cases the degree of polymerization was low (31 and 31.1). This result was not unexpected since as stated above only moderate or lower molecular weight polyesters have been prepared from dibasic acids containing 5 chain atoms or less. The relatively low boiling point of perfluoroglutaryl chloride (b.p. 110°C) might explain the still somewhat lower degree of polymerization obtained in these cases.

It is most enlightening to compare the approximate brittle temperature in the glutarate, perfluoroglutarate, and 3-perfluoroalkyl glutarates as listed in Table I. In the cases of glutarates vs. the corresponding perfluoroglutarates, no increases in approximate brittle temperatures are evidenced through the incorporation of the increased fluorine content. For the 3-perfluoroalkyl glutarates, however, the brittle temperatures of the polymers are increased with increasing length of the perfluoroalkyl side chain. It is clearly shown in this

series, how position of the fluorine in the linear polymer rather than total fluorine content, affects brittle temperatures. Rough solubility characteristics, on the other hand, are dependent on total fluorine content in any one series of polymers, as shown by the solubilities of the polymers listed in Table I.

Polyesters were also prepared from the fluorinated diols and 3,5-bis-(perfluoropropyl)-4-thiapimelyl chloride (synthesized at Purdue). This monomer was extremely slow in reacting and required four days of heating at elevated temperatures to obtain a polyester of moderate weight. The polymers had high brittle points (0° to -4°C) and did not crystallize because of the appended fluoroalkyl groups - as noted previously for polyesters containing appended fluoroalkyl groups in the glutarate series. In accord with their increased fluorine content, the polyesters were not soluble in most common solvents.

A sample of the acid chloride of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanoic dicarboxylic acid was also received from Purdue Research Foundation, and was polymerized with HFPD and OFHD. The reactions appeared to be slower than with adipyl chloride and only low molecular weight polyesters were obtained. The degree of polymerization for both polymers was between 21 and 25. Brittle temperatures were approximately -37°C and -40°C , respectively.

4. Physical Properties

Of primary importance in the development of these fluorinated elastomers are their solubility characteristics in various organic solvents and fluids. In general, solubility of the polyesters in a selected series of common liquids is decreased as total fluorine content of the polymers is increased.¹ In the copolyesters no unusual solubility characteristics were noticed other than what might be expected from the variations in the percentage of fluorine in the copolyester. Replacement of adipyl chloride by acid chlorides of about the same empirical formula gave copolyesters which had the same solubility characteristics as hexafluoropentylene adipate. However, when high mole percentages of acid chlorides of greater chain length than adipic were employed (i.e. azelate), solubility of the copolyesters in toluene increased. The polyesters prepared from diglycolyl chloride has about the same solubility characteristics as hexafluoropentylene glutarate.

The brittle points of the copolyesters and of the polyesters prepared from the new monomers in general confirm the conclusions previously reached concerning the effect of fluorine on brittle points.¹ The two perfluoropropyl groups in 3,5-bis(perfluoropropyl)-4-thiapimelate cause the brittle points of the polymers to be raised up to about 0°C . Somewhat surprising was the fact that hexafluoropentylene 3-oxaglutarate had about the same brittle point as the

corresponding glutarate, showing that the incorporation of an ether oxygen in the chain did not give improved low temperature characteristics to the polymer. Lack of increased flexibility at low temperatures was also shown for octafluorohexylene-3-oxaglutarate, which crystallized rapidly and had a melting point (77-80°C) some 40° above the corresponding glutarate.

When molecular weights above 25,000 are obtained, it becomes difficult to measure melt viscosities of the polyesters. For this reason, a study was made to determine the intrinsic viscosity-molecular weight relationship for hexafluoropentylene adipate. Intrinsic viscosities were determined for various molecular weight samples of the polyester, dissolved in chloroform and measured at 30°C, of known melt viscosity molecular weight. The samples covered the number average molecular weight range of 5,600 to 24,000. Intrinsic viscosity was found to be proportional to molecular weight over this range and is given by the equation.

$$[\eta] = 3.20 \times 10^{-5} M_n$$

One of the polyesters prepared for Materials Laboratory was found to have an intrinsic viscosity of 1.67 corresponding to a number average molecular weight of 50,000.

The effect of milling on the molecular weight of the elastomer was determined by measurement of intrinsic viscosities before and after the milling procedure for various intervals of time.

The results of these measurements are given in the following table.

EFFECT OF MILLING ON MOLECULAR WEIGHT

<u>Sample</u>	<u>Time (min.)</u>	<u>$[\eta]$</u>	<u>M_n</u>
#68	0	1.67	50,000
	30	0.64	19,000
	60	0.55	16,500
	90	0.52	15,500
#88	0	0.63	19,600
	90	0.55	17,200

The above data indicate that processing for 1.5 hours on the mill yields an elastomer with an intrinsic viscosity of 0.50-0.55 and M_n of about 16,000 in both cases of two materials of initially widely differing molecular weights.

Volume dilatometric methods have been established for determining melting transition, glass transition, and rates of crystallization of elastomer gums and elastomer vulcanizates.

The crystalline melting point of hexafluoropentylene adipate has been determined to be $34.0 \pm 0.5^\circ\text{C}$. The glass transition temperature (T_g) has been determined for two hexafluoropentylene adipate samples of different molecular weights and for the vulcanizate of the higher molecular weight sample.

<u>Sample</u>	<u>M_n</u>	<u>T_g ($^\circ\text{C}$)</u>
# 8-8-56	13,000	-58.3 ± 0.5
# 131	19,400	-57.2 ± 1.0
# 131 (Vulcanizate)	-	-51.0 ± 1.0

The vulcanizate has a transition temperature about six degrees above that of the linear polymer.

Rates of crystallization have been measured by following, dilatometrically, the change in volume of a sample at constant temperature as a function of time. Measurements on samples # 3-8-56 and #131 have been conducted at four and three temperatures respectively. A duplicate run at -10°C on sample #131 indicated good reproducibility.

Although analysis of the rate results is incomplete, some preliminary generalizations can be made. First, the maximum rate of crystallization, for both samples, occurs at about -10°C . At this temperature both the nucleation rate and the rate of crystal growth appear to be at a maximum. Second, the rate of crystallization, following the initial nucleation of the polymer, of the higher molecular weight sample (19,000), is about 60% of the corresponding rate for the sample of lower molecular weight (13,000) at -10°C . Third, ultimate degree of crystallinity, as judged by percent decrease in volume, is greater at each temperature, for the sample of 13,000 molecular weight. For both samples, equilibrium degree of crystallinity is greatest at the highest crystallization temperature (1°C) and decreases progressively as the temperature is lowered. These results are shown below.

<u>Sample</u>	<u>Temp. $^\circ\text{C}$</u>	<u>Percent Decrease in Volume</u>
#8-8-56	1	3.05
13,000	-5	2.82
	-10	2.77
	-30	1.60
#131	1	2.4
19,400	-10	2.3
	-30	1.0

The density of hexafluoropentylene adipate has been determined hydrostatically.

<u>Sample</u>	<u>Temp. °C</u>	<u>Density (gms/cc)</u>
#131	24.3	1.471
	29.9	1.465
#8-8-56	29.9	1.461

TABLE I

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~0.1 g/3 cc.)
Adipyl Chloride (AC) 1 Hexafluoropentanediol (HFPD) .5 Octafluorohexanediol (OFHD) .5	7,000 202°	22,800	131	-65°		Sol. B, CH, EA, A Insol. T, E, I, 20L, W.
AC 1, HFPD .75, OFHD .25	8,820 169°	20,800	124	-75°		Sol. B, CH, EA, A Insol. T, E, I, 20L, W.
Terephthaloyl Chloride (TPC) .25 AC .75, HFPD 1	12,160 202°	23,600	144	-65° crystallizes	~35°	Sol. B, CH, EA, A Insol. T, E, I, 20L, C.
AC .85, TPC .15, HFPD 1	6,580 198.5°	21,600	133	~-70°		Sol. B, CH, EA, A Insol. T, E, I, 20L, W, C
AC .95, TPC .05, HFPD 1	15,800 236°	26,800	164			
AC .975, TPC .025, HFPD 1	3,360 201°	19,700	122			
AC .75, Isophthaloyl Chloride (IPC) .25, HFPD 1	5,950	21,600	131	~-70°		
AC .85, IPC .15, HFPD 1	3,420 202°	19,800	123			
AC .90, IPC .10, HFPD 1	19,620 169°	22,800	140			
AC .95, IPC .05, HFPD 1	Too high to measure	> 25,000				

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises °C	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~0.1 g/3 cc.)
AC .975, IPC .025, HFPD	2,420 201°	18,700	116			Sol. B, CH, EA, A Insol. T, E, I, 20L, W, C
AC .85, Glutaryl Chloride (GC) .15 HFPD 1		>25,000				
AC .95, GC .05, HFPD 1		>25,000				
AC .80, Azelalyl Chloride (AzC) .20 HFPD 1	1,290 201°	17,400	105			Sol. B, T, CH, EA, A Insol. E, I, 20L, W, C
AC .93 AzC .07, HFPD 1	2,535 201°	18,900	116			
AC .95, Sebacyl Chloride (SeC) .05 HFPD 1		>25,000				
AC .95, Isebacyl Chloride (ISeC) .05 HFPD 1		>25,000				
GC 1, HFPD 1	42.5 169°	8,320	53.6		38-40°	
GC 1, HFPD 1	35.6 169°	7,980	51.5		38-40°	
3-Oxaglutaryl Chloride (DGC) 1, HFPD 1	88.8 169°	9,700	62.6	-55°		Sol. EA, CH, A Insol. B, T, E, C, 20L, W
DGC 1, OFHD 1	58.5 169°	9,500	53	-25 to -30°	77-82°C	Sol. EA, CH, A Insol. B, T, E, C, 20L, W

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises °C	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~0.1 g/3 cc.)
AC .80, DGC .20, HFPD 1	451 169 ^a	12,800	80.5			Sol. Insol. B, T.
AC .90, DGC .10, HFPD 1	757 169 ^a	14,000	87.3			Sol. B (d) Insol. T
3,5-Bis(perfluoropropyl)-4-thiapimelyl Chloride 1, HFPD 1	2.94 169 ^a	~7,480	21.7	-4°C		Sol. EA, E, A Insol. B, T, C, W, 20L, I
3,5-Bis(perfluoropropyl)-4-thiapimelyl Chloride 1, OBHD 1	2.38 169 ^a	~7,400	20	-0°C		Sol. EA, E, A Insol. B, T, C, W, 20L, I
AC 1.05, HFPD 1	37.9 110 ^a	5,430	33.8			
AC 1.10, HFPD 1	20.8 110 ^a	4,370	27.2			
Adipyl Chloride (AC) 1; 2,2,3,3,4,4-Hexafluoropentane diol (HFPD) 1 (intrinsic visc. 1.67)		50,000	310			
AC 1; HFPD 1	16,200 (205°)	24,600	152			
AC 0.80, Isophthalyl Chloride (IPC) 0.20; HFPD 1	-	>25,000	>150			
AC 0.75, IPC 0.25; HFPD 1	98 (205°)	11,400	70			
AC 0.75, IPC 0.25; HFPD 1	53 (205°)	10,200	62			

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~ 0.1 g/3cc.)
AC 0.75, IPC 0.25; HFPD 1	1,135 (205°)	17,150	105			
AC 0.75, IPC 0.25; HFPD 1	7,550 (205°)	22,600	138			
AC 0.75, IPC 0.25; HFPD 1	2,360 (205°)	19,500	118			
AC 0.65, IPC 0.35; HFPD 1	592 (205°)	15,700	95			
AC 0.5, IPC 0.5; HFPD 1	728 (205°)	16,300	100			
AC 0.98, Fumaryl Chloride (FC) 0.02; HFPD 1	2,445 (169°)	16,900	105			
AC 0.97, FC 0.03; HFPD 1	251 (184°)	12,100	75			
AC 0.96, FC 0.04; HFPD 1	193 (184°)	11,700	72			
AC 0.94, Itaconyl Chloride (ItC) 0.06; HFPD 1	gelled					
AC 0.96, ItC 0.04; HFPD 1	gelled					
AC 0.48, IPC 0.50, FC 0.02; HFPD 1	520 (205°)	15,600	93			
AC 0.46, IPC 0.50, FC 0.04; HFPD 1	471 (205°)	15,300	92			
AC 1; 2,2,3,3,4,4-Hexafluoropentanediol (HFPD) 1.01	57.5 (170°)	8,600	53.5			
AC .95; Fumaryl Chloride (FC), .05; HFPD 1.01	38 (170°)	7,900	48.9			

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~ 0.1 g/3 cc)
AC .80; Isophthalyl Chloride (IP) .20; HFPD 1.01	50.1 (170°)	8,350	51.6			
AC .75; IP .20; FC .05; HFPD 1.01	33.2 (170°)	7,700	47.6			
AC 1; HFPD 1	1,780 (205°)	18,200	112.5			
AC .80, IP .20; HFPD 1	640 (205°)	15,500	96			
AC .48, .02 FC, .50 IP; HFPD 1	520 (205°)	15,500	93			
AC .46 .04 FC, .50 IP; HFPD 1	471 (205°)	14,700	91.1			
AC .73, .02 FC, .25 IP; HFPD 1	2,060 (205°)	18,600	115			
AC .71, .04 FC, .25 IP; HFPD 1	>>20,000					
AC .69, .06 FC, .25 IP; HFPD 1	3,500 (205°)	20,000	124			
AC .70, .10 FC, .20 IP; HFPD 1	>>20,000					
AC .25, .05 FC, .70 IP; HFPD 1	326 (205°)	13,800	86			
AC .75, .05 FC, .20 IP; HFPD 1	392 (205°)	14,300	88.5			
AC .98, .02 Itaconyl Chloride; HFPD 1	Polymer Gelled					
AC .96, .04 Itaconyl Chloride; HFPD 1	Heating held to under 140°C					
Perfluoroglutarlyl Chloride 1; HFPD 1	24.7	6,450	31.0			

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises	No. Ave. Mol. Wt. (M_n)	Deg. of Pcly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility (~0.1 g/3 cc)
Perfluoroglutaryl Chloride 1; OFHD 1	32.9	6,700	31.1			
$(CF_2)_3-(CH_2-O-CH_2-C-Cl)_2$ 1; HFPD 1	12.5 (110°)	5,360	21.3			
$(CF_2)_3-(CH_2-O-CH_2-C-Cl)_2$ 1; HFPD 1	15.4 (110°)	6,850	24.7	-55°		Insol: benzene, ethyl acetate (d) acetone (d) chloroform (d) ether, toluene, CCl_4 , Plexol, iso-octane
$[OC(CF_2)_3CO_2CH_2(CF_2)_3CH_2O]_n$						
$[OC(CF_2)_3CO_2CH_2(CF_2)_4CH_2O]_n$				-55°		Insol: Et Acet (d), acetone (d), toluene, CCl_4 , $CHCl_3$, Plexol 201, benzene ether, iso-octane
$[OCH_2OCH_2(CF_2)_3CH_2OCH_2CO_2CH_2(CF_2)_3CH_2O]_n$				-37°		Sol: Ethyl Acetate Insol: H_2O , toluene, ether, CCl_4 , benzene, Plexol 201, iso-octane, chloroform (d)

TABLE I (CONT'D)

POLYESTERS FROM DICARBOXYLIC ACID CHLORIDES AND FLUORINE - CONTAINING DIOLS

Reactants	Melt Viscosity (η) Poises °C	No. Ave. Mol. Wt. (M_n)	Deg. of Poly. (X_n)	Approx. Brittle Temp. °C	Approx. Melting Temp. °C	Solubility
$[OCH_2OCH_2(CF_2)_3CH_2OCH_2CO_2CH_2(CF_2)_4CH_2]_n$				-40°		Sol: Ethyl Acetate Insol: H ₂ O, toluene, ether, CCl ₄ , benzene, Flexol 201, iso-octane, chloroform(d)

A = acetone
EA = ethyl acetone
CH = chloroform
201 = plexol 201
C = carbon tetrachloride

I = isooctane
W = water
T = toluene
B = benzene
(d) = dispersed

TABLE II
CRYSTALLIZATION TENDENCIES OF COPOLYESTERS AT -10°C

Copolyester	1 Day	2 Days	5 Days	6 Days	8 Days	19 Days
.75 AC, .25 IPC, H	Clear	Clear	Clear	Clear	Clear	Clear
.80 A, .20 IPC, H	Clear	Clear	Clear	Clear	Clear	Clear
.85 AC, .15 IPC, H	Clear	Clear	1/3-1/2 Opaque	1/3-1/2 Opaque	3/4 Opaque	
.90 AC, .10 IPC, H	1/3-1/2 Opaque		Opaque			
.95 AC, .05 IPC, H	Opaque					
.85 AC, .15 TPC, H	Opaque					
.95 AC, .05 TPC, H	Opaque					
.85 AC, .15 GC, H	Opaque					
.95 AC, .05 GC, H	Opaque					
.95 AC, .05 SeC, H	Opaque					
.95 AC, .05 ISeC, H	Opaque					
AC, I, .75 H, .25 O	Clear	Clear	1/3-1/2 Opaque	1/3-1/2 Opaque	3/4 Opaque	

H = HFFD

O = OFHD

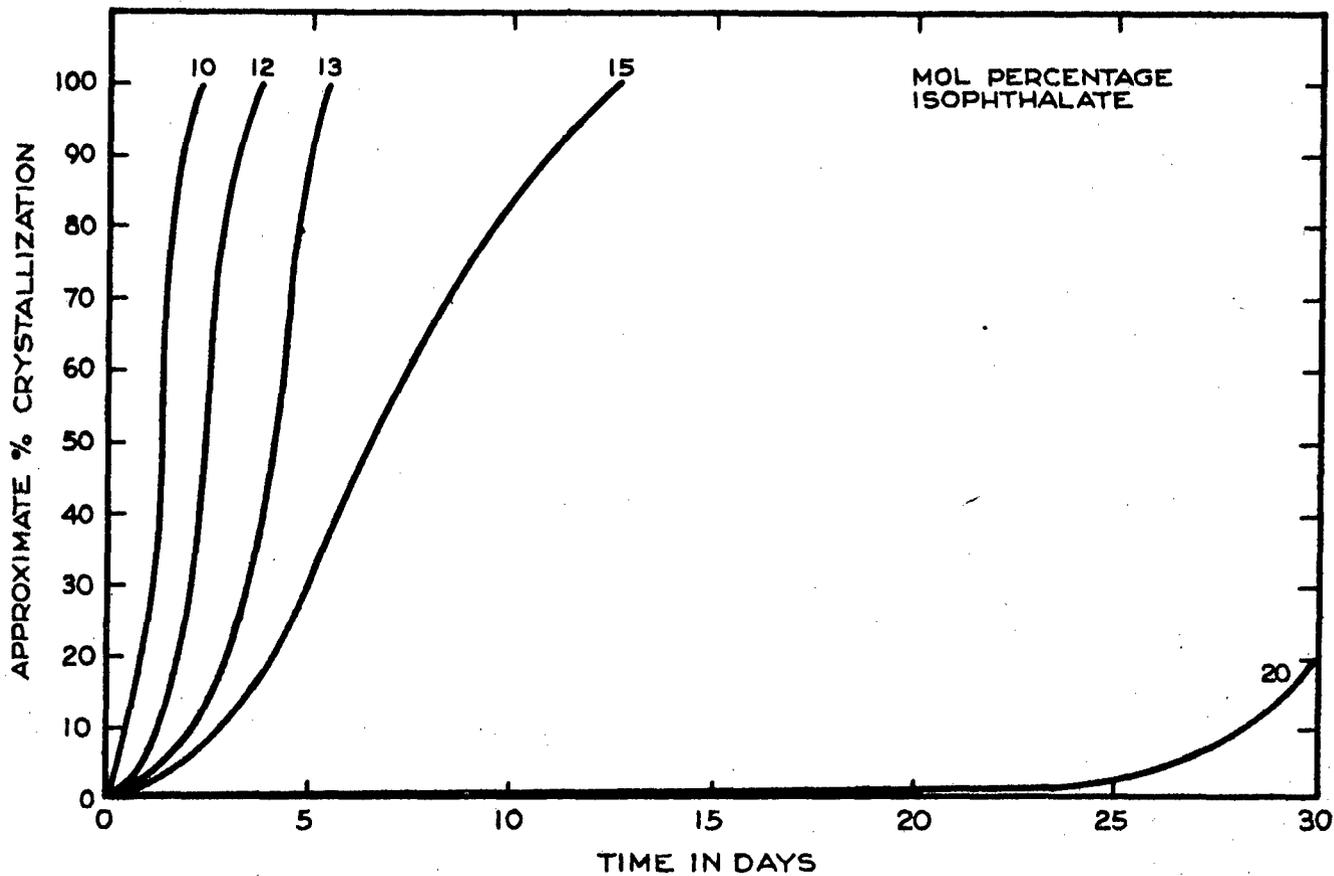


FIGURE 1
CRYSTALLIZATION RATES AT -10°C. OF RAW GUMS

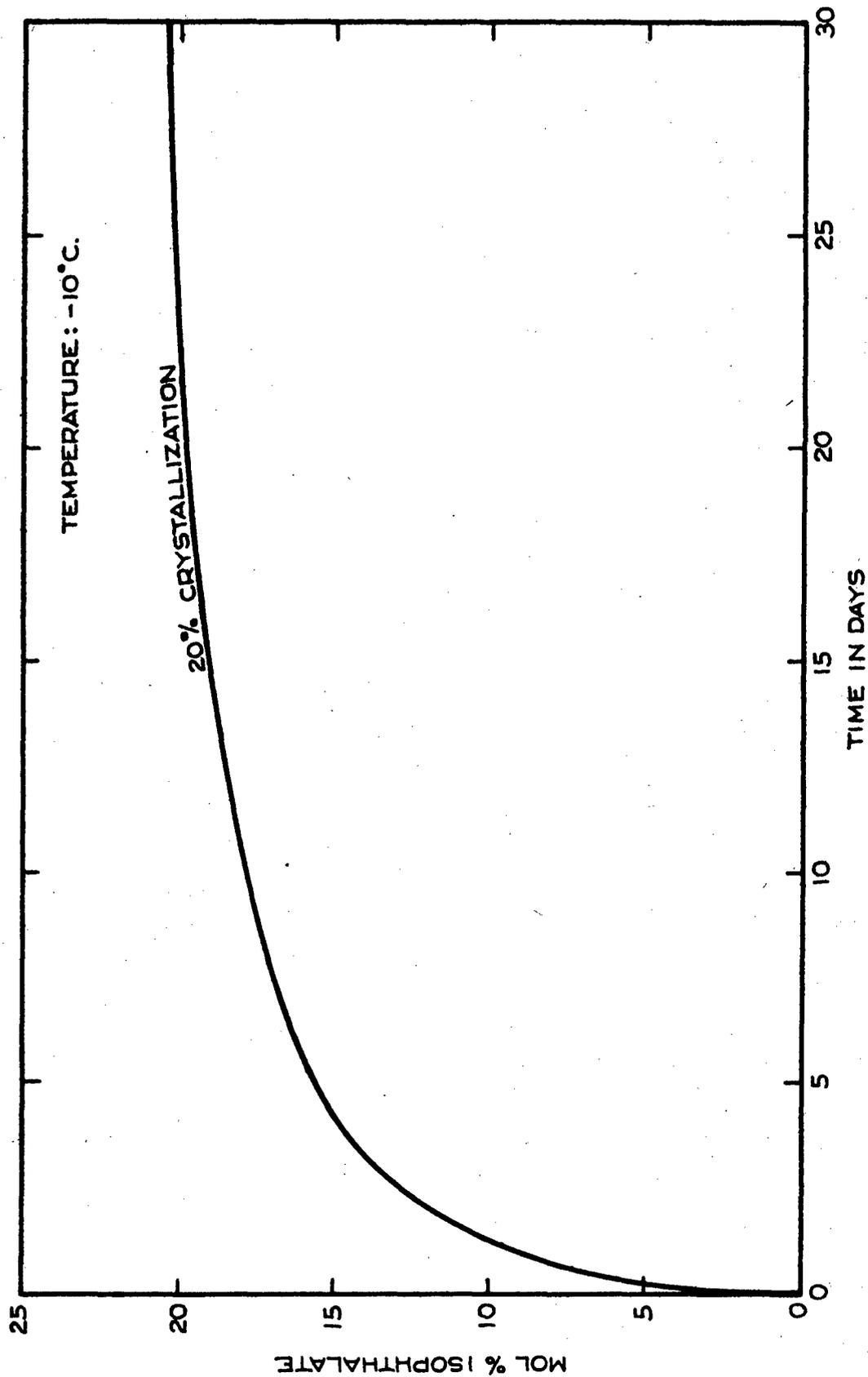


FIGURE 2

ISOPHTHALATE CONTENT VS DAYS TO 20% CRYSTALLIZATION
FOR RAW GUM POLYMERS

C. LINEAR POLYAMIDES CONTAINING FLUORINE

Investigations on the preparation and preliminary characterization of fluorine-containing N-substituted polyamides have been performed. The following two isomeric types of polyamides have thus far been prepared.

1. $(-\overset{\text{O}}{\parallel}{\text{C}}(\text{CF}_2)_3\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}}{\text{N}}(\text{CH}_2)_4\overset{\text{R}}{\text{N}}-)_n$
2. $(-\overset{\text{O}}{\parallel}{\text{C}}(\text{CH}_2)_4\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{R}}{\text{N}}\text{CH}_2(\text{CF}_2)_3\text{CH}_2\overset{\text{R}}{\text{N}}-)_n$

In the first type, reaction of stoichiometric quantities of perfluoroglutarate ester with bis(N-alkyl)1,6-hexanediamine led to rapid formation of the polyamide. To achieve higher molecular weights, heating the reaction mixture at relatively high temperatures under reduced pressure aided in apparently splitting out diamine and increasing melt viscosity of the linear polymers. Where the nitrogen substituent was methyl and *n*-butyl, higher molecular weights were easily achieved by this method, but where the nitrogen substituent was ethyl, decomposition of the polymer was caused by the elevated temperature. }

All of the fluorine-containing, N-substituted polyamides are best described as dark brown gums. As shown in Table III, preliminary characterizations indicate that approximate brittle temperatures of the polymers decrease as the nitrogen substituent goes from methyl to ethyl, and increases to butyl.

Solubility characteristics show that as the nitrogen alkyl substituent is lengthened, the polymers take on more non-polar characteristics and become more soluble in some of the common organic solvents. As shown in Table III, where the alkyl group is methyl and ethyl, the polyamides are insoluble in most organic solvents other than dimethylformamide and acetone. However, polyamides of the first type, where R = methyl or ethyl, are soluble in water and apparently hydrolyze; but where R = butyl the polyamide is soluble in the common organic solvents, but not in water.

In fluorine-containing, nitrogen substituted polyamides of the second type more difficulty in obtaining high molecular weight polymers is encountered. This is apparently due to the lowered basicity of the amine group caused by the strong inductive effect of the neighboring difluoromethylene moieties. As a result it is necessary to employ dicarboxylic acid chlorides in the reaction with the diamines. Two methods have given moderately high molecular weight polyamides from these reactants. In the first, the reactants are simply heated in a suitable solvent with evolution of hydrogen chloride; in the second, a tertiary amine base, i.e., pyridine, is added to aid in the formation of higher molecular weight polyamide. As shown in Table III, the first prototype of this kind of fluorinated polyamide, i.e., bis(N-methyl)2,2,3,3,4,4-hexafluoropentylene adipamide, is very similar in physical properties to its isomer, bis(N-methyl) hexamethylene perfluoroglutaramide, except that the former is not soluble (or hydrolyzed) in water.

Preliminary indications of thermal stability of the fluorine-containing polyamides suggest a wide variance of thermal stability with the nature of the alkyl substituent, and possibly with the purity of the polymer. For example, heating at elevated temperatures of about 205°C, caused some decomposition of bis(N-ethyl)hexamethylene perfluoroglutaramide, as noted by decrease in viscosity; however, an increase in viscosity, and further polymerization was manifested by heating at high temperatures in the case of the methyl and butyl analogs.

TABLE III

FLUORINE-CONTAINING, N-SUBSTITUTED POLYAMIDES

<u>Polyamide</u>	<u>Appearance</u>	<u>Approx. Brittle Temp.</u>	<u>Solubility</u>
$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}(\text{CF}_2)_3\text{C}-\text{N} \begin{array}{l} \text{CH}_3 \\ \text{(CH}_2)_6\text{N}- \end{array} \end{array} \right]_n$	Dark gum	25-30°C	<p>Sol: Dimethyl formamide, acetone. Hydrolysis in HOH.</p> <p>Insol: Ether, ethyl acetate, chloroform, benzene, toluene, Flexol 201, iso-octane, carbon tetrachloride.</p>
$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}(\text{CF}_2)_3\text{C}-\text{N} \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{(CH}_2)_6\text{N}- \end{array} \end{array} \right]_n$	Dark gum	5°C	<p>Sol: Dimethyl formamide, hydrolysis in water.</p> <p>Insol: Ether, ethyl acetate, chloroform, benzene, toluene, plexol carbon tetrachloride, iso-octane.</p>
$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}(\text{CF}_2)_3\text{C}-\text{N} \begin{array}{l} \text{C}_4\text{H}_9(n) \\ \text{(CH}_2)_6\text{N}- \end{array} \end{array} \right]_n$	Dark gum	20°C	<p>Sol: Acetone, benzene, toluene, iso-octane, dimethyl formamide, chloroform.</p> <p>Sl. Sol: Ether, ethyl acetate</p> <p>V. Sl Sol: Carbon tetrachloride</p> <p>Insol: Plexol, water</p>
$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}(\text{CH}_2)_4\text{C}-\text{N} \begin{array}{l} \text{CH}_3 \\ \text{(CF}_2)_3\text{CH}_2\text{N}- \end{array} \end{array} \right]_n$	Dark gum	15-25°C	<p>Sol: Acetone, dimethyl formamide</p> <p>Insol: Benzene, toluene, plexol 201, iso-octane, ether, dioxane, carbon tetrachloride, water.</p>

D. FLUOROPOLYESTER VULCANIZATES

1. Formulation and Cure

A recommended formulation and cure for fluorinated polyester vulcanizates is given in Table IV. The formulation works equally well on both hexafluoropentylene adipate and on its copolyesters containing up to 25 mol % isophthalate. The formulation consists of 100 parts gum, 50 parts SRF carbon black, 20 parts calcium carbonate, and 19 parts DI-CUP 40C (dicumyl peroxide curing agent).

Cure times of 50-55 minutes are arbitrarily used in research preparations, since there is no danger of overcure with the saturated polyesters. Less time is actually required for the vulcanization, however; and short curing cycles could be used. While an oven post cure is not necessary to obtain completely cured vulcanizates with good properties, it is recommended for reducing weight losses of aged specimens and for giving slightly higher elongations.

2. Original Properties

Table V gives typical original properties of vulcanizates compounded and cured as recommended in Table IV. It should be noticed that both hexafluoropentylene adipate and its copolyesters containing up to 25 mol % isophthalate exhibit essentially equivalent properties except for low temperature characteristics.

3. Air Aging at High Temperatures

The vulcanizates compounded and cured as in Table IV, have been submitted to air aging at temperatures of 350° and 400°F for up to 1000 hours. As shown in Figure 3, there is an initial drop in tensile strength at both temperatures generally to values of 800-1000 psi, with an increase in elongation to values of 200-250%. At 400°F, tensile strength then gradually increases with further heating to a value of about 1100 psi after 1000 hours. Elongation gradually decreases during this period to about 50% after 1000 hrs. At 350°F, tensile strength then remains at about 800-1000 psi and elongation at about 200% through 1000 hrs.

At 450°F in air, the vulcanizates become brittle and hard in about 168 hours. Tensile strength after 70 and 168 hrs. at 450°F is 500-600 psi, elongation after 70 hrs. is 175%, after 168 hrs. 9-25%.

There is a slight trend for copolyesters containing 25 mol % isophthalate to exhibit better resistance to aging at high temperatures than the homopolymer vulcanizates. The differences between the aged vulcanizates are barely significant, however, in view of

the fairly wide test results obtained on any one compound. For example, a few results of air aging at 400°F have given specimens with tensiles as high as 1400-1800 psi after 168 hrs. aging, but these results are not reproducible at will, and at this time must be considered anomalous.

4. Diester Oil Aging at 350°F

Table VI gives properties of vulcanizates (compounded and cured as in Table IV) after aging in diester oil at 350°F for 70 hrs. The oil used is Plexol 201 with 0.5% phenothiazine added, or Anderol 774, which pass specifications for MIL-L-7808 lubricating oil. Another MIL-L-7808 oil, Turbo Oil #15, degraded the vulcanizates at 350°F.

There is no significant difference in resistance to the oils between the homopolymer and copolymer vulcanizates. The range of values listed in Table VI covers differences in test procedures used, mainly in the amount of air flowing over the oil surface. It is seen that good resistance with very low swell (0-3%) is shown by the vulcanizates to the oils at 350°F for 70 hrs.

At 400°F, a temperature at which the oil itself is decomposing, after 70 hrs. a decrease in volume of about 5-10% is manifested by the vulcanizates, and tensile strengths and elongations are lowered to about 300-600 psi, and 100-150%, respectively.

5. Fuel Aging at 250°F

Table VII gives properties of vulcanizates (compounded and cured as in Table IV) after aging in JP-4 or JP-5 jet fuels, and in 70/30 iso-octane-toluene for 70 hours at 250°F. Tensile and elongation changes are similar in both types of fuels, but swell is about doubled in the aromatic fuel compared to the jet fuels (7-12% vs. 19-24%).

At about 325°F in JP-5 for 24 hours (pressure bomb) swell was 14-16%, and tensile strength was 500-700 psi, with corresponding elongations of 220-280%.

At 350°F in 70-30 iso-octane-toluene for 70 hrs. the vulcanizates were seriously degraded.

The homo and copolymers are essentially equivalent with respect to fuel aging resistance.

6. Hydraulic Fluid Aging at 316°F

After aging in MIL-O-5606 (low swell hydraulic fluid) for 168 hrs. at 316°F, the rubber (compounded and cured as in Table IV) exhibited similar properties to the diester oil aged vulcanizates. Table VII

gives results of the hydraulic fluid aging, showing the good resistance of the vulcanizates to this aircraft hydraulic fluid. The rubber is not resistant to Skydrol hydraulic fluid at 350°F.

7. Effect of Fluids at Room Temperature

The rubbers are resistant to common fuels and oils at room temperature, as well as to 10% aqueous solutions of hydrochloric acid and sodium chloride. Concentrated or fuming nitric acids degrade the rubbers at room temperature, as does 10% sodium hydroxide solution.

Table IX lists volume swells of the vulcanizates in various fluids at room temperature.

8. Low Temperature Properties

The major difference between the homopolymer, i.e., hexafluoropentylene adipate, and its copolyesters containing up to 25 mol % isophthalate is in their low temperature characteristics. The linear homopolymer crystallizes in less than 1 day at -10°C. Increasing amounts of isophthalate reduce the crystallization rate at -10°C, until at 20 mol % isophthalate content, crystallization does not begin for at least 25 days. However, temperature retraction tests on the vulcanizates show that rubber-like behavior of the 25 mol % isophthalate is lost at a higher temperature than the homopolymer during very short time exposures to low temperatures. Figure 4 shows how temperature retraction values vary with isophthalate content, assuming a straight line function applies between the two known values at 0 and 25 mol % isophthalate. The TR-10 values are significant in showing approximately at what temperature good rubber-like properties are lost by the vulcanizates. The TR-50 and TR-70 values shown in Figure 4 illustrate that the homopolymer is crystallizing during the testing period.

Figure 5 illustrates the Gehman low temperature torsional curve for hexafluoropentylene adipate vulcanizates, showing the excellent short-term low temperature properties exhibited by this rubber. Table X gives the Gehman data and ASTM D-746 brittle temperature (brittle at -98°F) for the homopolymer vulcanizate.

9. Vulcanizates From Unsaturated Polyesters

The unsaturated polyesters, described in Section B of this report, require considerably less curing agent for equivalent or tighter degrees of cure than do the saturated polyesters, depending on how much unsaturation is contained in the linear polymers. This is illustrated in Table XI, which also gives aged properties of the vulcanizates. Preliminary compounding studies have shown, however, that optimum physical properties will probably be found for less highly loaded vulcanizates in the case of the unsaturated polymers. Original and aged properties of some of the vulcanizates of these unsaturated polyester, from the preliminary results, appear to be

at least equivalent to the more extensive data listed above for the saturated polymers. Much more work is required to standardize and recommend a particular amount of unsaturation and compounding recipe which will give an overall balance of superior properties.

TABLE IV

RECOMMENDED FORMULATION AND CURE

	<u>Parts by Weight</u>
Fluoroelastomer gum	100
SRF Carbon Black ¹	50
Calcium Carbonate ²	20
DI-CUP 40C3 (40% dicumyl peroxide on calcium carbonate)	19

Mill: cold, fraction speed, about 1 hr. milling time.

Press cure: 50-55 minutes at 320°F.

Oven post cure: 16 hours at 350°F.

1. Furnex and sterling carbon black have been used and are essentially equivalent.
2. Ultrafine precipitated calcium carbonate. Purecal U has been used. Wyandotte Chemicals Corp., Wyandotte, Michigan.
3. Hercules Powder Co., Wilmington, Delaware.

TABLE V

VULCANIZATE ORIGINAL PROPERTIES
(Compounded and Cured as in Table IV)

	<u>Hexafluoropentylene Adipate</u>	<u>25% Isophthalate</u>
Tensile Strength, psi	2000-2500	2000-2500
Elongation, %	125-200	125-200
Hardness, Shore A	76-86	76-86
Set at Break, %	0-4	0-4
Compression Set -B*		
70 hrs. at 250°F.	48.5-50	41

*Very preliminary values measured on plied-up samples at WADC; the rubbers are not specially compounded to obtain low set.

TABLE VI

MIL-L-7808 OIL* AGING AT 350°F

Time: 70 hours

Tensile Strength, psi	1200-1700
Elongation, %	150-250
Hardness, Shore A	63-73
Set at Break, %	0-8
Volume Swell, %	0-3

* Plexol 201 with 0.5% phenothiazine, Rohm and Haas Co., or Anderol 774.

TABLE VII

FUEL AGING AT 250°F

Time: 70 hrs.

	<u>JP-4 or JP-5</u>	<u>70/30 Iso-octane/toluene</u>
Tensile Strength, psi	1100-1800	1000-1500
Elongation, %	150-250	125-225
Hardness, Shore A	55-70	43-70
Set at Break, %	0-6	0-6
Volume Swell, %	7-12	19-24

TABLE VIII

MIL-O-5606 HYDRAULIC FLUID AGING AT 316°F

Tensile Strength, psi	1440
Elongation, %	200
Hardness, Shore A	68
Set at Break, %	3-4
Volume Swell, %	5

TABLE IXVOLUME SWELL AT ROOM TEMPERATURE

<u>Fluid</u>	<u>Time Hrs.</u>	<u>Volume Swell, %</u>
70/30 iso-octane/toluene	70-168	9-14
JP-4 jet fuel	70-168	4-5
Benzene	70-168	20-40
Plexol 201 lubricating oil	70-168	1-2
Turbo Oil #15 lubricating oil	70-168	2-3
Skydrol hydraulic fluid	70-168	31-44
10% hydrochloric acid	168	negligible
10% sodium chloride	168	negligible
10% sodium hydroxide	168	degraded
Fuming nitric acid	8	degraded
90% nitric acid	8	degraded

TABLE X

LOW TEMPERATURE PROPERTIES OF HEXAFLUOROPENTYLENE ADIPATE VULCANIZATES

TORSIONAL MODULUS AND BRITTLE TEMPERATURE

Gehman T ₂	-42°F	Torsional Modulus (C) at room temperature	188 psi
T ₅	-56°F		
T ₁₀	-62°F	Freeze Point.	-71°F
T ₁₀₀	-72°F	Brittle Temperature (ASTM D-746)	-98°F

* Tests performed at B F Goodrich Co. on 0.075" thick specimens.

TABLE XI

UNSATURATED VULCANIZATES*

Comp. of Gum	Parts DI-CUP 40C	Original Properties		AGED PROPERTIES																	
				Flexol 350°F, 70 hours					Air 70 hrs, 400°F					Air 168 hrs. 400°F							
				T	E	S	H	% Wt Loss	T	E	S	H	% Wt Loss	T	E	S	H	% Wt Loss			
98A2F	10	1960	200	1-2	72-76	1250	200	5-6	65-70	3.8	+1.1	826	250	5-6	64-68	3.8	875	225	6-7	70-74	7.8
98A2F	5	1417	250	1-2	68-72	863	325	11-12	61-65	4.7	-0.9	652	425	31-32	58-62	3.9	409	350	43-44	66-70	8.9
*73A25IP2F	15	2045	125	0-1	85-80	1217	125	2-3	79-74	4.8	+ .1						1120	125	2-3	86-81	6.35
73A25IP2F	10	1912	125	0-1	84-79	1083	150	1-2	76-72	5.9	- .4	1185	200	4-5	80-75	2.8	760	150	6-7	81-76	6.03
71A25IP4F	10	1625	100	0-1	88-83	1230	125	3-4	80-75	10.78	-8	1200	175	3-4	82-77	3.4	1417	175	6-7	75-80	6.8
69A25IP6F	10	2482	100	0-1	89-85	1392	100	2-3	79-75	5.9	-1.9	1730	125	2-3	83-79	3.3	1720	100	3-4	81-82	6.5
70A20IP10F	10	2356	50	0-1	91-87	1613	75	0-1	82-78	2.7	+2.9						2034	100	2-3	87-83	7-6
70A20IP10F	5	2606	50	0-1	92-87	1677	75	0-1	84-80	2.8	+2.1						1966	75	2-3	90-86	7.1
48A50IP2F	10	2038	275	2-3	73-77	1037	350	17-18	69-73	8.9	-3.8	1880	350	8-9	71-75	1.6	600	525	75-76	65-69	7.3
48A50IP2F	5	2034	375	7-8	73-77	1200	300	11-12	71-76	9.6	+0.6	760	750	200	67-71	2.8	385	750	300	62-67	5.7
46A50IP4F	10	2448	200	2-3	79-83	1519	200	7-8	72-75	5.7	+ .1	852	475	30-31	67-71	5.9	1230	400	25-26	69-74	5.5
46A50IP4F	5	1706	175	0-1	71-76																
25A70IP5F	19	2255	100	0-1	91-88	1650	125	1-2	82-78	5.6	- .5						1633	250	11-12	87-84	4.1
25A70IP5F	10	2460	100	0-1	87-84																

* Compounded with 50 parts Furnex, 20 parts Purecal U, DI-CUP 40C variable as indicated

A = Adipate

IP = Isophthalate

F = Fumarate

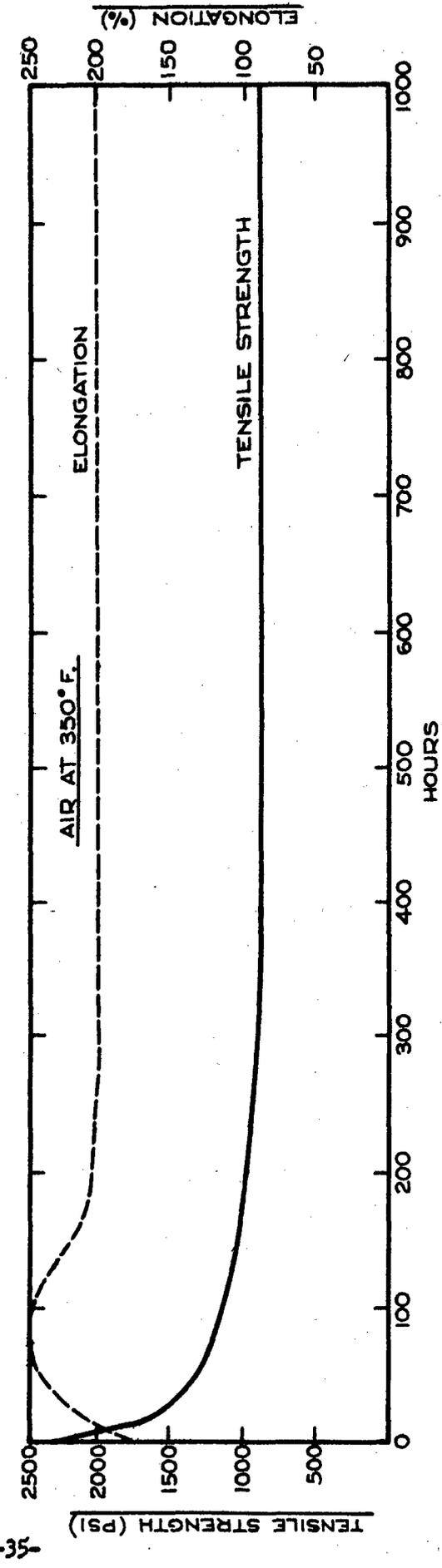
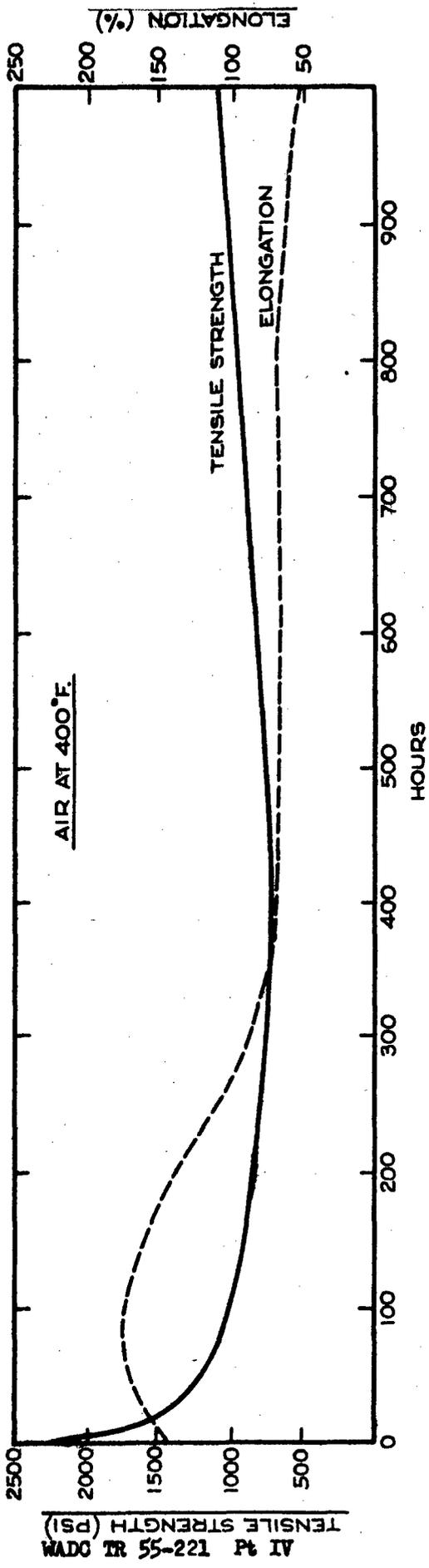


FIGURE 3
TENSILE-ELONGATION FOR HEAT AGED VULCANIZATES IN AIR

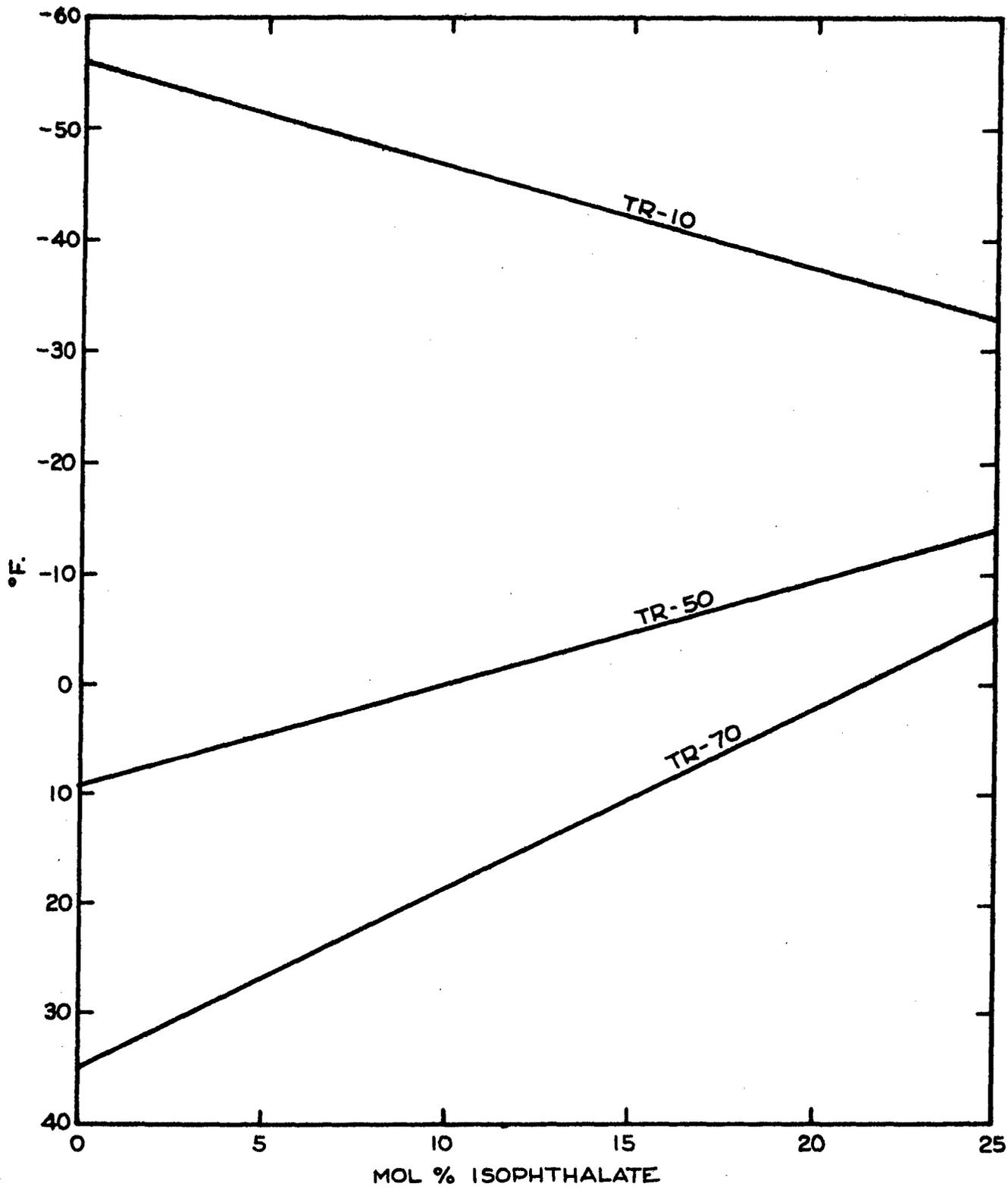


FIGURE 4
TEMPERATURE RETRACTION DATA
ON VULCANIZATES

GEHMAN LOW TEMPERATURE TORSION
 TEST OBTAINED FROM A.E. JUVE, DIRECTOR,
 TECHNICAL SERVICE RESEARCH,
 B.F. GOODRICH CO.

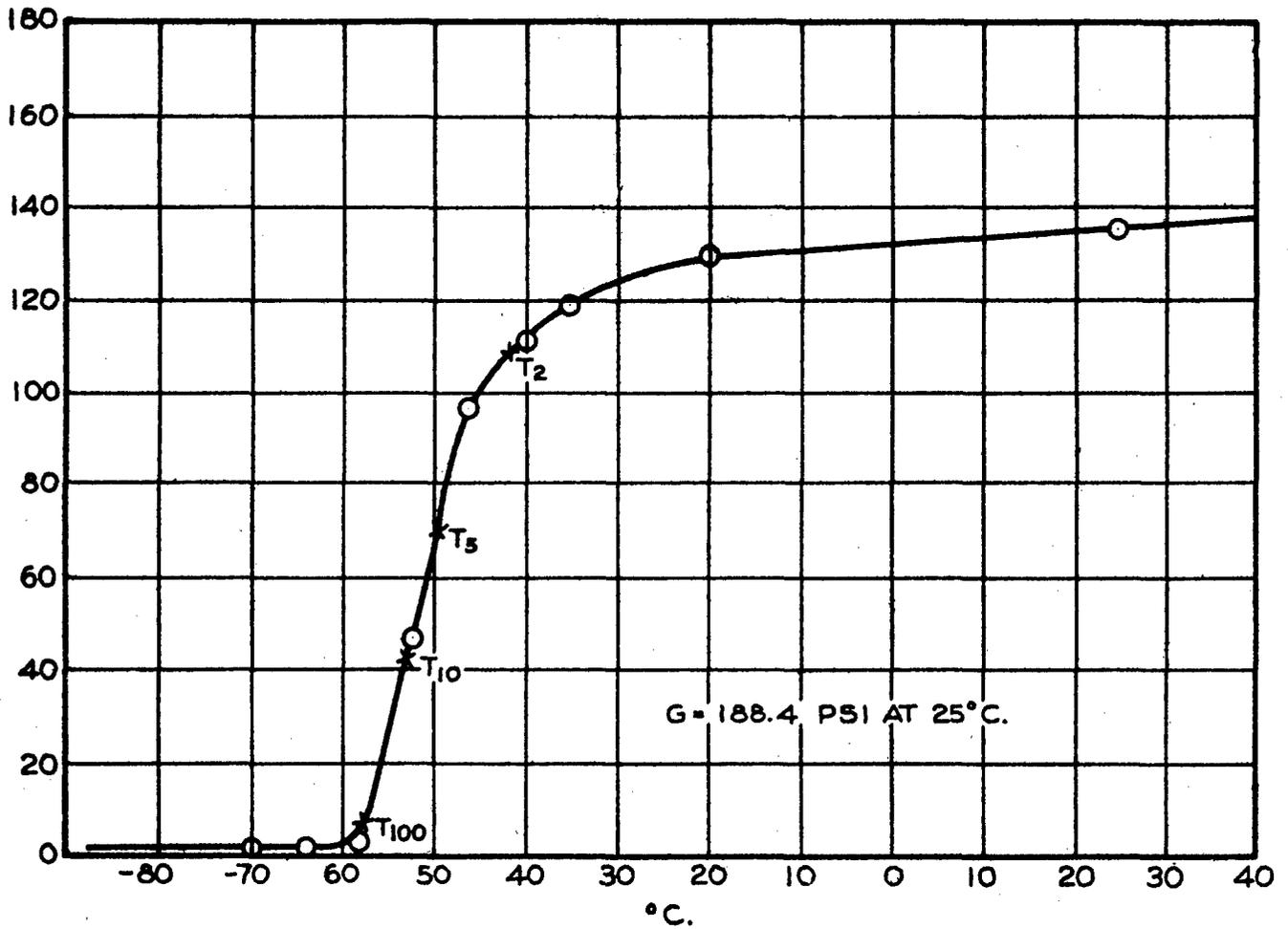


FIGURE 5

LOW TEMPERATURE FLEXIBILITY OF HEXAFLUOROPENTYLENE
 ADIPATE CARBON BLACK REINFORCED VULCANIZATES

IV. EXPERIMENTAL

A. INTERMEDIATES

Research on the preparation of certain novel or unusual fluorine-containing intermediates considered desirable for polymerization in this project was performed at Purdue Research Foundation under sub-contract to Hooker Electrochemical Company and details of that synthetic work comprise Appendix I of this report. The materials described below were prepared at Hooker Electrochemical Company laboratories, and further details of known compounds may be found in the references cited.

Perfluoroglutaric Acid was prepared by aqueous permanganate oxidation of 1,2-dichlorohexafluorocyclopentene according to the method described by McBee, Wiseman, and Bachman;² b.p. 121-126°C/1.4-1.8 mm.

Diethyl Perfluoroglutarate² was prepared by refluxing a mixture of perfluoroglutaric acid and 100% excess ethanol with a small amount of sodium bisulfate in benzene, as described previously;¹ b.p. 57°C/0.6 mm.

2,2,3,3,4,4-Hexafluoropentane-1,2-diol was prepared by reduction of diethyl perfluoroglutarate with lithium aluminum hydride according to the method reported by McBee, Marzluff and Pierce;³ m.p. 77-78.5°C.

Perfluoroadipic Acid², Diethyl Perfluoroadipate², and 2,2,3,3,4,4,5,5-Octafluorohexane-1,2-diol³ were prepared in a manner similar to that outlined above for the perfluoroglutarate series, starting with 1,2-dichlorooctafluorocyclohexene, as described previously.¹

Preparations of Bis(N-alkyl) 1,6-Hexanediamines and Their Precursors

Bis(N-acetyl) 1,6-hexanediamine - To 58 g. (0.5 m) of 1,6-hexanediamine was added dropwise 150 g. (1.47 m) of acetic anhydride. The reaction became exothermic after approximately 30 ml. of the acetic anhydride had been added. The reaction mixture was cooled and the remainder of the acetic anhydride was added. After addition, the reaction mixture was heated at reflux for 1 hour, and the acetic acid and excess anhydride were then removed under reduced pressure (water aspiration) to yield 73 g. (73% yield) of a white precipitate; m.p. 125-126°C. Literature⁸ report a m.p. of 125-126°C.

Bis(N-isopropyl)adipamide - In 1-l. of ether was dissolved 180 g. (3.05 m) of isopropylamine, and to this reaction mixture was added dropwise 91.5 g. (0.5 m) of adipyl chloride. During the addition the reaction flask was cooled with a dry-ice acetone bath, but after addition the reaction was allowed to warm to room temperature and stand overnight. The reaction mixture was filtered and the filtrate evaporated down to yield less than 1 g. of solid. The precipitate from the filtration was efficiently washed with water to remove amine hydrochloride. There remained 90 g., 86.5% of water insoluble residue, a white solid melting 190-191°C. The product was recrystallized from chloroform-hexane and melted 192-192.5°C.

Bis(N-n-butyl)adipamide - To a stirred and cooled solution of 97.4 g. (1.33 mole) of n-butylamine in 200 ml. of chloroform was added 61 g. (0.33 mole) of adipyl chloride. The reaction mixture was stirred overnight. The amine hydrochloride salt was removed by filtering and the solvent removed from filtrate to yield 57 g. of a white solid residue; m.p. 159-160.5°C yield 67%.

Analysis for $C_{14}H_{28}N_2O_2$

Calcd. C, 65.62; H, 10.94; N, 10.94
Found. C, 65.74; H, 11.00; N, 10.99

Bis(N-tert-butyl)adipamide - To a stirred and cooled solution of 160 g. (2.1 mole) of tert-butylamine in 200 ml. of chloroform was added 91.5 g. (0.5 mole) of adipyl chloride. After addition the reaction mixture was stirred overnight. The amine hydrochloride salt was removed by filtering and n-hexane was added to the filtrate to precipitate a white solid. The yield was 116 g. (90.6%); m.p. 209-210°C. Literature m.p. 208°C⁹ and 212°C.

Bis(N-ethyl)1,6-hexanediamine - In a 5-l. 3-necked creased flask fitted with stirrer, condenser, dropping funnel, and protected from atmosphere moisture was placed 35 g. (0.92 mole) of lithium aluminum hydride and 2 liters of anhydrous ether. To this was added dropwise 38 g. (0.19 mole) of bis(N-acetyl)1,6-hexanediamine slurried in 1.5 liters of anhydrous ether. After about one-half of the diamide had been added, large clumps developed which interfered with the stirring. The reaction mixture was heated to reflux and after a time the clumps were reduced sufficiently to permit stirring. Further addition was continued under the reflux conditions. The reaction mixture was stirred under reflux for an additional 72 hours.

The excess lithium aluminum hydride was destroyed by the dropwise addition of the following:

1. Water - 35 g.
2. 15% Sodium hydroxide-35 g.
3. Water - 105 g.

The inorganic salts were removed by filtration and the filter cake washed several times with ether. The filtrate and washings were combined and dried over anhydrous magnesium sulfate. After filtering the mixture, dry hydrogen chloride gas was bubbled into the filtrate and a white precipitate formed. There was obtained 76 g. of the amine hydrochloride which was treated with 30% sodium hydroxide solution. This basic solution was extracted five times with ether. The combined ether extractions were dried over sodium hydroxide pellets, filtered and the filtrate distilled. There was obtained 8.8 g. of a material of b.p. 92°C (5 mm.) N_2^5 1.4429. Yield 34%.

Literature¹¹ reports a b.p. of 105°C (6 mm.), N_2^5 1.4434.

Bis (N-isopropyl)1,6 hexanediamine - In an apparatus protected from atmospheric moisture, 2.5 liters of anhydrous ether was stirred with 45.6 g. (1.2 mole) of lithium aluminum hydride. To this was added, with stirring, a slurry of 57 g. (0.25 mole) of bis (N-isopropyl) adipamide in 1 liter of anhydrous ether. After addition, the reaction mixture was stirred under reflux for 48 hours.

Excess lithium aluminum hydride was destroyed by the dropwise addition of the following:

1. Water - 5 ml.
2. 15% Sodium hydroxide
3. Water - 120 ml.

The reaction mixture was filtered and the filter cake washed twice with ether. The combined ether washings and filtrate were dried over anhydrous magnesium sulfate. The drying agent was removed and anhydrous hydrogen chloride gas bubbled into the filtrate. There was obtained 36 g. of the hydrochloride salt of the amine. The salt was treated with a 30% sodium hydroxide solution and the basic solution then extracted 5 times with ether. The combined ether extracts were dried over sodium hydroxide pellets, filtered and the ether removed. The residue was distilled and a fraction, 15.1 g., of b.p. 88-94°C (2.9 mm.) was collected. N_D^{29} 1.4392. Literature¹² reports a b.p. of 77°C. (2 mm.) N_D^{25} 1.4391.

Bis(N-n-butyl)1,6-hexanediamine - This preparation was run similarly to the preparation of bis (N-isopropyl) 1,6-hexanediamine. Reduction of 51.2g. (0.2 mole) of bis (N-butyl) adipamide was carried out with 34.2 g. (0.9 mole) of lithium aluminum hydride. The reflux period was extended to 60 hours.

The hydrochloride salt turned light brown at 190°C but had not melted at 280°C. Yield 50 g. Neutralization, extraction and distillation gave 23 g. of the product, b.p. 140°C/6 mm., N_D^{30} 1.4453. Yield 50.5%. Literature¹¹ reports a b.p. of 141°C (6 mm.).

Bis(N-tert-butyl)1,6-hexanediamine - This preparation was run similarly to the preparation described for bis (N-isopropyl)1,6-hexanediamine. Sixty grams of hydrochloride salt were collected which did not melt at 270°C. The free base distilled and the product collected at 100°C (1.6 mm.). The yield was 24.2 g. (53%), $N_D^{29.5}$ 1.4398

Analysis for $C_{14}H_{32}N_2$

Calcd. C, 73.68; H, 14.04; N, 12.28
Found. C, 73.89; H, 13.96; N, 12.59

Preparation of Bis(N-alkyl)2,2,3,3,4,4-Hexafluoropentanediamines and Their Precursors and Derivatives

Bis(N-ethyl)perfluoroglutaramide - Monoethylamine gas was bubbled into a solution of 176 g. (0.5 mole) of dibutyl perfluoroglutaramide in 250 ml. of tetrahydrofuran and 200 ml. of ether. The reaction flask was cooled while the exothermic reaction continued. When no more heat was produced by the reaction, the addition of the amine was discontinued, and the reaction mixture allowed to stand for 2 hours.

The solvent was stripped off at reduced pressure with the aid of a water aspirator to yield a white solid. Recrystallization from benzene gave a m.p. 119-120°C, yield 134 g. or 91.3%.

An analytical sample was prepared by three further recrystallizations from benzene; m.p. 122-122.5°C.

Analysis for $C_9H_{12}F_6N_2O_2$

Calcd. C, 36.72; H, 4.08; F, 38.78; N, 9.52

Found. C, 36.79; H, 4.12; F, 38.92; N, 9.17

Bis(N-isopropyl) perfluoroglutaramide - To a stirred cooled solution of 62 g. (1.05 m) of isopropylamine and 250 ml. of dry ether was added dropwise 176 g. (0.5 mole) of dibutylperfluoroglutarate. The addition rate was slow with the temperature of the reaction mixture kept at 20°C. After the addition, the ice bath was removed and the temperature rose due to the exotherm of the reaction.

Two portions of 5 ml. each of isopropyl amine were added in order to insure complete reaction, as well as 100 ml. of tetrahydrofuran. The reaction mixture was allowed to stir overnight.

The solvent was stripped off at reduced pressure (water aspirator) to yield a yellow white precipitate. This was recrystallized with carbon black from benzene and melted 125-128°C. Further recrystallization from methanol-water gave 100 g. or 62%, m.p. 132-134°C. An analytical sample was prepared by 2 further recrystallizations from ether-hexane (excess ether used to solublize precipitate and some boiled off after hexane addition); m.p. 138.75-139.25; shiny, extremely fine needles.

Analysis for $C_{11}H_{16}N_2O_2F_6$

Calcd. C, 41.0; H, 4.97; N, 8.69; F, 35.4

Found. C, 41.2; H, 5.18; N, 8.64; F, 35.69

Bis(N-n-butyl) perfluoroglutaramide - To a solution of 176 g. (0.5 m) of dibutylperfluoroglutarate, 250 ml. ether, and 100 ml. of dioxane was added dropwise with cooling and stirring 75 g. (1.03 m) of n-butylamine. The reaction temperature was kept below 30°C. After the addition, the reaction mixture was allowed to stir for 18 hours after which the solvent was stripped off under reduced pressure to yield a yellow white precipitate; m.p. 114.5-115.5.

Recrystallization three times from ether-hexane gave fine feathery needle-like crystals which melted at 117.25-117.75°C.

Analysis for $C_{13}H_{20}N_2F_6O_2$:

Calcd. C, 44.6%; H, 5.72; N, 8.0; F, 32.59

Found. C, 44.81; H, 6.00; N, 8.22, F, 32.48

Bis(N-tert-butyl) perfluoroglutaramide - To a solution of 92 g. (0.33 m) of perfluoroglutaroyl chloride and 200 ml. of dry tetrahydrofuran was added dropwise and with stirring 100 g. (1.37 m) of t-butylamine. Reaction was quite vigorous and required external cooling. After the addition the reaction mixture was stirred over the weekend (66 hours).

The reaction mixture was filtered to remove the amine hydrochloride and the solvent stripped from the filtrate at reduced pressure to yield a white precipitate. This was treated with decolorizing charcoal and recrystallized from ether-hexane, giving 77 g. (66% yield) of product melting at 119-120°C.

An analytical sample was prepared by three further recrystallizations from ether-hexane, m.p. 120-121°C.

Analysis for $C_{13}H_{20}N_2O_2F_6$:

Calcd. C, 44.6; H, 5.72; N, 8.0; F, 32.59
Found. C, 44.76; H, 6.02; N, 7.99; F, 32.63

Bis(N-methyl)2,2,3,3,4,4-hexafluoropentanediamine was synthesized by reduction of the diamide with an ether slurry of lithium aluminum hydride.

Because of the reported instability and violent decomposition of certain fluorinated amide reductions with lithium aluminum hydride⁵, a very small sample of the reaction mixture of Bis(N-methyl)perfluoroglutaramide and lithium aluminum hydride was heated cautiously to about 80°C. No sign of decomposition was noted until at about 80°C some darkening of the reaction product occurred.

On a larger scale, 6.9 g. (.182 mole) of lithium aluminum hydride was slurried in a 3-necked 3-liter flask with 2 lbs anhydrous ether. After one hour, 10 g. (.0375 mole) of finely powdered and screened bis(N-methyl)perfluoroglutaramide in 250 ml. of anhydrous ether was added dropwise so as to maintain moderate ether reflux. The reaction mixture was stirred at room temperature for 43 hours before the excess hydride was destroyed by dropwise addition of water. After filtration and drying of the ethereal solution, anhydrous hydrogen chloride was added until no more precipitate formed. About 6.5 g. of hydrochloride salt, m.p. 198-201°C (d), was collected. The salt was neutralized with 50% sodium hydroxide solution, and the mixture extracted with five 50 ml portions of ether. After drying and filtering, and removal of the ether, the residual yellow oil was fractionally distilled to give 4 g. (43.8%) of bis(N-methyl)2,2,3,3,4,4-hexafluoropentanediamine, b.p. 55-57°C/10 mm, $N_D^{25} = 1.3779$.

An analytical sample was redistilled, b.p. 55-56°C/10.5 mm, $N_D^{26.5} = 1.3771$.

Analysis for

Calcd. C, 35.3; H, 5.04; F, 47.8; N, 11.76
Found. C, 35.54; H, 4.82; F, 47.85; N, 11.72

About 2 g. of starting material was recovered by evaporation of the filtrate from the hydrochloride salt separation.

When the above procedure was modified by using tetrahydrofuran to dissolve the bis(N-methyl)perfluoroglutaramide, lower yields of the desired diamine were obtained, and increased amounts of starting material and by-products were obtained. When tetrahydrofuran-ether was used, a substance melting at 103-103.5°C was isolated from the reaction mixture after four recrystallizations from carbon tetrachloride.

Bis(N-methyl)2,2,3,3,4,4-hexafluoropentanediamine hydrochloride was prepared by passing anhydrous hydrogen chloride through an ether solution of the fluorinated diamine. Recrystallization of the precipitate from ethanol-ether gave white crystalline product; m.p. 213°-215° (d).

Analysis for $C_7H_{13}F_6N_2Cl$:

Calcd. Cl, 12.91
Found. Cl, 12.62

When the above salt was dissolved in methanol and treated with further hydrogen chloride, a precipitate was collected which analyzed low in chlorine for the dihydrochloride salt.

Analysis for $C_7H_{14}F_6N_2Cl_2$:

Calcd. Cl, 22.83
Found. Cl, 22.01

Preparation of Bis(N-ethyl)2,2,3,3,4,4-hexafluoropentanediamine - In a 3-necked 5-l. flask fitted with a stirrer, condenser, dropping funnel, and protected from atmospheric moisture, was placed 1800 ml. of anhydrous ether and 25 g. (.66 mole) of lithium aluminum hydride. The mixture was stirred for approximately one hour whereupon a slurry of 40 g. of bis(N-ethyl)perfluoroglutaramide in 1200 ml. of anhydrous ether was added dropwise so as to maintain a slow but constant reflux of the ether. After the addition, the reaction mixture was heated at reflux for 3 days with the stirring maintained. The excess lithium aluminum hydride was destroyed by the cautious dropwise addition of water. After filtration and drying of the ethereal solution, anhydrous hydrogen chloride was added until no more precipitate formed. The precipitate, 20 g., melted 243-245° with decomposition.

The free base was obtained by treating the hydrochloride salt with 30% sodium hydroxide solution followed by extracting the mixture with five 100 ml. aliquots of ether. After drying, filtering, and removal of the ether, the residual yellow oil, b.p. 46°C at .05 mm, $N_D^{27} = 1.3864$.

Analysis for $C_9F_6H_{16}N_2$:

Calcd. C, 40.60; H, 6.02; N, 10.53; F, 42.86
Found. C, 40.86; H, 6.11; N, 10.23; F, 42.92

Preparation of Bis(N-isopropyl)2,2,3,3,4,4-hexafluoropentanediamine -

The preparation was run similarly to the synthesis of bis(N-ethyl)2,2,3,3,4,4-hexafluoropentanediamine. The hydrochloride salt browned slightly at 155°C and finally melted at 245-247°C. The neutralization of hydrochloride by 30% sodium hydroxide solution, extraction with ether, drying, and removal of ether gave the diamine as the residue. This was distilled to give a 41.4% yield of a slightly yellow oil of b.p. 66°C (0.43 mm.) $N_D^{26} = 1.3924$.

Analysis for $C_{11}H_{20}N_2F_6$

Calcd: C, 44.90; H, 6.80; N, 9.56; F, 38.78
Found: C, 44.98; H, 7.13; N, 9.75; F, 38.67

Preparation of Bis(N-n-butyl)2,2,3,3,4,4-hexafluoropentanediamine -

The preparation was run similarly to the synthesis of bis(N-ethyl)2,2,3,3,4,4-hexafluoropentanediamine. The hydrochloride salt melted at 250°C with decomposition. After removal of the hydrochloride salt, evaporation of the solvent from the ether filtrate yielded 29% of the starting material. Neutralization of the hydrochloride salt in the same manner as in the preparation of bis(N-ethyl)2,2,3,3,4,4-hexafluoropentanediamine yielded 39.8% of a water white oil, b.p. 70°C/0.5 mm, $N_D^{25} = 1.4038$.

Analysis for $C_{13}H_{24}N_2F_6$

Calcd: C, 48.45; H, 7.45; N, 8.70; F, 35.40
Found: C, 48.50; H, 7.80; N, 8.89; F, 35.38

Preparation of Bis(N-tert-butyl)2,2,3,3,4,4-hexafluoropentanediamine -

The preparation was similar in all respects to synthesis of bis(N-ethyl)2,2,3,3,4,4-hexafluoropentanediamine. The hydrochloride was a yellowish sticky material and no strenuous attempt was made to obtain its melting point. The freshly distilled amine was a water white oil, b.p. 67°C (0.37 mm.) $N_D^{26} = 1.4020$, 39.2%. From the ether filtrate after removal of the hydrochloride salt was obtained 25% of the starting material.

Analysis for $C_{13}H_{24}N_2F_6$

Calcd: C, 48.45; H, 7.45; F, 35.40; N, 8.70
Found: C, 48.80; H, 7.72; F, 35.69; N, 8.97

Preparation of Bis(N-fluoroalkyl)2,2,3,3,4,4-Hexafluoropentane-
diamine and Precursors

Preparation of Perfluorobutylamide - Ammonia gas was bubbled into an ice-bath cooled solution of 400 ml. of anhydrous ether and 139 g. (0.575 mole) of ethylperfluorobutyrate. After the addition, the solvent was distilled off to yield 86 g. of product m.p. 103-105°C (70%); m.p. 105°C reported.⁷

Preparation of 1,1-dihydroperfluorobutylamine - In 1200 ml. of anhydrous ether in a 3-l. 3-necked round bottom flask fitted with a stirrer, condenser, dropping funnel, and protected from atmospheric moisture was dissolved 20.4 g. (.536 mole) of lithium aluminum hydride. To the ether solution was added dropwise a solution of 40 g. (0.188 mole) of perfluorobutyramide dissolved in 450 ml. of anhydrous ether. The addition was slow so that an even controlled reflux of the ether was maintained. After addition, the reaction mixture was stirred overnight at room temperature.

Excess lithium aluminum hydride was destroyed by the cautious dropwise addition of water. The reaction mixture was filtered from the inorganic salts. The filtrate was dried over anhydrous magnesium sulfate and filtered. Hydrogen chloride gas was bubbled into the reaction solution. This yielded 37 g., (83.7%) of hydrochloride salt which sublimes from 206°-230°C.

The free base was obtained by neutralization with 15% sodium hydroxide solution followed by ether extraction of the amine. The ether extracts were dried over anhydrous magnesium sulfate, filtered and the ether removed to yield the amine residue which was distilled.

Preparation of Bis(N-n-1,1,-dihydroperfluorobutyl)perfluoroglutaramide - To an ether solution containing 150 ml. of ether and 49 g. (0.246 mole) of N-1,1-dihydroperfluorobutylamine (obtained in the neutralization of the amine hydrochloride salt with 15% sodium hydroxide followed by ether extraction and drying of the ether extracts over anhydrous magnesium sulfate) was added slowly dropwise 16.12 g. (0.058 mole) of perfluoroglutaryl chloride. Upon completion of the addition, 100 ml. of tetrahydrofuran was added to dissolve the diamide. The reaction mixture was allowed to stand overnight and filtered the next morning to remove 33.5 g. of n-1,1-dihydroperfluorobutylamine hydrochloride. The filtrate was evaporated down to yield 13 g., 45% of the residue believed to be the diamide, m.p. 135-136°C.

Preparation of Bis(N-n-1,1-dihydroperfluorobutyl)2,2,3,3,4,4-hexafluoropentanediamine - In 800 ml. of anhydrous ether was dissolved 10.6 g. (0.279 mole) of lithium aluminum hydride, and to this mixture was added dropwise with stirring, using the usual precautions for this type of reaction, 24 g. (0.0399 mole) of bis(N-n-1,1-dihydroperfluorobutyl)glutaramide dissolved in 400 ml. of anhydrous ether. After addition, the reaction was heated at reflux for 64 hours. Excess lithium aluminum hydride was destroyed by the cautious addition of water, followed by filtering off the inorganic salts. The filtrate was dried over anhydrous magnesium sulfate, filtered to remove the drying agent, and dry hydrogen chloride gas bubbled into the ether solution. This yielded 18 g. of hydrogen chloride salt which browned at 170°C and melted to a brown liquid at 180°C.

The hydrogen chloride salt was treated with 15% sodium hydroxide solution and extracted 3 times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered and the ether evaporated off. The residue distilled at 72°C (.04 mm.) to yield 12 g., 52.5%, $N_D^{25} = 1.3278$.

B. POLYMERS

The methods and techniques employed in the preparation and characterization of the linear polyesters have been described previously.¹

Viscometer tubes and methods described by Flory⁶ for the determination of melt viscosities (η) and molecular weights (M_n), etc. of hydrocarbon polyesters were applied in this work to the fluorine-containing polyesters. Intrinsic viscosities were measured in chloroform at 30°C, and related to number average molecular weights as determined above.

Dilatometer measurements were performed on the fluorinated polyesters using General Electric Silicon Oil SF-81(40) as the confining liquid.

Polymerization of Dimethylperfluoroglutarate and Bis(N-alkyl) 1,6-Hexanediamine

Poly-Bis(N-methyl) hexamethyleneperfluoroglutaramide - Into a polymerization tube fitted with a Claisen adapter, a nitrogen inlet tube, condenser, Barrett water trap, and drying tube was placed 11.8138 g. of dimethylperfluoroglutarate and a stoichiometric equivalent (6.3477 g.) of bis (N-methyl)1,6-hexanediamine, as well as 5 ml. of dry redistilled tetrahydrofuran which was used to wash the reactants from the weighing vessels and sides of the tube.

In order to obtain mechanical mixing of the reactants, purified nitrogen was bubbled into the polymerization tube. A rapid reaction with heat evolution ensued which within 15 minutes resulted in a very viscous reaction mixture. To slow the reaction, cooling was instituted during the initial 15 minutes of reaction.

After the initial heat surge the viscous liquid was immersed in an 85°C bath for 3 hours, followed by 1 hour at 120°C, 1 hour at 150°C, $\frac{1}{2}$ hour at 202°C. A high vacuum was applied at 200°C to the reaction mixture for 15 minutes, and then at 225°C for 1 hour.

The polymer was a dark brown gum with a brittle point of approximately 29°C and a melt viscosity of 86.5 poises at 110°C.

The polymer was heated at 205°C with nitrogen bubbling through the tube for 2 hours, and the melt viscosity increased to 317 poises at 205°C. Further heating at 205°C with nitrogen bubbling through the tube resulted in further increased viscosity beyond the range of measurement of the viscometer tubes.

Poly-Bis(N-ethyl) hexamethyleneperfluoroglutaramide - To 10.8526 g. of dimethylhexafluoroglutarate was added a stoichiometric quantity 6.9651 g. of bis(N-ethyl)1,6-hexanediamine, as well as 6 ml. of dry ether which was used to wash the reactants from the weighing vessels and sides of the tube. No immediate reaction was noted probably due to lack of mixture. The polymerization tube was placed in an oil bath at 63°C with a nitrogen bubbler in operation for 3 hours after which time the reaction mixture had

become quite viscous with very slight discoloration. The reaction temperature was raised to 80° for 1 hour resulting in further discoloration and increased viscosity. Three ml. of o-dichlorobenzene were added. Polymerization was continued for 1 hour more at 95°C, before discontinuing the heating of the polymerization mixture for 16 hours.

The next morning the polymerization tube was heated to 105°C under nitrogen for $\frac{1}{2}$ hour then subjected to high vacuum to remove solvent, giving a brown colored polymer with a melt viscosity of 54.2 poises. The polymer was heated to 140°C for 2 hours, under nitrogen (bubbler), followed by drawing a high vacuum on the polymer to give a brown gum with a melt viscosity of 104 poises and a brittle point of +5°C.

In another run the temperature was raised from 105°C to 160°C for 3-4 hours under nitrogen with a large increase in viscosity as well as increased discoloration of the polymer. This was followed by 2 hours more at 170°C followed by reduced pressure removal of solvent. The polymer was initially of greater viscosity than the one previously made, but on attempting to build up the molecular weight at 205°C with a nitrogen purge (bubbler) the polymer became less viscous with chunks of polymer which clogged up the viscometer tubes making melt viscosity determination impossible. This occurred even though basic material was evolved from the reaction mixture.

Poly-Bis(N-butyl)hexamethyleneperfluoroglutaramide - The methods and techniques employed in polymerization of this polymer are similar to the previously described polymerization of dimethylperfluoroglutarate and bis(N-methyl)1,6-hexanediamine.

To 7.0234 g. of dimethylhexafluoroglutarate was added a stoichiometric quantity or 5.9751 g. of bis(N-n-butyl) 1,6-hexanediamine, as well as 6 ml. of dry ether which was used to wash the reactants from the weighing vessels and sides of the tube. Reaction was noted as heating commenced and solid formed which was not initially soluble in the reaction mixture.

<u>Bath Temp.</u>	<u>Time</u>	<u>Operation of N₂Bubbler</u>	<u>Remarks</u>
R.T.	0	Yes	Reaction noted
58°	25 min.	Yes	
78°	1 hr. 15 min.	Yes	
93°	2 hrs. 45 min.	Yes	Thickening of Reaction Mixture
130°	4 hrs. 0 min.	Yes	3 ml. o-dichlorobenzene added
150°	4 hrs. 30 min.	Yes	
150°	6 hrs. 30 min.	Yes	Polymer still light in color
Left standing at room temperature for 16 hours			
150°	0	Yes	
160°	1 hr.	Yes	Polymer turning brown in color
170°	2 hrs.	Yes	Further darkening but large increase in viscosity of resin
190°	3 hrs. 30 min.	Yes	
190°	4 hrs. 30 min.	Yes	High vacuum pulled on resin to rid polymer of solvent

It was noted that the high vacuum also tended to draw off a basic white vapor. The polymer was a dark brown gum with a melt viscosity of 159.3 poises a brittle temperature of +20°C.

Polymerization of Adipyl Chloride and Bis(N-methyl)2,2,3,3,4,4-Hexafluoropentanediamine

Poly-Bis(N-methyl)2,2,3,3,4,4-hexafluoropentamethyleneadipamide -
The preparation of fluorine-containing polyamides by two general methods utilizing bis(N-methyl)2,2,3,3,4,4-hexafluoropentanediamine and adipyl chloride was investigated.

Method I:

Stoichiometric amounts of the diamine were added to adipyl chloride resulting in the immediate formation of a white precipitate. Anhydrous ether was used to rinse out flasks and to aid in stirring the salt. A solvent, selected from either the aromatic, chloroaromatics, chloroform, or esters, was then added to the mixture and nitrogen was bubbled through the flask. Reaction temperature was raised to the reflux temperature of the mixture and held until no further hydrogen chloride evolution was noted. The solvent was then removed under reduced pressure leaving the polymer in the flask. Higher temperatures and more polar solvents caused faster reaction, but too high a temperature resulted in some decomposition as noted by the black color of the polymers.

Method II:

The initial polymerization was carried out as above in chloroform, and then 2 moles of pyridine per mole of adipyl chloride was added to the reaction mixture. The mixture was heated at 62°C for 24 hours and then at 90°-95°C for a further 24 hours. The solvent was removed under reduced pressure leaving the polymer in the flask. Pyridine odor of the polymer was removed by dissolving in methanol and precipitating with water.

The polyamides prepared by the latter method appeared to be, in general, higher in molecular weight than those prepared without pyridine addition. Brittle temperatures of the polymers varied from about -15°C to 15°C. They are brown, viscous liquid and gum-like materials of low to apparently moderately high molecular weights.

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APPENDIX I

SUB-CONTRACT WORK PERFORMED AT PURDUE UNIVERSITY

Research on the synthesis of certain difunctional compounds containing fluorine, or fluorine in combination with hetero atoms interspersed in the carbon chain, such as sulfur, oxygen, and nitrogen, has been performed at the Department of Chemistry and Purdue Research Foundation, Purdue University, under sub-contract to Hooker Electrochemical Company. In general, novel fluorocarbon compounds considered desirable as starting materials for polymer reactions for this project, at the present stage, consist of dicarboxylic acids from which the corresponding dicarboxylic acid chlorides can be made. It was considered important to investigate the effects produced on the polymers after polymerization of compounds such as those containing fluorine on pendent groups attached to the linear chain as well as those containing fluorine directly on the linear chain, but not alpha or beta to the carbonyl function.

This appendix comprises the summary report of the research performed at Purdue University under sub-contract to Hooker Electrochemical Company during the 1957 contract year.

Summary Progress Report

FLUORINE CONTAINING MONOMERS

FOR CONDENSATION POLYMERS

Earl T. McBee

Department of Chemistry and The Purdue Research Foundation

Purdue University

December 1, 1956 to November 1, 1957

Subcontract with the

Hooker Electrochemical Company

Niagara Falls, New York

on

Contract AF 33(616)-2421 RDO No. 617-11 SR3N

Task Number 73404

FOREWORD

This summary progress report was prepared by the Department of Chemistry, Purdue University on work concerned with the investigation and development of new fluorine-containing monomers suitable for condensation type polymers. This work was performed on a subcontract with the Hooker Electrochemical Company as part of Contract AF 33(616)-2421, RDO No. 617-11 SR-3N, Task Number 73404.

The personnel assigned to this project were Mr. Gordon Wilson, Jr. (2 months only), Mr. L. David Moore, and Mr. Abraham E. Martin under the direct supervision of Dr. E. T. McBee.

Abstract

A. Sulfur Containing Monomers

1. The exhaustive chlorination of thiophene has produced hexachloro-3-thiolene in yields of 88-93%.

2. The reaction between hexachlorothiolenene and antimony trifluoride catalyzed with antimony pentachloride has produced 2,2,5,5-hexafluoro-3,4-dichloro-3-thiolene in a 59% yield and 2,5-difluoro-3,4-dichlorothiophene in a 21% yield.

3. The attempted oxidations of tetrafluorodichlorothiolenene to perfluorothiodiglycolic acid with basic permanganate or acidic dichromate solutions have not been successful.

B. Oxygen-Containing Monomers

1. Hexachlorofuran has been prepared in a 47% yield by the chlorination of furan at -60°C followed by exhaustive chlorination at room temperature.

2. No tetrafluorodichlorofuran has been isolated from exchange reactions on hexachlorofuran with antimony trifluoride.

3. Diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate has been prepared in a 63.5% conversion by the action of ethyl bromoacetate on the disodium salt of hexafluoropentanediol.

4. 5,5,6,6,7,7-Hexafluoro-3,9-dioxaundecanedioic acid has been prepared from the ester in an 87.9% yield by ester interchange with formic acid.

5. 5,5,6,6,7,7-Hexafluoro-3,9-dioxaundecanedioyl chloride has been prepared from the acid in an 84.6% yield by the use of thionyl chloride.

6. 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanenitrile and 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedinitrile have been prepared in conversions of 10.3% and 32.6% respectively by the cyanoethylation of hexafluoropentanediol.

7. Diethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate has been prepared in a 59.8% conversion by the ethanolysis of the corresponding dinitrile.

8. The hydrazide of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioic acid has been prepared in a 60.3% conversion by the action of hydrazine hydrate on the corresponding diethyl ester.

C. Nitrogen Containing Monomers

1. Diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate has been prepared by treating ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl bromoacetate and anhydrous potassium carbonate in a sealed tube.

D. Carbon-Chain Monomers

1. All attempts to prepare ethyl trifluoropropionate by the interaction of silver trifluoroacetate and ethyl iodoacetate have produced ethyl trifluoroacetate as the only identified product. This reaction was, therefore, never attempted on silver perfluoroglutarate.

2. A mixed ester condensation between diethyl perfluoroglutarate and ethyl acetate has produced diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelaate in a 6% conversion and diethyl 3-keto-4,4,5,5,6,6-hexafluoropimelate in a 20% conversion. The yields were 6.5% and 21.5% respectively.

3. Perfluoroglutaryl chloride has been prepared from perfluoroglutaric anhydride in an 85% yield.

4. Diethyl 3,3,4,4,5,5-hexafluoropimelate has been prepared from perfluoroglutaryl chloride in a 43% yield by the Arndt-Eistert synthesis.

5. 3,3,4,4,5,5-Hexafluoropimelic acid has been prepared from its diethyl ester by acidic hydrolysis in an 82% yield.

6. Perfluoroglutaryl chloride and ethyl sodiomalonate have been reacted to produce diethyl 2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelaate in a 28.6% yield. This reaction also produced a substance thought to be 1,1,-dicarbethoxy-2,6-diketo-3,3,4,4,5,5-hexafluorocyclohexane in a 58% yield.

7. 1,3-Dibromo-1,1,2,2,3,3-hexafluoropropane has been prepared by a Hunsdiecker reaction on silver perfluoroglutarate.

8. Several attempts have been made to react hexafluorodibromopropane with ethyl sodiomalonate. The desired adduct was produced only in extremely small yields.

9. The reaction between hexafluorodibromopropane and the silver salt of diethyl malonate is now being investigated.

E. Repeated Preparation

1. Perfluoroglutaric acid has been prepared by the established procedure.

2. Diethyl perfluoroglutarate has been prepared by an improved method.

3. Hexafluoropentanediol has been prepared by the established procedure.

4. Yields for 3,3,4,4,5,5-hexafluoro-2,6-heptanediol have been established.

Summary and Conclusions

A major portion of this contract period has been spent in the preparation of starting materials and the development of new syntheses for the preparation of fluorine-containing difunctional monomers.

Major new efforts are being directed at the development of successful syntheses for the preparation of diacids and diols having fluorine in the backbone. In particular, satisfactory methods are being developed for compounds of the following general structure:

1. $\text{HOOCCH}_2\text{CH}_2(\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{COOH}$
2. $\text{HOOCF}_2\text{SCF}_2\text{COOH}$
3. $\text{HOOCF}_2\text{OCF}_2\text{COOH}$

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DISCUSSION

A. Sulfur-Containing Monomers

It has been thought that the interruption of the series of CF_2 groups in the backbone of a polyester chain by the introduction of a freely rotating group such as an atom of sulfur would give the resultant elastomer better low temperature properties. With this purpose in mind, it was decided to prepare perfluorothioldiglycolic acid by the oxidation of the double bond in 2,2,5,5-tetrafluoro-3,4-dichloro-3-thiolene. This thiolene was successfully prepared by an exchange reaction on hexachlorothiolenes using antimony trifluoride. Attempts to oxidize this compound with the use of basic permanganate and acidic dichromate have given oxidative cleavage at the double bond and also at the sulfur atom. No acidic material has been isolated from either of these experiments. The catalytic oxidation performed on this compound at the Hooker Electrochemical Company has not been fully investigated at this time.

B. Oxygen-Containing Monomers

Perfluorodiglycolic acid would possibly give the same desirable low-temperature characteristics as perfluorothioldiglycolic acid. In order to prepare this acid, furan was chlorinated to hexachlorofuran. No successful synthesis has yet been found to convert this compound to the desired tetrafluorodichlorofuran.

Diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate was prepared by reacting the disodium salt of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol with ethyl bromoacetate, using dioxane as solvent. Because the commercially available dioxane contains some sodium sensitive impurities, it was necessary to purify the dioxane before use by refluxing over sodium for several hours and subsequently distilling. The diester was prepared for use as an intermediate in the synthesis of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioyl chloride. A sample of the acid chloride was sent to Hooker Electrochemical Company.

Cyanoethylation of hexafluoropentenediol produces mainly the mono-adduct. However, it is possible to convert some of the mono- to the di-adduct by further reaction with more acrylonitrile in ether as solvent and aqueous potassium hydroxide as catalyst.

Diethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate was prepared by the alcoholysis of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedinitrile. This compound has been prepared and characterized before¹. Although a 59.8% conversion to the desired product is claimed in this report, it is quite possible that the final fractions contain both the diethyl ester and the dinitrile. The infrared spectra taken on a sample of the diethyl ester prepared by alcoholysis of the dinitrile indicated trace amounts of the dinitrile still present. The boiling points and indices of refraction for these two compounds are very close.

The method of L.A. Carpino² seems to be a possible synthetic route to the desired 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioyl chloride. The method depends on the fact that hydrazides can be converted to the corresponding acid chlorides. The reaction is conducted by successively passing hydrogen chloride gas and chlorine through a solution of the hydrazine in nitromethane or nitroethane as solvent. The hydrazide of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioic acid has already been prepared. In order to learn the experimental techniques involved and check the possibilities of the reaction on dihydrazides, the reaction was carried out on a sample of succinic dihydrazide which was prepared from diethyl succinate. When the reaction was carried out, only a 30.3% conversion to succinyl chloride was obtained. The relatively low conversion was probably due to failure to solubilize the hydrazide completely, and possibly also due to the use of too little chlorine and/or hydrogen chloride.

C. Nitrogen-Containing Monomers

The only nitrogen-containing monomer prepared during this contract period was diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate which was prepared by heating ethyl 3-methyl-4,4,5,5,6,6,6-heptafluorohexanoate with ethyl bromoacetate and anhydrous potassium carbonate in a sealed tube.

D. Carbon-Chain Monomers

The primary interest in carbon-chain monomers is in the preparation of dibasic acids which contain a methylene "cushion" between the carboxylic acid group and the perfluorinated part of the molecule. Such acids would give esters or polyesters which would be much more resistant to hydrolysis than the esters or polyesters of perfluoroacids. The only previous work which has been done in preparing a homologous series of perfluoroacids, has been by the use of the Arndt-Eistert synthesis³, but since this synthesis requires the acid chloride as a starting material, it could not be applied to perfluoroglutaric acid without first preparing perfluoroglutaryl chloride. Many attempts previously have been made to prepare this compound, but none have been successful^{4,5}. It therefore seemed as if unusual synthetic routes were necessary to prepare the desired acids. One of these synthetic routes was the investigation of the reaction between the silver salt of a perfluoroacid such as silver trifluoroacetate and ethyl iodoacetate under free radical conditions in hopes of getting a Hunsdiecker-type reaction. Since ethyl trifluoroacetoxyacetate was the only product obtained from this reaction, this synthesis route was not applied to silver perfluoroglutarate.

A mixed ester condensation between diethyl perfluoroglutarate and ethyl acetate could possibly give diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate which could then be reduced to diethyl hexafluoroazelate. This acid would have the carboxylic acid groups cushioned from the perfluorinated group by two methylene groups and thus should give a hydrolysis-resistant polyester. This mixed ester condensation was attempted several times. A great amount of tarry polymeric material was formed each time, and a great amount of ethyl acetoacetate and higher non-fluorinated esters were produced. The

best yields of the fluorinated mono-condensate and the di-condensate that were obtained were respectively 21.5% and 6.5%. An attempt to reduce the di-condensate by the Clemmenson procedure was not successful.

Perfluoroglutaryl chloride has been successfully prepared in yields of 85% by the action of oxalyl chloride on perfluoroglutaric anhydride. This acid chloride has been converted into diethyl hexafluoropimelate in yields of 41-43% by means of the Arndt-Eistert synthesis. Acid hydrolysis of this ester has produced the acid in an 82% yield.

In order to prepare hexafluoroazelaic acid in somewhat better yields than could be obtained by means of the procedure involving the mixed ester condensation, perfluoroglutaryl chloride was reacted with ethyl sodiomalonate. This reaction has produced two products: diethyl 2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate in a 29% yield and a lower boiling material which is thought to be 1,1-dicarbethoxy-2,6-diketo-3,3,4,4,5,5-hexafluorocyclohexane in a 58% yield. The first compound would result from simultaneous attack on both chlorine atoms by separate ethyl malonate ions; the second would result from attack by one ethyl malonate ion, the second chlorine being displaced by the second hydrogen on the attached ethyl malonate group. The geometry of the six membered ring and the increased acidity of the hydrogen atom which is now alpha to a ketone as well as two carbethoxy groups makes this a very feasible reaction. The IR spectra shows ester groupings, carbonyls, C-F and C-H bonds. The elemental analysis has not as yet confirmed the proposed structure for this material. It is now being hydrolyzed and reduced in hopes of preparing 1,5-dihydroxy-2,2,3,3,4,4-hexafluorocyclohexane, a glycol which might give a polyester with improved low temperature properties. An attempt has been made to reduce the straight chain diketone catalytically using a palladium on charcoal catalyst. This attempt was not successful. A modified Wolff-Kishner reduction was also unsuccessful since the strong base employed removed fluorine from the molecule.

Another possible synthetic route for hexafluoropimelic acid would be by preparing the dibromohexafluoropropane from the silver salt of perfluoroglutaric acid by means of a Hunsdiecker reaction, and then performing a malonic ester synthesis on this halide. 1,3-Dibromo-1,1,2,2,3,3-hexafluoropropane was prepared by the method of Hauptschein⁶. Its reaction with ethyl sodiomalonate has been tried at various temperatures in diethyleneglycol, dimethyl sulfoxide, and ethyl alcohol. The reaction in ethyl alcohol gave small amounts of a viscous oil distilling at about 160°C under 1 mm. pressure. This oil can be hydrolyzed to hexafluoropimelic acid. The yield represented by this oil is only about 5%. Since silver salts are often superior to sodium salts in displacing halogens, silver diethyl malonate was prepared by precipitation from an aqueous mixture of ethyl sodiomalonate and silver nitrate. The reaction between this salt and dibromohexafluoropropane is now being investigated.

E. Repeated Preparations

Fairly large amounts of perfluoroglutaric acid have been prepared by the basic permanganate oxidation of hexafluorodichlorocyclopentene in the usual manner. This acid was used to prepare diethyl perfluoroglutarate by an improved method, to prepare perfluoroglutaryl chloride by the use of perfluoroglutaric anhydride as an intermediate, and to prepare dibromohexafluoropropane by means of the silver salt of perfluoroglutaric acid.

Fairly large amounts of hexafluoropentanediol have been prepared in the usual manner. This glycol was used in the preparation of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioyl chloride. Definite yields recently have been determined for the previously reported 3,3,4,4,5,5-hexafluoro-2,6-heptanediol.

EXPERIMENTAL

A. Sulfur Containing Monomers

1. Preparation of 2,2,3,4,5,5-hexachloro-3-thiolene - The procedure used is essentially that of Coonradt and Norris.⁷ Thiophene (840 grams, 10.0 moles) and 10 grams of iodine crystals were placed in a 2-liter, 3-necked round-bottomed flask fitted with stirrer, thermometer and gas inlet tube, and reflux condenser which was connected to a gas wash bottle containing water. The gas inlet tube was connected to a gas wash bottle containing concentrated sulfuric acid which was, in turn, connected to a cylinder of chlorine. The chlorine was introduced to the well stirred thiophene-iodine solution at such a rate that the reaction temperature could be maintained at 40-60°C. by means of an ice bath. After 3 1/2 hours, the reaction temperature started dropping to 40°C and continued to drop below this temperature even after the removal of the ice bath. This signalled the completion of the reaction. The resultant liquid was dissolved in twice its volume of ether, washed twice with water, twice with 5% potassium carbonate solution, twice with a 5% sodium thiosulfate solution, and twice with water. The resultant ethereal solution was dried over anhydrous magnesium sulfate and evaporated on a steam bath. The residue material was distilled in vacuo and the product collected at 104-108°C under 4-5 mm. pressure.

2. Preparation of 2,2,5,5-tetrafluoro-3,4-dichloro-3-thiolene and 2,5-difluoro-3,4-dichlorothiophene - Hexachlorothiolenene (400 grams, 1.365 moles), antimony trifluoride (400 grams, 2.235 moles, 23% excess of theory) and catalytic amounts (a few drops) of $SbCl_5$ were placed in a 2-liter, 3-necked, round bottomed flask fitted with stirrer, thermometer, and reflux condenser. An exothermic reaction began immediately and in 15 minutes the reaction temperature had reached 70°C where dense white fumes were given off. The reaction temperature continued to rise to 75°C where a violent refluxing began which had to be controlled by a water-cooled bath. The mixture was kept at gentle reflux (about 55°C) for as long as the reaction continued (about one hour). After the reaction had subsided, the mixture cautiously was heated with stirring to 90°C and held there for an additional 45 minutes. An additional amount of dense white fumes (small in volume compared to the first evolution) and a small amount of refluxing occurred during this heating period. Total reaction time was about two hours.

The resultant dark brown organic liquid was decanted from the inorganic salts. The salts were extracted with benzene until white. The benzene washings were combined with the decanted organic liquid, washed with 17% HCl until the HCl washings showed no salt precipitation when diluted with water (usually two washings were sufficient) and washed with water. The benzene was removed by distillation at atmospheric pressure. The residue was distilled and two distinct products were obtained. At 214-215°C, a bright yellow oil distilled over which crystallized out when it came in contact with the cold parts of the distillation apparatus. From 216°C to 219°C, this solid material was mixed with another oil which doesn't crystallize at room temperature. At 220-222°C, only liquid distills over. The crystalline

material was separated and recrystallized twice from petroleum ether to give white plates having a melting point of 86°C. This material is 2,5-difluoro-3,4-dichlorothiophene. The yield is 54.0 grams or 21%. The liquid was redistilled at 72°C under 1.5 mm. pressure. This material is 2,2,5,5-tetrafluoro-3,4-dichloro-3-thiophene. The yield is 185 grams or 58.4%.

Analysis for $C_4Cl_2F_2S$

Calcd: C, 25.4%; H, 0.0%; Cl, 37.6%
Found: C, 25.2%; H, 0.0%; Cl, 37.8%

Analysis for $C_4Cl_2F_4S$

Calcd: C, 21.2%; H, 0.0%; Cl, 31.4%
Found: C, 21.4%; H, 0.0%; Cl, 31.5%

3. Attempted oxidation of tetrafluorodichlorothiophene to perfluorothiodiglycolic acid - Tetrafluorodichlorothiophene (22 grams, 0.097 mole), potassium permanganate (20.4 grams, 0.129 mole), sodium bicarbonate (21.7 grams, 0.258 mole), and water 100 ml) were placed in a 500 ml, 3-necked, round bottomed flask fitted with stirrer and reflux condenser. The mixture was stirred and refluxed for 48 hours. At the end of this period, no more gas was emitted from the reaction mixture. The mixture was cooled and acidified with 45 ml concentrated sulfuric acid in 50 ml of water. The mixture was filtered with suction to remove the insoluble manganese dioxide. A two-layer liquid system resulted. The organic layer was separated and identified as 10.6 grams of recovered starting material (48.2% recovery.) The aqueous layer was extracted several times with ether. The ether extracts were dried and distilled at atmospheric pressure. No organic materials were extracted by the ether. Evaporation of the aqueous layer left only a deposit of inorganic salts (sodium sulfate). When a similar oxidative attempt was made substituting sodium hydroxide for sodium bicarbonate, a gaseous evolution was still observed. This gaseous evolution gives a precipitate with a barium hydroxide solution. Thus these oxidation attempts seem to have exhaustively oxidized the ring compound. Similar results were noted when acidic dichromate was used as the oxidizing medium.

B. Oxygen-Containing Monomers

1. Preparation of 2,2,3,4,5,5-hexachlorofuran - Furan (248 grams, 3.65 moles) and 1500 grams of methylene chloride were placed in a 2-liter, 3-necked, round-bottomed flask fitted with stirrer, reflux condenser, and rubber stopped containing a gas inlet tube and a low temperature (-100 to +50°C) thermometer. The gas inlet tube was connected to a gas wash bottle filled with concentrated sulfuric acid which was connected to a chlorine cylinder. The flask was placed in a well insulated acetone-dry ice bath and the charge was cooled with stirring to -60°C. Chlorine was introduced to the well stirred mixture at such a rate that the reaction temperature could be maintained at -55 to -60°C. It was possible to introduce the gas at about 1400 ml/minute and still maintain this low temperature. After five hours, the reaction was no longer exothermic so the mixture was allowed to

warm slowly with stirring to room temperature. At -30°C , the excess chlorine was passed out of the reaction mixture. The mixture warmed to room temperature without any visible polymerization occurring, although the mixture had darkened slightly. The methylene chloride was distilled off at atmospheric pressure at head temperatures of $30-46^{\circ}\text{C}$. The head temperature then jumped rapidly to 80°C , remained there for a very short time and then rapidly climbed to 145°C . These head temperatures correspond to the boiling points of dichlorofuran (80°C) and tetrachlorofuran (145°C). A clear, slightly yellow oil (436 grams) distilled at $145-200^{\circ}\text{C}$. This is probably a mixture of tetra- and hexa-chlorinated furans. It does not polymerize when chlorine is introduced at room temperature indicating that all the hydrogen has been removed from the furan ring. This oil was placed back in the chlorinating apparatus described above and chlorinated at temperatures up to 70°C . After three hours of rapid chlorination (again about 1400 ml/minute) the exothermic reaction stopped. The oil was distilled at atmospheric pressure to give no boiling material and 471 grams (47% yield) of a clear, slightly yellow oil at $207-213^{\circ}\text{C}$. This oil is essentially 2,2,3,4,5,5-hexachlorofuran although small amounts of the 2,2,3,3,4,5-hexachlorofuran isomer are present.

2. Attempted preparation of tetrafluorodichlorofuran - Hexachlorofuran (100 grams, 0.361 mole) and antimony trifluoride (120 grams, 0.67 mole - a 40% excess) were placed in a 500 ml, 3-necked, round-bottomed flask fitted with a stirrer, a thermometer, and a reflux condenser. A catalytic amount of antimony pentachloride was added and the solution immediately became black and tarry. No exothermic reaction occurred, so the material was heated with stirring to 85°C and held at this temperature for two hours. The material was very tarry in appearance. It was extracted with several volumes of benzene. The benzene solution was washed with 17% HCl and water and distilled. Approximately 4 grams of a yellow oil distilled at $135-155^{\circ}\text{C}$. The residual tarry material which was not extracted by benzene was insoluble in benzene, ethyl ether, and several other organic solvents. Its weight corresponds to about 96% of the weight of the reacting materials.

3. Preparation of diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate - In a two-liter, three-necked flask equipped with a stirrer, and a 35 cm. Bigreux column connected to a total reflux distillation head were placed 42.4 grams (0.2 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, 320 ml of dioxane, and 9.2 grams of sodium dissolved in 300 ml of absolute ethyl alcohol. The ethyl alcohol was removed by distillation. A solution of 66.8 grams (0.4 mole) of ethyl bromoacetate in 150 ml of dioxane was added and the mixture refluxed for five hours. The dioxane was removed by distillation and the residue was taken up in benzene. The benzene solution was washed several times with water. The benzene was dried over drierite, stripped off, and the residue distilled to give 48.8 grams of the desired product, b.p. $142-149$, $n_{\text{D}}^{21.5}$ 1.3990. This represents a 63.5% conversion to the diester. D

4. Preparation of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioic acid - A three-necked flask was fitted with a stirrer and a 35 cm. Vigreux column connected to a total reflux distillation head and charged with 44.0 grams (0.115 mole) of diethyl 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioate and 120 ml of 88% formic acid. Ethyl formate and some formic acid was removed. The reaction mixture was allowed to reflux (with stirring) for a twelve-hour period before any ethyl formate was removed. The rest of the ethyl formate was removed over a twelve-hour period. The reaction mixture was allowed to cool and the formic acid remaining was removed by means of a water aspirator and a warm-water bath.

5. Preparation of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioyl chloride - A flask fitted with a condenser was charged with 25.24 grams (0.08 mole) of 5,5,6,6,7,7-hexafluoro-3,9-dioxaundecanedioic acid and an excess of thionyl chloride. The solution was refluxed for a period of 3.5 hours. The excess thionyl chloride was taken off with the aid of a warm-water bath and an aspirator. The residue was fractionated to give 24.7 grams of the acid chloride, b.p. 106-126 at less than 1.0 mm. This represents an 84.6% yield. Purification by recrystallization from hexane gave a white solid, m.p. 52.5 (uncorrected).

6. Preparation of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedinitrile and 9-hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanenitrile - A three-necked flask was fitted with a stirrer, condenser, an addition funnel and charged with 2,000 ml of water, 4.6 grams of potassium hydroxide, and 169.6 grams (3.2 moles) of acrylonitrile. A solution of 169.6 grams (0.8 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol in 600 ml of water was put in the addition funnel and added drop-wise over a two-hour period. Stirring was continued for an additional hour. The layers were separated. The non-aqueous layer was washed with water and dried over anhydrous magnesium sulfate. Distillation gave an 11.9% conversion to the di-adduct, and a 62.7% conversion to the mono-adduct, boiling at 140-160 C/1.5 mm., n_D^{20} 1.3923.

7. Preparation of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedinitrile from 9-Hydroxy-6,6,7,7,8,8-hexafluoro-4-oxanonanenitrile - In a three-necked flask fitted with a stirrer and condenser were placed 150 ml of ether, 2 ml of 40% aqueous potassium hydroxide and 42.4 grams (0.8 mole) of acrylonitrile plus the mono-adduct from the reaction above. The mixture was stirred at room temperature for 19 hours. The ether solution was washed free of alkali and dried over anhydrous magnesium sulfate. The residue remaining after the ether was stripped off was fractionated to give an overall 32.6% conversion to the di-adduct, boiling at 186-194 C/1.5 mm., n_D^{20} 1.4040.

8. Preparation of diethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate - In a one-necked flask fitted with a reflux condenser (with a drying tube attached) was placed 100 ml of absolute ethyl alcohol and 6.23 grams of concentrated sulfuric acid. The flask was cooled and 10.0 grams (0.0314 mole) of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedinitrile was added. The solution was refluxed for a period of thirty-six hours. The solution was poured into ice water. An immiscible layer separated out immediately. This layer was separated from the aqueous layer, and the aqueous layer was

extracted with ether. The ether extracts and the previously separated layer were combined and shaken with 10% sodium bicarbonate solution. After washing several times with water, the ether solution was dried over anhydrous magnesium sulfate. The ether was removed by distillation. Subsequent fractionation of the residue gave a 59.8% conversion to diethyl 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate, boiling point, 168-170°C at 1.2 mm. pressure, n_D^{20} 1.4041.

9. Preparation of the hydrazide of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioic acid - A one-necked flask was fitted with a reflux condenser and charged with 21.9 grams (0.0533 mole) of 6,6,7,7,8,8-hexafluoro-4,10-dioxatridecanedioate, 0.14 mole of hydrazine hydrate (85% in water), and 100 ml of absolute ethyl alcohol. The solution was refluxed for a period of twelve hours. No solid was noted in the flask. The solvent was stripped off by means of an aspirator and a warm water bath. When this was done, an oil formed that would not solidify when subjected to the usual methods of crystallization. The oil was poured into cold water; however, no solid formed. The oil remained in the water overnight. The water was removed by means of a hot-water bath and an aspirator. After standing at room temperature for a day, the oil solidified to an orange, wax-like substance. Recrystallization from ethyl alcohol and petroleum ether gave 12.3 grams of material. This represents a 60.3% conversion to the hydrazide. Purification gave a white solid, melting point, 102-105°C. (uncorrected).

C. Nitrogen-Containing Monomers

1. Preparation of Diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate - Into a combustion tube were placed 20.9 grams (0.07 mole) of ethyl 3-methylamino-4,4,5,5,6,6,6-heptafluorohexanoate, 11.7 grams (0.07 mole) of ethyl bromoacetate and 11.0 grams (0.08 mole) of anhydrous potassium carbonate. The tube was sealed and heated at 125°C for 24 hours. The contents were washed from the tube with 200 ml of ether and the ether solution was washed with water and dried with magnesium sulfate. Fractionation led to 8.55 grams (40% recovery) of the methylamino ester and 9.15 grams (34% conversion, 56% yield) of diethyl 4-perfluoropropyl-3-methyl-3-azahexanedioate, b.p. 95°C (1.9 mm.), n 1.3860, d 1.298.

Analysis for $C_{13}H_{18}F_7NO_4$

Calcd: C, 40.52; H, 4.71; N, 3.64; MR_D , 69.68

Found: C, 40.46; H, 4.99; N, 3.94; MR_D , 69.70

D. Carbon-chain Monomers

1. Preparation of ethyl trifluoroacetoxyacetate - Silver trifluoroacetate (30 grams, 0.136 mole) and ethyl iodoacetate (22 grams, 0.103 mole) were placed in a 200 ml, 3-necked flask fitted with thermometer, stirrer, and reflux condenser to which was connected in series, two gas wash bottles, the first containing concentrated sulfuric acid and the second containing a saturated solution of barium hydroxide. The charge reaction was stirred and an immediate exothermic reaction took place which raised the reaction temperature to 110°C.

in the matter of a very few minutes. At this point the temperature started dropping and the reaction was considered to be complete. The mixture was cooled to room temperature and taken up in ethyl ether. The insoluble silver iodide was filtered off and the resultant liquid distilled to give 14.8 grams of a clear liquid, boiling at 154-56°C and having a refractive index (n_D^{20}) of 1.3599. This is a 74% yield of $CF_3COOCH_2COOC_2H_5$, substantiated by elemental analysis and saponification equivalent. Other reaction conditions (U. V. light, higher temperatures, etc.) have produced only this compound, and in somewhat lesser yields.

Analysis; saponification equivalent for $CF_3COOCH_2COOC_2H_5$

Calcd: 100
Found: 100.1 and 100.9

Analysis for $C_6H_7O_4F_3$

Calcd: C, 36.0%; H, 3.5%
Found: C, 36.14%; H, 4.02%

2. Preparation of diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelaate and diethyl 3-keto-4,4,5,5,6,6-hexafluoropimelate - Diethyl perfluoroglutarate (209 grams, 0.7 mole) was dissolved in 300 ml of dry benzene and the resultant solution dried over calcium hydride. It was placed in a 1-liter, 3-necked flask fitted with a reflux condenser stopped with a $CaCl_2$ drying tube, a stirrer, and an addition funnel. Ethyl acetate (185 grams, 2.1 moles) was dissolved in 200 ml of dry benzene and the resultant solution dried over calcium hydride. Sodium hydride (48 grams, 2.0 moles) was added to the diethyl perfluoroglutarate in benzene solution and the dried ethyl acetate solution was placed in the addition funnel. The charge in the flask was stirred and heated to 50°C. The ethyl acetate solution was added dropwise over a ten hour period to the well stirred diethyl perfluoroglutarate solution maintained at 50-65°C. After the addition was complete, the mixture was stirred for an additional fourteen hours. It was cooled and hydrolyzed by pouring into 1000 grams of ice and 200 grams of concentrated sulfuric acid. The resultant aqueous layer was separated and extracted twice with ether. The organic layers were combined and dried over anhydrous magnesium sulfate. Distillation gave 77 grams of ethyl acetoacetate, 16 grams recovered diethyl-perfluoroglutarate, 48 grams of a light yellow oil, b.p. 118-20°C under 6 mm. pressure, and 15 grams of a dark brown oil at 147-8°C under 6 mm. pressure. There was also obtained 41 grams of a black, tarry resinous residue. The lower boiling oil has been identified as diethyl 3-keto-4,4,5,5,6,6-hexafluoropimelate. This quantity represents a 21.5% yield. The higher boiling oil has been identified as a 6.5% yield of diethyl-3,7-diketo-4,4,5,5,6,6-hexafluoroazelaate.

Analysis; molar refractivity for $C_{11}H_{12}F_6O_5$

Calcd: 56.78
Found: 56.94

Analysis for $C_{14}F_6O_6$

Calcd: 66.04

Found: 66.46

3. Preparation of oxalyl chloride - Anhydrous oxalic acid (90 grams, 1.0 mole) and phosphorus pentachloride (416 grams, 2.0 moles) were mixed thoroughly in a 1-liter flask and allowed to stand for three days. The resultant liquid was filtered from the solid and distilled to give 66 grams (52% yield) of oxalyl chloride, b.p. 63-4°C.

4. Preparation of perfluoroglutaric anhydride - This anhydride was prepared by the method of Hauptschein⁵. The yields were 76-82% of the clear liquid distilling at 71-74°C.

5. Preparation of perfluoroglutaryl chloride - Perfluoroglutaric anhydride (124 grams, 0.56 mole) and oxalyl chloride (160 grams, 1.26 moles, a 2.25 to 1 molar ratio) were placed in a 500 ml, 1-necked, round-bottomed flask fitted with a reflux condenser to which is connected a gas wash bottle in order to observe the evolved gases. A zinc chloride catalyst was added (about 3 grams) and the resultant solution was refluxed until no more gas was evolved (about 28 hours). Careful fractionation gave 82 grams of oxalyl chloride, at 61-62°C. (a 92% recovery of the excess) and 131 grams of perfluoroglutaryl chloride at 109-110°C. This represents an 84% yield. There was also obtained 26 grams of an isomeric material boiling at 101-104°C.

Analysis for $C_5O_2Cl_2F_6$

Calcd: C, 21.6%; H, 0.0%; Cl, 25.6%

Found: C, 21.4%; H, 0.0%; Cl, 25.8%

6. Preparation of diethyl 3,3,4,4,5,5-hexafluoropimelate - An ethereal solution of diazomethane was prepared by a standard procedure.⁸ Reaction of an aliquot with benzoic acid and back titration of the excess acid showed this solution to contain 1.9 moles of diazomethane in 3 liters of ordinary ethyl ether. This solution was dried over pellets of KOH for 3 hours and filtered into a 5-liter, 3-necked flask fitted with stirrer, reflux condenser and addition funnel. All the fittings were rubber stoppers rather than ground glass. This ethereal solution was cooled to 5°C and perfluoroglutaryl chloride (111 grams, 0.4 mole) dissolved in 300 ml anhydrous ether was placed in the addition funnel. The acid chloride was added slowly to the cold diazomethane over a 3-hour period at such a rate that a smooth evolution of gaseous products was maintained from the reacting solution. The solution was stirred for an additional 3 hours while being allowed to warm to room temperature. The ether was removed at 35°C under reduced pressure to give 96 grams of a dark red liquid which contains nitrogen, fluorine, and no chlorine. This liquid crystallizes to yellow needles when evaporated on a watch glass. Without further purification, this liquid was dissolved in 200 ml of absolute ethanol and heated to 65°C with stirring. A slurry of 7 grams of silver oxide in 50 ml of absolute ethanol was added to the alcoholic solution in small batches over a 45 minute period. The resultant solution was

refluxed for 18 hours, treated with activated charcoal, refluxed, cooled, filtered, and distilled. A viscous, light yellow oil distilled at 113-115°C under 3 mm. pressure. This oil weighed 31.8 grams which represented a 41.8% yield of diethyl hexafluoropimelate.

Saponification equivalent

Calcd: 162
Found: 159, 160

7. Preparation of 3,3,4,4,5,5-hexafluoropimelic acid - A 3-necked flask of 300 ml capacity was fitted with a thermometer, stirrer, and 20 cm. Vigreux column connected to a total reflux head. Diethyl hexafluoropimelate (21.8 grams, 0.067 mole) and 150 ml of 17% HCl were placed in the flask and heated with stirring at 105°C so that the temperature in the reflux head was maintained at less than 85°C. Over a 26 hour period approximately 15 ml of distillate was removed. The aqueous solution was extracted with three 100 ml portions of ether, the ether extracts were combined and extracted with three 50 ml portions of a 10% sodium carbonate solution. The carbonate extracts were combined, acidified with concentrated sulfuric acid, and extracted with three 100 ml portions of ether. The ether extracts were combined, dried over magnesium sulfate and distilled to remove the ether. The residue oil solidified on cooling to give 14.1 grams of solid material. This represents an 82% yield of 3,3,4,4,5,5-hexafluoropimelic acid. This solid was recrystallized from benzene.

Neutral Equivalent

Calcd: 134
Found: 132, 134

8. Preparation of diethyl 2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate - Sodium (11.5 grams, 0.5 mole) was cut into very small cubes and placed in one pound of anhydrous ether in a 1-liter, 3-necked flask fitted with a stirrer and reflux condenser. Diethyl malonate (80 grams, 0.5 mole) was added in portions over a two hour period. The resultant slurry was stirred until no more gas was evolved (about 18 hours). A solution of perfluoroglutaryl chloride (63 grams, 0.227 mole) in 100 ml anhydrous ether was placed in an addition funnel and added dropwise to the well stirred slurry of ethyl sodiomalonate in ether. The addition was made at such a rate that the ether was kept at a gentle reflux. After the addition was complete, the solution was refluxed for three hours and cooled. It was poured into 200 ml of water and stirred to dissolve the salts. The ethereal layer was washed once with water and the combined aqueous layers extracted with two 50 ml portions of ether. The combined ether layers were dried over magnesium sulfate and the ether removed by distillation. Fractionation under reduced pressure gave 47.3 grams of an unidentified fluorine-containing ester at 105-108°C under 1 mm. pressure and 34 grams of a viscous oil at 184-186°C under 1 mm. pressure. The latter compound is diethyl 2,8-dicarbethoxy-3,7-diketo-4,4,5,5,6,6-hexafluoroazelate, having a refractive index (n_D^{20}) of 1.4342. This quantity represents a yield of 28.6%

Analysis for $C_{19}H_{22}F_6O_{10}$

Calcd: C, 43.5; H, 4.2

Found: C, 43.5; H, 4.1

9. Attempted preparation of 2,8-dicarbethoxy-4,4,5,5,6,6-hexafluoroazolate by catalytic reduction - A $PdCl_2$ -C catalyst was prepared by standard methods.⁹ It was placed in a Parr hydrogenator with 20 ml glacial acetic acid and reduced. Diethyl dicarbethoxydiketohexafluoroazolate (20 grams, 0.0382 mole) in 25 ml glacial acetic acid was added to the catalyst and heated to 80°C. The Parr hydrogenator was placed at 40 lbs initial pressure and reacted for 24 hours. No pressure loss was indicated. Fractionation of the residual solution gave a 90% recovery of the starting material.

10. Preparation of silver perfluoroglutarate - Perfluoroglutaric acid (540 grams, 2.25 moles) was dissolved in 1000 ml distilled water and placed in a 2000 ml flask fitted with a reflux condenser. Silver oxide (523 grams, 2.26 moles) was added and the mixture refluxed for two hours. The resultant solution was filtered into a porcelain evaporating dish and left in an electric drying oven at 110°C for 24 hours. The resultant silver perfluoroglutarate weighs 990 grams (97% yield).

11. Preparation of 1,3-dibromo-1,1,2,2,3,3-hexafluoropropane - This method of preparation is essentially that given by Hauptschein.⁵ Silver perfluoroglutarate (226.9 grams, 0.5 mole) was placed in a 1000 ml, 1-necked flask. Bromine (230 grams, 1.44 moles) was added to the dry silver salt and a reflux condenser added to the flask. The flask was placed in a water bath which was heated to 90°C and kept at 90-100°C until no more carbon dioxide was evolved from the reacting mixture (about 5 hours was necessary). The water bath was removed and the reaction mixture allowed to cool to room temperature. The reflux condenser was replaced by a distillation apparatus and all the liquid distilled from the flask. This dark red liquid was washed until colorless with a 10% aqueous NaOH solution. The lower, water-white liquid weighed 103 grams. It was distilled to give 97 grams of pure $C_3F_6Br_2$ at 73-75°C. This represents a 62.8% yield. The IR spectra exactly matches that given by Hauptschein.

12. Preparation of the silver salt of diethyl malonate - Sodium (23 grams, 1.0 mole) was dissolved with cooling in 500 ml of absolute ethanol. Diethyl malonate (160 grams, 1.0 mole) was added and 350 ml ethanol distilled from the reaction mixture. The solution was cooled and 400 ml of water was added. Distillation was continued until the head temperature reached 100°C. The aqueous solution of ethyl sodiomalonate was cooled and poured with stirring into a solution of silver nitrate (170 grams, 1.0 mole) in 300 ml of water. The white precipitate of silver diethylmalonate formed immediately. After washing with several volumes of water and drying at room temperature in a vacuum desiccator, the white salt weighed 235 grams (an 87% yield). This solid is insoluble or very slightly soluble in acetone, acetonitrile, benzene, chloroform, diethyl malonate, dibutyl ether, dimethyl formamide, dioxane, ethyl ether, ethyl acetate, acetic acid, hydrochloric acid, triethylamine and tetrahydrofuran. It is soluble in pyridine and concentrated ammonium hydroxide.

E. Repeated Preparations

1. Preparation of perfluoroglutaric acid - Hexafluorodichlorocyclopentene (296 grams, 1.21 moles), potassium permanganate (267 grams), potassium hydroxide (180 grams), and water 1000 ml) were placed in a 3-liter, 3-necked flask fitted with stirrer and a reflux condenser. This charge was stirred and refluxed for 40 hours. Steam distillation gave recovery of 29 grams of unreacted hexafluorodichlorocyclopentene. Concentrated sulfuric acid (505 ml) was added with cooling and the resultant acidic solution was cooled to 2°C. At this temperature, the aqueous medium was extracted with five 300 ml portions of ether by adding the ether, rapidly stirring the mixture for at least 20 minutes, and removing the ethereal layer by means of a suction tube. The resultant ethereal solution was dried over magnesium sulfate and distilled. Perfluoroglutaric acid was collected at 114-121°C under 1 mm pressure. The yield was 235 grams which represents a 90% yield or an 81% conversion. Other attempts have given conversions as high as 86%.

2. Preparation of diethyl perfluoroglutarate - The ethereal extracts mentioned above were distilled to a head temperature of 85°C. The residue was dissolved in a 100% excess of absolute ethanol and placed in a 3-necked flask, fitted with a stirrer, a reflux condenser, and an addition funnel. One mole of concentrated sulfuric acid per mole of original hexafluorodichlorocyclopentene was placed in the addition funnel and added dropwise to the well stirred alcoholic solution at such a rate that refluxing does not occur. This addition takes about one hour. The resultant two layer system was separated, the acid (top) layer was extracted twice with ether, the resultant organic layers were combined, neutralized by washing with 5% NaHCO₃, separated, dried, and distilled. Diethyl perfluoroglutarate was collected at 85°C under 4 mm pressure. The overall yield is about 86%, C₅Cl₂F₆ to ester. This esterification step takes only about four hours including distillation and thus is greatly preferred to the Dean-Stark trap method.

3. Preparation of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol - Hexafluoropentanediol was prepared as originally reported.¹⁰

4. Preparation of 3,3,4,4,5,5-hexafluoro-2,6-heptanediol - From a reduction of diethyl perfluoropentanedioate with methylmagnesium iodide and isopropylmagnesium bromide identical to that first reported,¹¹ a total of 35.75 grams (59%) of 3,3,4,4,5,5-hexafluoro-2,6-heptanediol was isolated by allowing the viscous oil to crystallize over a period of 2 months and recrystallizing the solid product from benzene.

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