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AFML-TR-67-261
PART III
AD0862951

SYNTHESIS AND CHARACTERIZATION OF PERFLUOROALKYL HETEROCYCLIC ELASTOMERS

N. L. Madison
C. D. Burton
The Dow Chemical Company

Technical Report AFML-TR-67-261 PART III

October 1969

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SYNTHESIS AND CHARACTERIZATION OF PERFLUOROALKYL HETEROCYCLIC ELASTOMERS

N. L. Madison
C. D. Burton

FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. F33615-68-C-1120. The contract was initiated under Project Number 8M30770/7340, "Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers." This work was sponsored and administered by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Fred E. Arnold, MANP, as Project Engineer.

This report represents the work performed on this contract for the period 1 September 1968 to 1 September 1969, and is being submitted by the authors in September, 1969. It is Dow Report Nr. PH(2)-1F-69. The manuscript was released by the authors September, 1969 for publication.

Management direction at Dow was under Mr. G. F. Mackenzie, Division Leader of the Product Department Laboratories. Dr. N. L. Madison and Mr. C. D. Burton are the principal investigators, and were assisted by Mr. W. J. Jensen.

This technical report has been reviewed and is approved.

WE Gibbs
W. E. Gibbs
Chief, Polymer Branch
Nonmetallic Materials
Division

ABSTRACT

Perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers have been prepared from carefully purified monomers. DTA measurements show the glass transition temperature is -15°C. and the onset of thermal decomposition occurs at 350°-400°C. in nitrogen. The highest intrinsic viscosity attained was 0.28.

Polymers prepared from dihydroxybenzidine and methyl perfluoro-4,9-dioxadodecanediimidate soften at ~65°C. with a T_g near 21°C. Thermal decomposition takes place above 400°C., and intrinsic viscosities to 0.38 have been attained.

A new polymer has been prepared from the reaction of 3,3'-diamino-4,4'-dihydroxybenzophenone with methyl perfluorosebacimidate. The polymer softens at 205°C., forms films and has excellent thermal stability. Whereas the reactions with dihydroxybenzidine are heterogeneous, this polymerization reaction is completely homogeneous since the polymer and both monomers are soluble in hexafluoroisopropanol. The parameters of this faster reaction are being investigated to determine if molecular weights higher than those attained with the bibenzoxazoles are possible. The intrinsic viscosity of the initial polymer was 0.23

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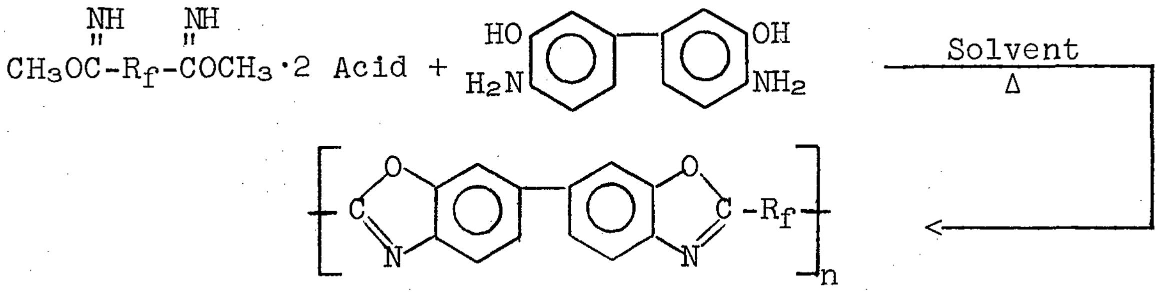
SECTION I

INTRODUCTION

The purpose of this research program is to synthesize heterocyclic fluorine-containing polymers for use as high temperature elastomers. Initially, selected model compounds were prepared and, after evaluation, a family of bibenzoxazole polymers, congeneric to the most attractive model compound, was selected for synthesis and evaluation.

The most attractive route to the models was found to be the following high yield reaction which was also applicable to polymer synthesis[1]:



The first polymers, $R_f = (CF_2)_8$, were prepared either in dioxane with trifluoroacetic acid as the acid promoter or in acetic acid which acted as both solvent and promoter. Although polymer yields were good, molecular weights were low. The failure to achieve high molecular weights was attributed primarily to the heterogeneity of these two systems since one monomer, dihydroxybenzidine, and the polymer were insoluble in both dioxane and acetic acid. Therefore, two solvents, hexamethylphosphoramide and hexafluoroisopropanol, which were good solvents for the polymers, were tried as reaction media. Hexamethylphosphoramide, which also dissolved the dihydroxybenzidine, was used in combination with acetic acid to produce a completely homogeneous reaction mixture. However, the polymer produced contained some form of phosphorus and the infrared spectrum was entirely different from the previous bibenzoxazole polymers. The polymerization in a trifluoroacetic acid hexafluoroisopropanol system resulted primarily in the formation of dihydroxybenzidine bis(trifluoroacetate) rather than polymer.

The use of acetic acid as the promoter in hexafluoroisopropanol solvent gave an excellent yield of light colored polymer, and osmotic pressure measurements confirmed that this system

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[1] The Dow Chemical Company, Technical Report AFML-TR-67-261, Part I, September 1967, "Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers," Contract Nr. AF 33-(615)-5268.

produced higher molecular weights than any previous system. Again, dihydroxybenzidine was insoluble in the solvent, but after two days a single phase formed, and the later stages of polymerization took place in solution.

The high melting points, 235-240°C., of the dihydroxybenzidine-methyl perfluorosebacimidate polymers precluded their use in elastomeric applications, but the ready availability of the monomers afforded an opportunity to optimize the acetic acid-hexafluoroisopropanol system before committing more sophisticated and expensive reactants[1].

The most significant variables involved the purity of reactants and, concomitantly the stoichiometry. Methyl perfluorosebacimidate was readily purified by fractional distillation under high vacuum but dihydroxybenzidine required exhaustive charcoal treatment of its dihydrochloride in solution followed by isolation in the absence of light and air. Storage in other than a completely inert atmosphere caused the dihydroxybenzidine to discolor. Combining highly purified materials in careful 1:1 stoichiometry, with vigorous exclusion of air and moisture to protect monomers from decomposition, resulted in polymers having molecular weight values in the 15,000-20,000 range, as determined by membrane osmometry. The polymers were light colored solids which softened at ~240°C., and tough, flexible films or long fibers could be formed from the melt. The decomposition temperature was ~500°C., as determined by TGA, and the weight loss in air was 5.5% in 24 hours, as measured by isothermal TGA at 300°C.

The polymerization promoted by acetic acid is a rather slow reaction, and the kinetics were studied for five weeks to determine the optimum reaction time. Membrane osmotic pressure measurements indicated that the molecular weight values reached a maximum as soon as all the dihydroxybenzidine dissolved (~48-70 hrs.) and did not increase thereafter. Thus, the reaction seemed to resemble an interfacial polymerization, but the physical differences in the sample suggested that the molecular weight was increasing with time. With the poor reproducibility of the molecular weight values and the poor correlation of these values with viscosities, the kinetic study was judged to be inconclusive.

Attempts were made to increase the rate of the polymerization reaction through the use of other imidate esters. The reactivity of the perfluoroalkyl imidates was attributed to the presence of the strongly electronegative perfluoroalkyl group. Therefore, trifluoroethyl perfluorobutyrimidate with two fluorinated groups was used in the established reaction to prepare Model I.

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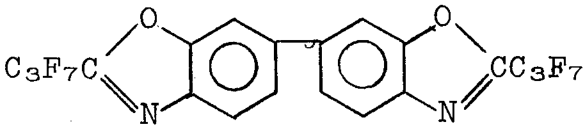
[1] The Dow Chemical Company, Technical Report AFML-TR-67-261, Part II, December 1968, "Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers," Contract Nr. AF 33-(615)-5268.



Model I

However, the reaction rate was no faster than with methyl perfluorobutyrimidate.

To improve the polymer flexibility and thereby enhance the chances of obtaining elastomeric properties, a longer chain perfluoroalkyl imidate, methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate, was reacted with dihydroxybenzidine under the previously established conditions to form the polymer, where $R_f = (CF_2CF_2OCF_2CF_2)_4$. The polymers were isolated by evaporation of the solvent and heated to 205°C./<1 μ to remove coproduced ammonium acetate and low molecular weight material. The yield of polymer after this treatment was 85% or less.

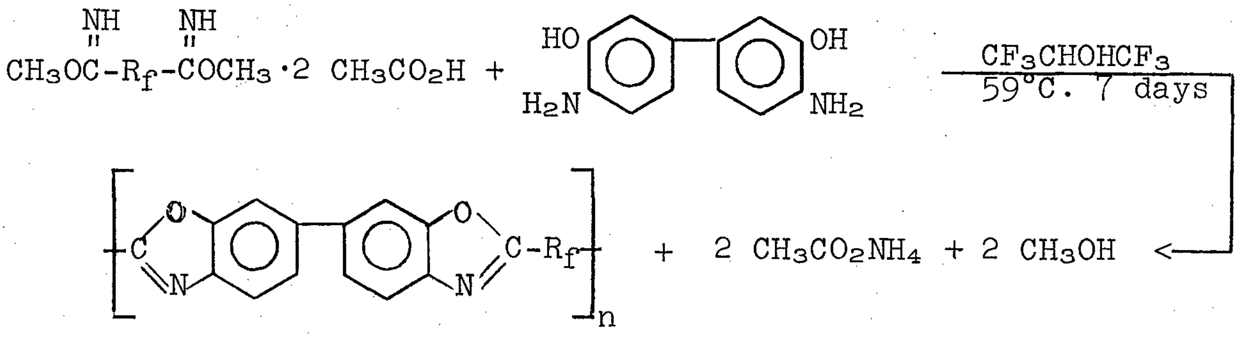
The dihydroxybenzidine-methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate polymers are tacky, resilient materials with only a slight tendency to flow at room temperature. At -30°C., the polymer becomes hard but not brittle. When heated to 300°C., the polymer crosslinked to an elastomer, but further heating had no effect indicating the crosslinks were very limited.

A polymer was prepared from methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate varying in purity from crude to fractionally distilled, but in all cases osmotic pressure measurements indicated the molecular weights were similar, $\sim$11,500. Infrared analysis showed the spectral features expected of the proposed structure plus a carbonyl band absorbing at 1745 cm.$^{-1}$. This band was present in the spectra of all polymers, but was diminished with increasing imidate purity, indicating the source of the band was an impurity, possibly associated with the end groups.

SECTION II

DISCUSSION

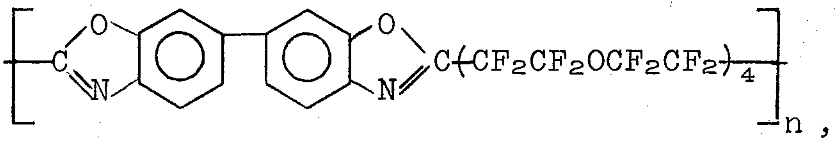
The preparation of bibenzoxazole polymers was continued using the following optimized reaction:



The emphasis was placed on improving the purity of the polymer with $R_f = \left(CF_2CF_2OCF_2CF_2 \right)_4$, either through the use of better quality starting materials or by treatment of the product after polymerization. Other polymers were also prepared to study the effect of structure on softening point and glass transition temperature.

A. METHYL PERFLUORO-4,9,14,19-TETRAOXADOCOSANEDIIMIDATE-DIHYDROXYBENZIDINE POLYMERS

Although the analyses indicated these polymers conformed predominantly to the proposed structure,



impurities were detectable by infrared analysis. As expected, the amount of impure functions decreased with increase in monomer purity until the only infrared absorbance not attributable to the proposed polymer structure was a carbonyl band at 1745 cm.$^{-1}$ (Figure 1). This band was present in all of the polymers, but was very small in the spectra of the highest molecular weight perfluorosebacimidate-dihydroxybenzidine polymers (Figure 2). The band was most prominent in the methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers. The use of fractionally distilled methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate did not reduce the absorbance to the level of the best sebacimidate polymers. The presence of the carbonyl group could be attributed to either imperfect sites along the chain or to adulterated end groups. In either case, the purity

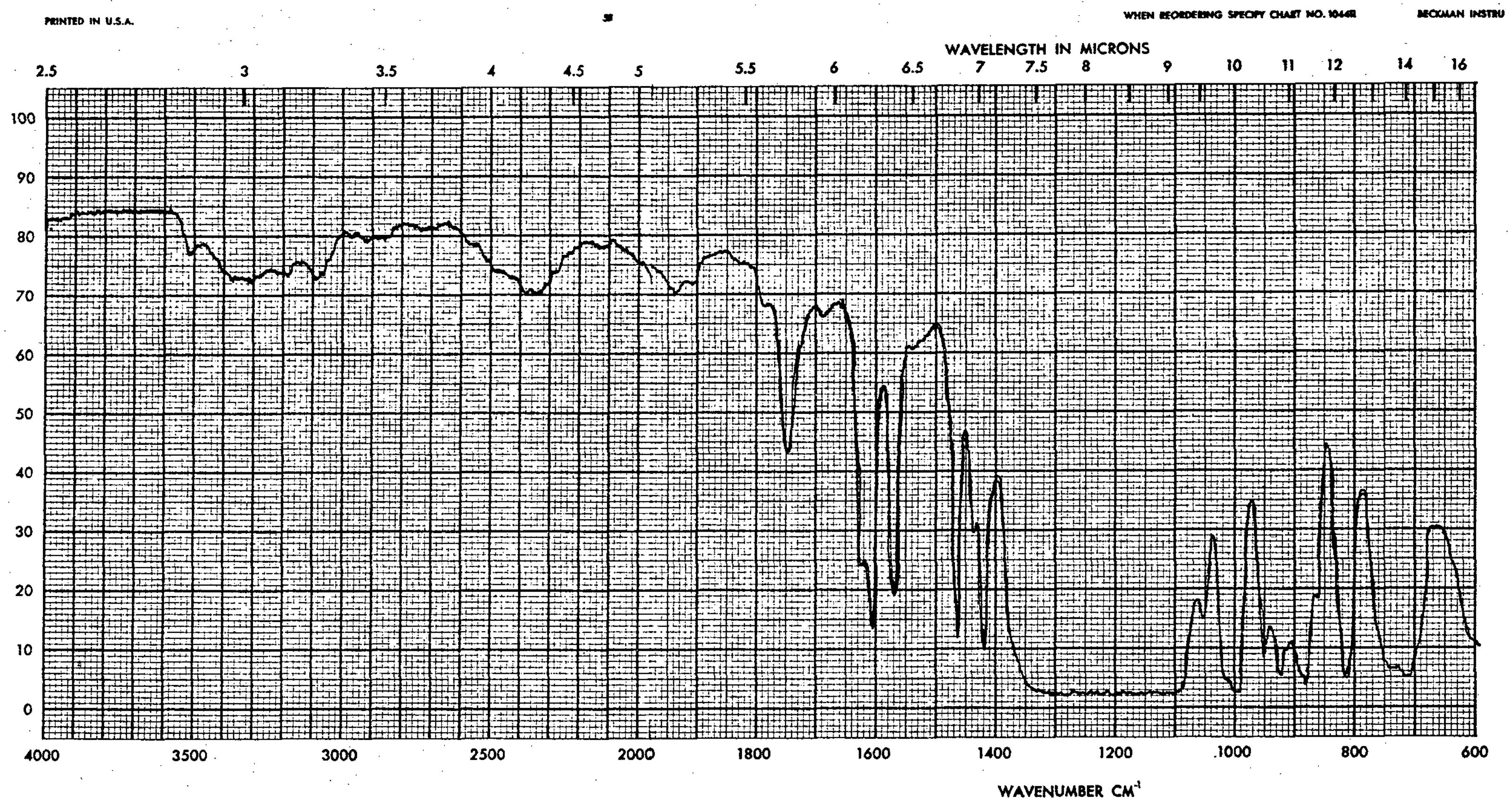


Fig. 1 - Infrared Spectrum of Methyl Perfluoro-4,9,14,19-tetraoxadocosanediimidate-Dihydroxybenzidine Polymer

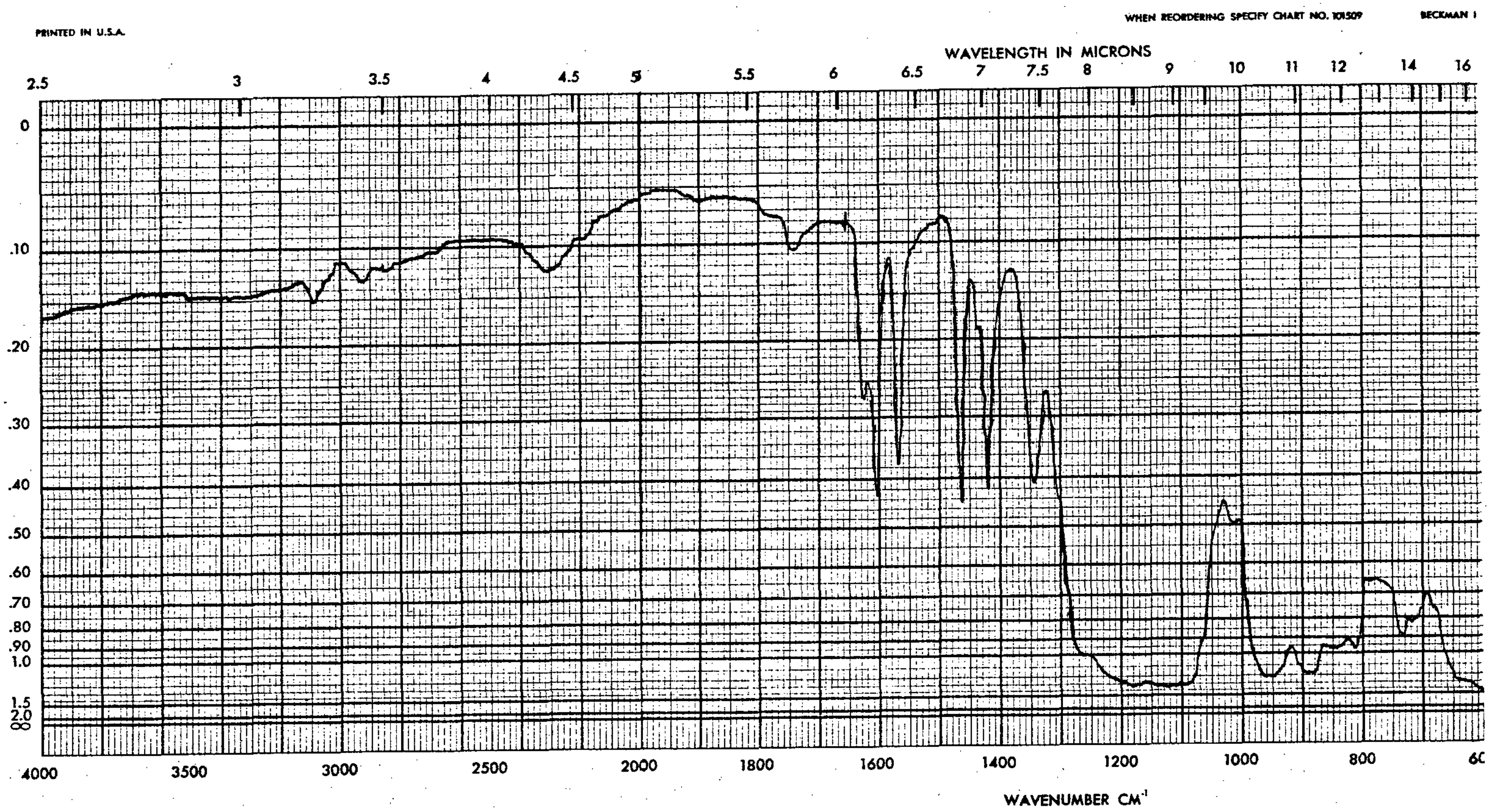


Fig. 2 - Infrared Spectrum of Methyl Perfluorosebacimidate-Dihydroxybenzidine Polymer

of the monomers was questionable, and a more intensive monomer purification program was undertaken.

Perfluoro-4,9,14,19-tetraoxadocosanedinitrile was prepared by dehydration of the corresponding diamide and fractionally distilled. VPC and infrared analyses confirmed the high purity of the dinitrile, which was then converted to methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate and again fractionally distilled. Infrared analysis indicated the forerun from the fractional distillation contained a trace of ester (C=O band at 1790 cm.$^{-1}$) while the residue showed absorbance at 1745 cm.$^{-1}$. Since the main fractions appeared to be highly pure, this imidate ester was polymerized with dihydroxybenzidine. Although the color of the polymer was lighter than any previous polymer, the small unidentified carbonyl band at 1745 cm.$^{-1}$ was again present. A subsequent study of a number of derivatives of perfluorinated acids established that the 1745 cm.$^{-1}$ band is not associated with the acid, its esters, amides or N-methyl amides, the functions most likely to be present as the terminal groups or to result from incomplete cyclization. The intrinsic viscosity of this polymer was only 0.19, whereas values as high as 0.28 had been attained with previous methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers.

The purification of dihydroxybenzidine is difficult because of its low solubility in most solvents and its sensitivity toward oxidation. Two methods of purification were explored. Under full vacuum, <1 μ, dihydroxybenzidine sublimed very slowly at 150°C.; at 200°C. the rate of sublimation was still not sufficient to warrant further investigation. Purification of dihydroxybenzidine in the form of its dihydrochloride salt by recrystallization from water was also evaluated. In the salt form, dihydroxybenzidine is stable in aqueous solution and impurities indicated by the presence of color can be removed by repeated treatment with charcoal. In addition, the salt can be recrystallized since increasing the hydrogen chloride content precipitates dihydroxybenzidine dihydrochloride. By this method, old dark brown samples were purified to white dihydroxybenzidine. Although the polymerization reaction with this material was normal, the final polymer solution turned dark after standing two weeks and the polymer, after purification, crosslinked to an elastomer when heated to 160°C. for two hours. However, since other factors were involved which could have caused the crosslinking, this method of purification will have to be reevaluated.

The investigation into a better dihydroxybenzidine purification procedure was prompted by erratic results of some methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymerizations. A few of these reactions failed to go to completion and small amounts of solids remained suspended in the final reaction mixture. This phenomenon occurred only with certain lots of dihydroxybenzidine. However, by color and infrared and elemental analysis, the difference between these lots and satisfactory dihydroxybenzidine was indistinguishable. The present methods of analysis apparently are not sufficiently accurate to guarantee the absolute purity of dihydroxybenzidine.

Contaminants in the early methyl perfluoro-4,9,14,19-tetraoxadosanediimidate-dihydroxybenzidine polymers were readily discernible by infrared analysis. In addition, the crosslinking was too limited for this reaction to be a function of the polymer since continued heating did not cause embrittlement. Differential thermal analysis of crude polymer also confirmed the presence of minor crystalline components.

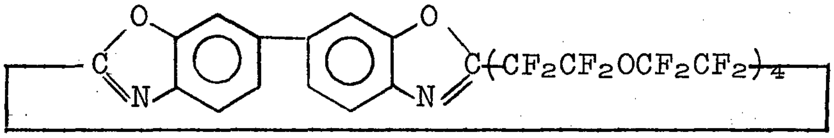
The isolation and purification of the polymers were difficult due to their viscous consistency. When precipitated by dilution of the polymer solutions with water, methanol, etc., the polymers which were prepared in very small quantities adhered to any surface and could not be collected without loss of product. Therefore, polymers were isolated by removal of the solvent under vacuum. This, however, was ineffective in removing most byproducts and impurities. The polymer was partially purified by heating to 200°C. under full vacuum to remove volatile materials.

Since the sebacimidate polymers, $R_f = \left(CF_2 \right)_8$, were obtained in a reasonably pure state simply through a filtration and washing procedure, a similar method, applicable to the tacky docosanediimidate polymer, was devised. In essence the polymer was extracted in a Soxhlet using a small beaker rather than a porous cup. Since the extracting fluid flowed across rather than through the polymer, the process required considerable reflux time to be effective. Non-solvents for the polymer were tested and the most effective was dimethylformamide (DMF). The high boiling point of DMF gave the polymer greater mobility and thereby improved contact between the solvent and the polymer mass. After extraction and solvent removal, the polymer could be heated to 240°C. for three hours without elastomer formation and loss of solubility in hexafluoroisopropanol. The amount of dark tacky material extracted from the polymer was too small to be accurately identified.

Although most extracted polymers would not crosslink when heated, a few remained heat-sensitive, and in one case crosslinking occurred during extraction. Due to the inconsistency of the results and because the unidentified carbonyl absorption at 1745 $cm.^{-1}$ remained undiminished after extraction, other methods of polymer purification were sought. Further, if the carbonyl band was associated with incomplete ring closure, the high temperatures associated with DMF extraction might destroy any chances of completing the cyclization by some designed reaction.

The purification of polymers by repeated precipitation from hexafluoroisopropanol solution with polymer non-solvents was then investigated. The polymer solution was rapidly added to the precipitating medium which was stirred at medium speed in a Waring Blendor. The polymer deposited on the sides of the glass container, and the liquors were separated by decantation. Methanol, acetonitrile, diglyme and dimethylformamide effectively precipitated the polymer, but only methanol, diglyme and dimethylformamide appeared to be removing impurities as indicated by the presence of color in the liquors. Although these precipitations did not alter the infrared spectra of the polymers to any great extent, impurities have been isolated from the decanted liquors.

One polymer was precipitated three times with methanol and the liquors were distilled. The distillate at atmospheric pressure was composed entirely of methanol and hexafluoroisopropanol. When the residual material from the distillation was heated under vacuum, a white solid sublimed to the top of the flask. The material had a sharp melting point (89-90°C.) and the infrared spectrum (Figure 3) was similar to that of the polymer with no absorbance above 1620 cm.$^{-1}$. NMR analysis indicated there was only one type of ring, and the fluorine spectrum was consistent for the $\left(CF_2CF_2OCF_2CF_2\right)_4$ chain. The molecular weight, by ebulliometric measurements, was 1025. Although the latter figure is below the theoretical value of 1098, a cyclized mer,



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would fit the data reasonably well. This solid accounted for about 10% of the theoretical yield. The residue from the sublimation was a tacky material which appeared to be polymer, but with a preponderance of end groups, and the carbonyl band at 1745 cm.$^{-1}$ was larger than the precipitated polymer. The amount of sublimable solid and tacky residue rapidly diminished with each succeeding precipitation.

The methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers are resilient materials which vary from amber to black depending upon monomer quality. Low temperature differential thermal analysis (DTA) (Figure 4) indicates the glass transition temperature is about -15°C. The thermogravimetric analyses (Figure 5) concurs with the DTA curve that decomposition begins at 350-400°C. The TGA curves in nitrogen or air are identical until decomposition is well under way, and then the decomposition appears to be sensitive to air.

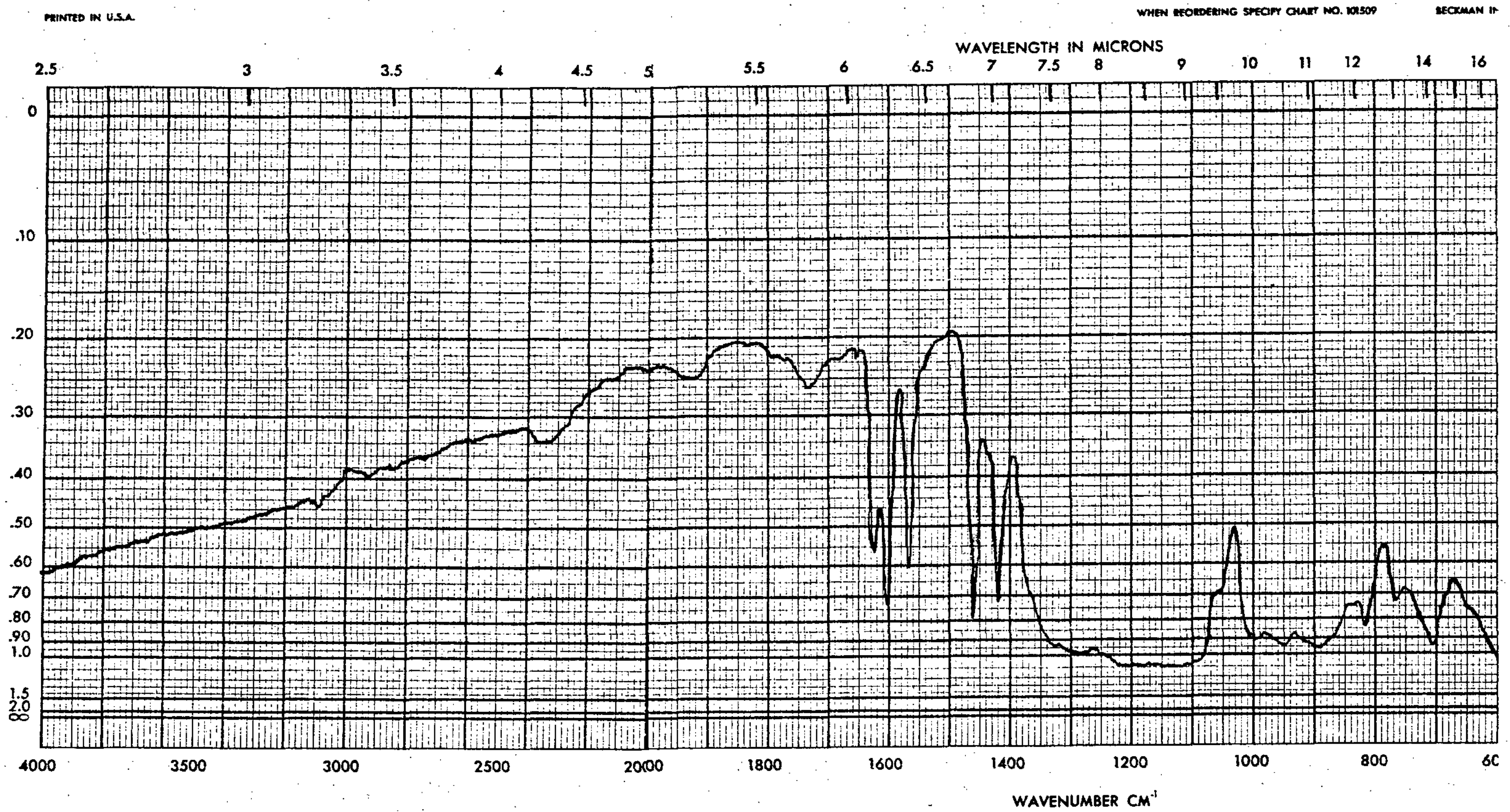


Fig. 3 - Infrared Spectrum of Sublimed Solid from Methyl Perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine Polymer

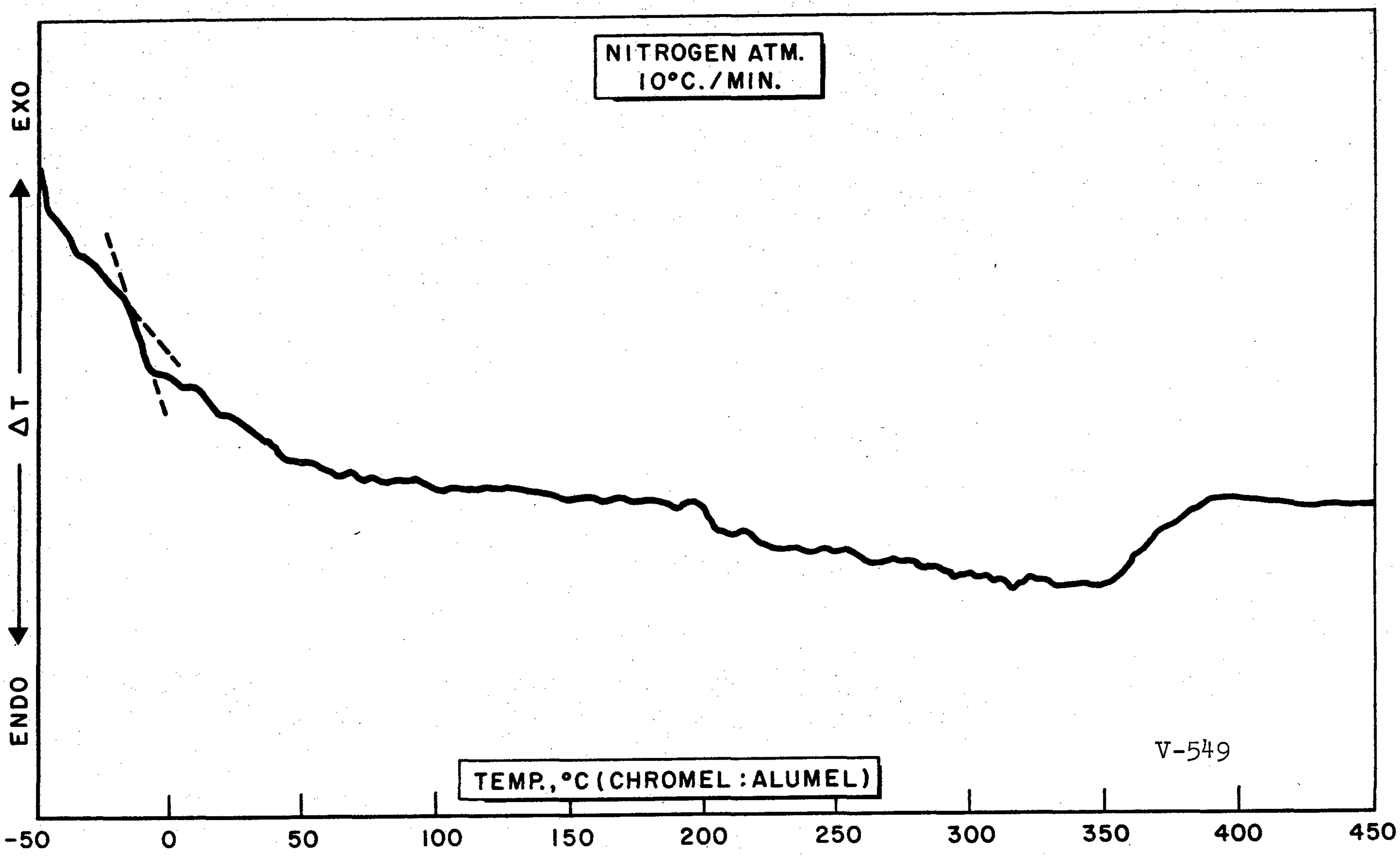


Fig. 4 - DTA of Methyl Perfluoro-4,9,14-19-Tetraoxadocosanediimidate-Dihydroxybenzidine Polymer

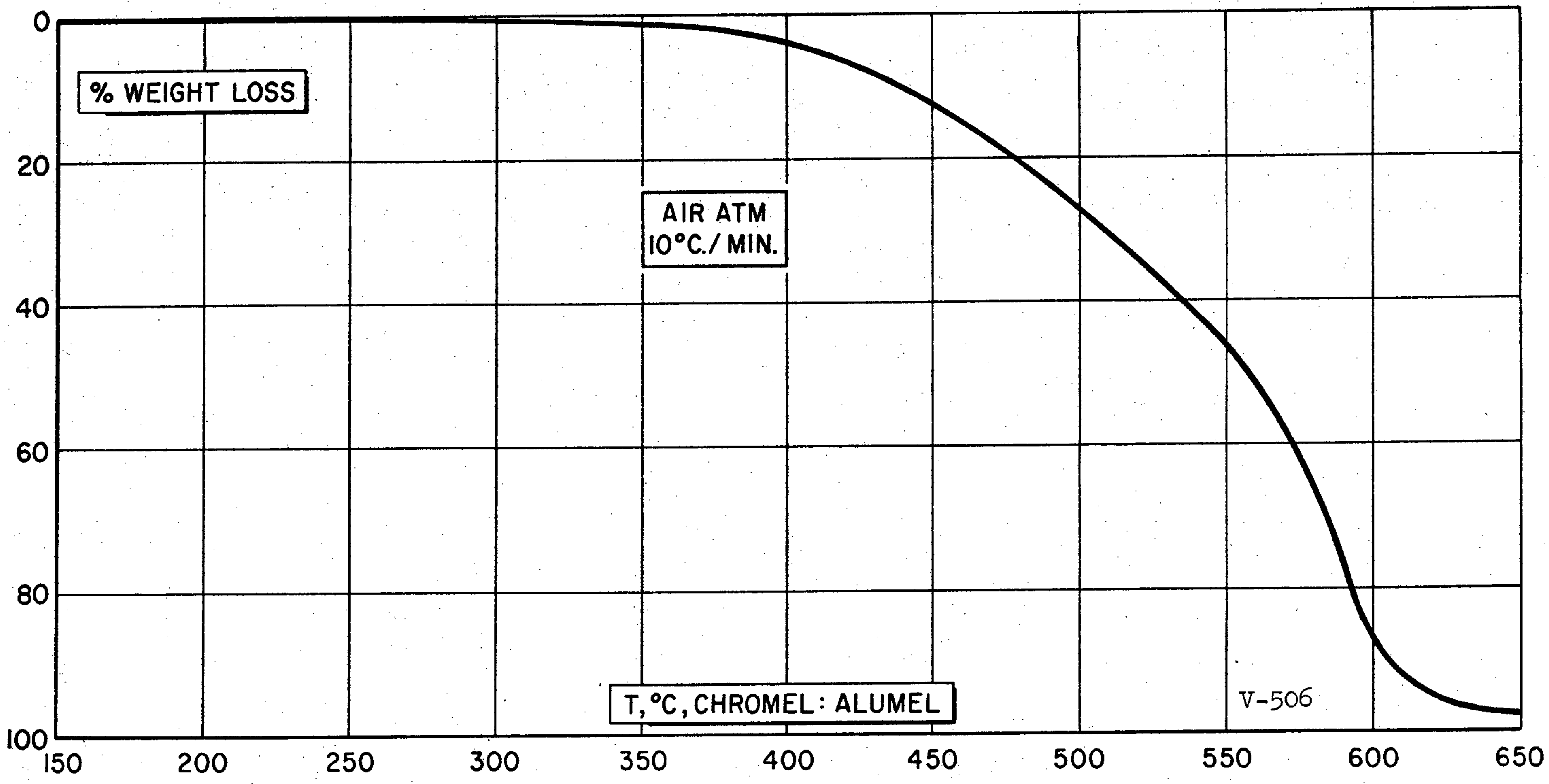


Fig. 5 - TGA of Methyl Perfluoro-4,9,14,19-Tetraoxadocosanediimidate-Dihydroxybenzidine Polymer

Although the polymerizations were carried out with highly refined starting materials, and the polymers were repeatedly reprecipitated to remove contaminants, molecular weight values greater than 11,600 or intrinsic viscosities higher than 0.28 have not yet been attained. Efforts to identify and remove the source of the carbonyl absorbance, which may be a factor in suppressing high molecular weights, have been unsuccessful, and further work on this polymer will be necessary.

B. METHYL PERFLUORO-4,9-DIOXADODECANEDIIMIDATE - DIHYDROXYBENZIDINE POLYMERS

Since the perfluoroinated oxydipropionic acid dimer is more readily prepared than the tetramer, the dimer imidate was polymerized with dihydroxybenzidine to determine if this polymer might also be soft and resilient at room temperature. The methyl perfluoro-4,9- dioxadodecanediimidate was prepared from distilled dinitrile and methanol in the presence of a triethylamine catalyst. The imidate was purified by distillation and fractional redistillation before use.

These dioxapolymers were prepared by the same procedure developed for the methyl perfluoro-4,9,14,19-tetraoxadocosane-dihydroxybenzidine polymers and the two polymerizations appeared to behave identically. The reactions were run for seven days and homogeneity was attained after 48 hours. Isolation was accomplished by removal of the solvent and ammonium acetate under vacuum. Further heating to 210°C. for two hours sublimed a material which appeared to be low molecular weight polymer. However, the sublimate was only 2% of theoretical and the yield of non-volatile material was 95%.

Extraction of the crude polymers with hot DMF gave poor results. One polymer, after extraction, was no longer soluble in hexafluoroisopropanol and did not soften at 65°C., indicating that crosslinking had occurred during its residence in the Soxhlet extractor. Another polymer was extracted without crosslinking, but polymer recovery was only 70%, and purification, as analyzed by infrared spectroscopy, was poor.

The highest intrinsic viscosities attained were 0.29 for unextracted polymer and 0.38 after extraction.

Due to the lack of the fluorinated monomer, only a limited number of reactions were carried out, and no further variations in the purification could be attempted.

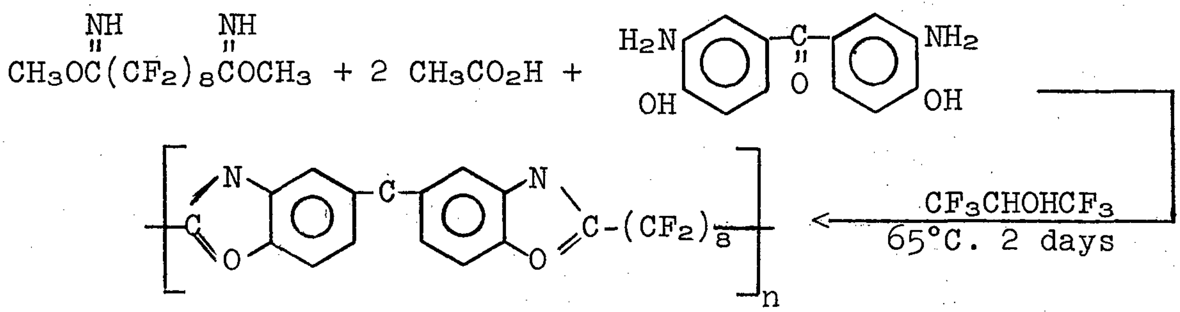
The methyl perfluoro-4,9-dioxadodecanediimidate-dihydroxybenzidine polymers, which are tough, amber, leathery materials at room temperature, elongate under stress, but show complete, though slow, recovery upon removal of the stress. The flow point of the polymer appears to be about 65°C. The DTA curve

(Figure 6) is not well defined, perhaps due to a wide molecular weight range, but a glass transition temperature of about 21°C. is indicated. The endotherm accompanying the glass transition apparently reflects the release of stresses in the sample at the glass temperature. The TGA curve (Figure 7) shows the polymer has lost only 2% of its weight at 400°C. Beyond this, the weight loss increases, but 45% of the polymer still remains at 600°C. The infrared spectrum (Figure 8) shows about the same impurity functions as the tetramer polymer.

The methyl perfluoro-4,9-dioxadodecanediimidate-dihydroxybenzidine polymers, $R_f = (CF_2CF_2OCF_2CF_2)_2$, are identical in structure to the methyl perfluorosebacimidate-dihydroxybenzidine polymers, $R_f = (CF_2)_8$, except for the two ether linkages per mer, but this modification is sufficient to lower the softening point 175°C. without loss of thermal stability.

C. METHYL PERFLUOROSEBACIMIDATE-3,3'-DIAMINO-4,4'-DIHYDROXYBENZOPHENONE POLYMERS

All previous polymers were prepared from dihydroxybenzidine which was insoluble in the solvent causing the reaction to be heterogeneous in the initial stages. The poor contact between monomers in the two phases decreased the reaction rate, and all attempts to promote a faster reaction with dihydroxybenzidine had failed. Therefore, polymers were prepared with 3,3'-diamino-4,4'-dihydroxybenzophenone to determine if this monomer would have sufficient solubility in hexafluoroisopropanol to produce a homogeneous system or, at least, a faster reaction. The 3,3'-diamino-4,4'-dihydroxybenzophenone was prepared by reduction of 4,4'-dihydroxy-3,3'-dinitrobenzophenone and purified by recrystallization from concentrated hydrochloric acid. The polymer was prepared by reaction with methyl perfluorosebacimidate under the following conditions:



When the reaction temperature reached 65°C., the 3,3'-diamino-4,4'-dihydroxybenzophenone had dissolved giving a clear amber solution. After an arbitrarily selected reaction time of two days, the clear solution was mixed with methanol to precipitate a quantitative yield of pale yellow polymer. The polymer was purified by reprecipitation twice with methanol, but there was

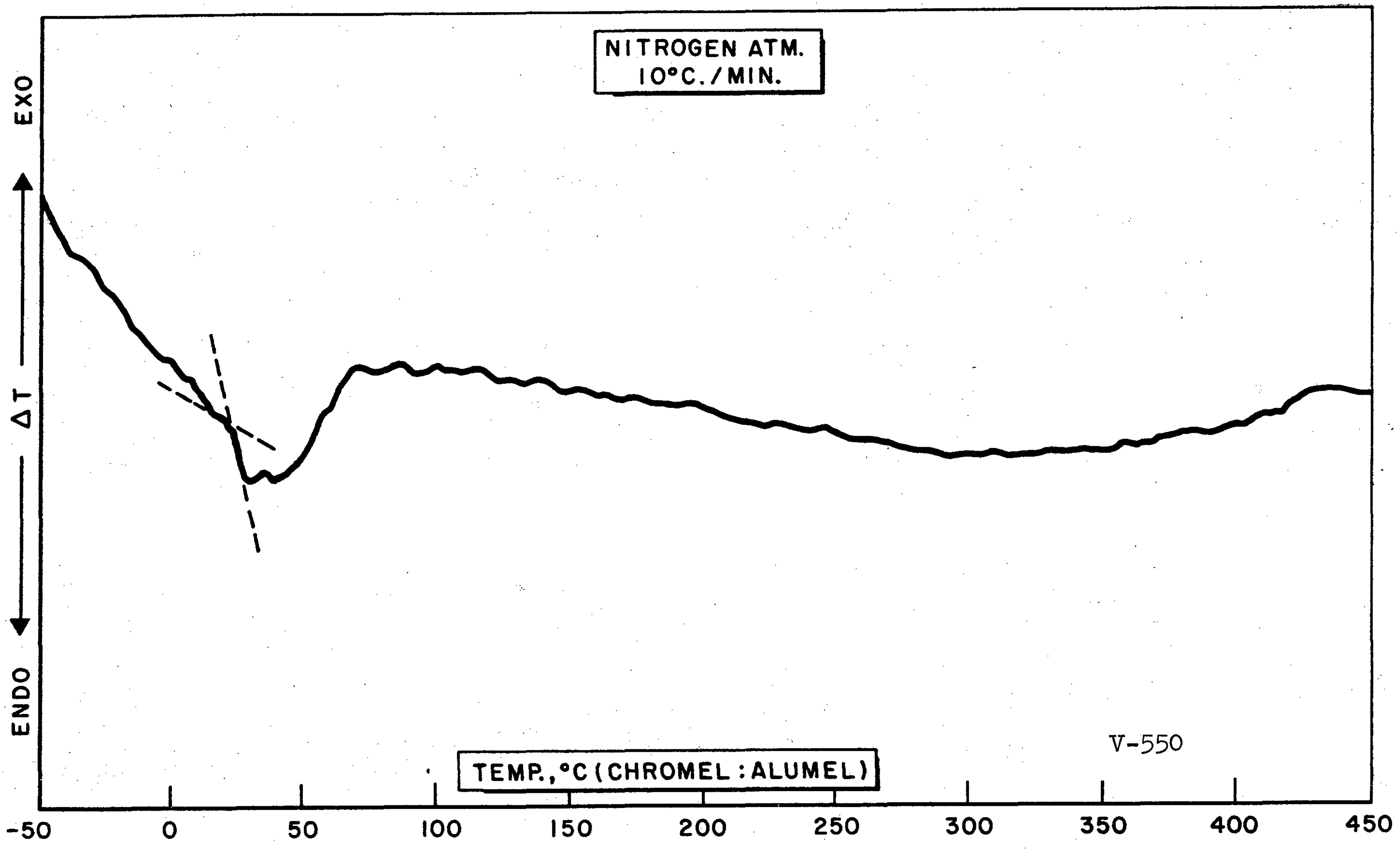


Fig. 6 - DTA of Methyl Perfluoro-4,9-Dioxadodecanediimidate-Dihydroxybenzidine Polymer

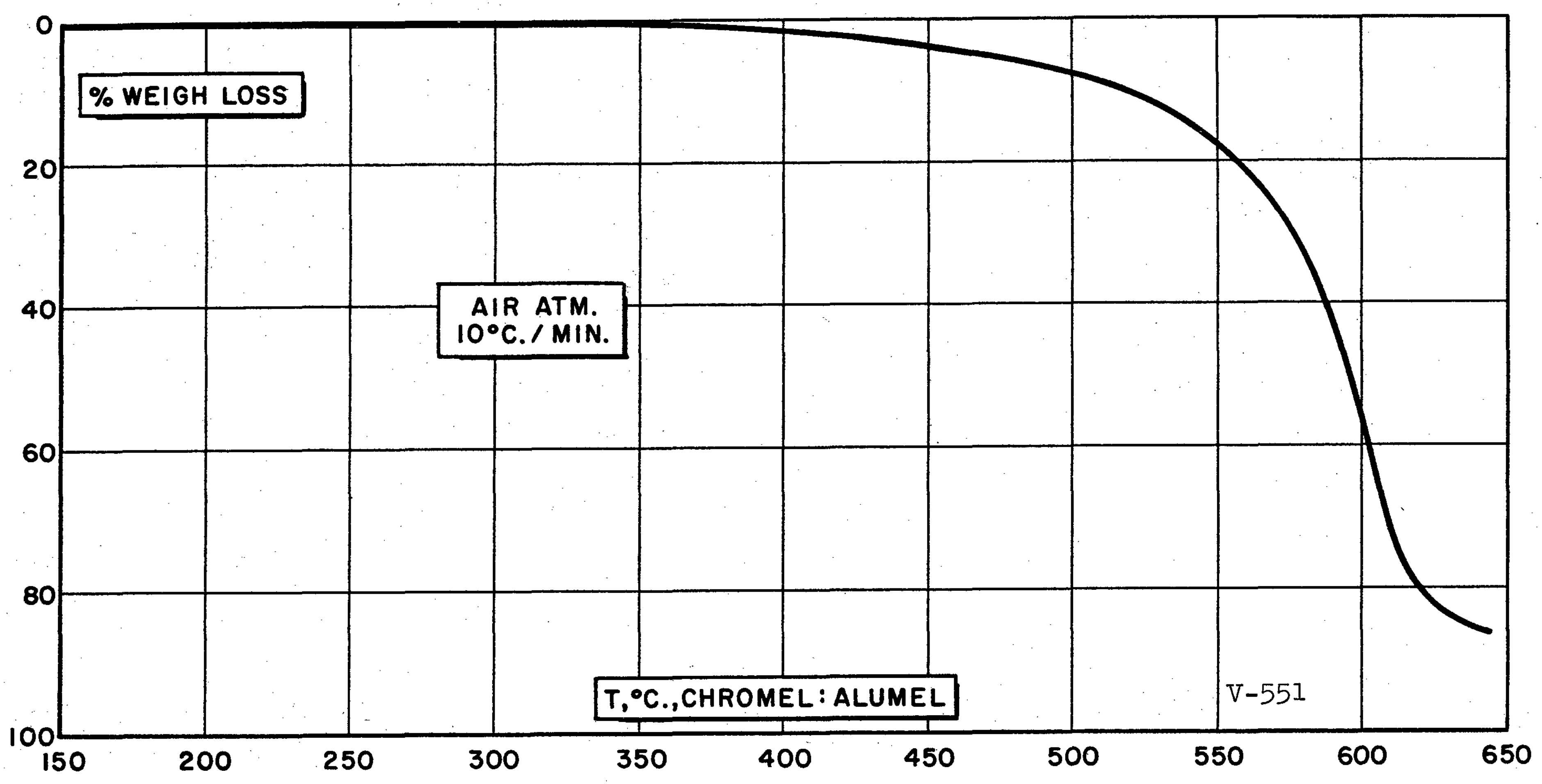


Fig. 7 - TGA of Methyl Perfluoro-4,9-Dioxadodecanediimidate-Dihydroxybenzidine Polymer

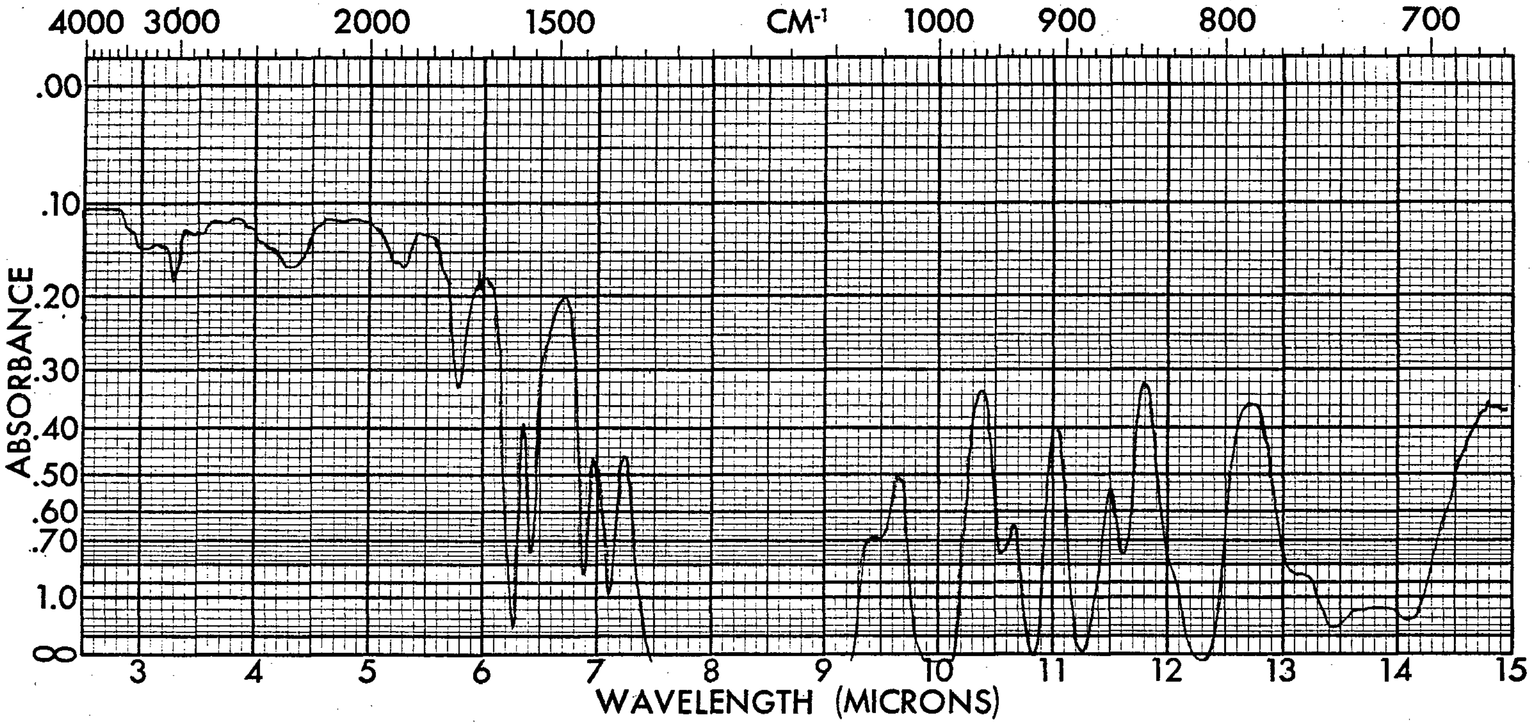


Fig. 8 - Infrared Spectrum of Methyl Perfluoro-4,9-Dioxadodecane-Diimidate-Dihydroxybenzidine Polymer

no weight loss, and the infrared spectrum (Figure 9) was unchanged. By DTA measurements (Figure 10), melting occurs at 205°C., and the onset of decomposition is about 420°C. TGA (Figure 11) shows the weight loss at 400°C. is less than 2% and at 500°C. more than 94% of the polymer still remains. Isothermal TGA at 300°C. in air resulted in a weight loss of 4.5% in 24 hours with 1% of the loss occurring in the first hour. The infrared spectrum shows the contaminant carbonyl band at 1745 cm.$^{-1}$ also present in this polymer.

Although elemental analysis indicated the 3,3'-diamino-4,4'-dihydroxybenzophenone was reasonably pure, the presence of impurities was indicated by the slight yellow tint of the solid and the amber color produced by its dissolution in the solvent. However, even in the absence of extremely high monomer purity, an intrinsic viscosity of 0.23 was attained on the initial polymer.

Efforts were continued to purify the 3,3'-diamino-4,4'-dihydroxybenzophenone. Whereas the dihydroxybenzidine was best purified by recrystallization of its dihydrochloride salt, this has not been entirely successful with the benzophenone monomer. Purification has been thwarted by the presence of small amounts of chromophoric materials which have solubility characteristics similar to the 3,3'-diamino-4,4'-dihydroxybenzophenone. Charcoal treatment of the dihydrochloride salt in aqueous solution initially reduced the color to a bright yellow but further treatment was ineffective.

In concentrated hydrochloric acid, both the product and impurities precipitate, leaving the mother liquors essentially colorless. The dihydrochloride salt has been recrystallized from water with complete exclusion of air, and the first crop (~50%) of crystals was colorless. However, a very short exposure to air before this sample was completely dry regenerated the yellow color. Washing the free base with copious quantities of water elutes most of the yellow chromophore, but the product is usually grey or tan. Present efforts are being directed toward finding a good recrystallization solvent for the free base. Combinations of methanol and water appear promising.

D. REACTION STUDIES

The polymerization reaction with dihydroxybenzidine is a slow reaction due to the insolubility of this monomer. The reaction is particularly slow when promoted by acetic acid. Trifluoroacetic acid produces a faster reaction but, unfortunately, this promoter also rearranges imidate esters to unreactive amides, thereby destroying the polymerization stoichiometry. To determine if the side reaction could be avoided by reacting thioimidates in the presence of trifluoroacetic acid, Model I was prepared in the following manner:

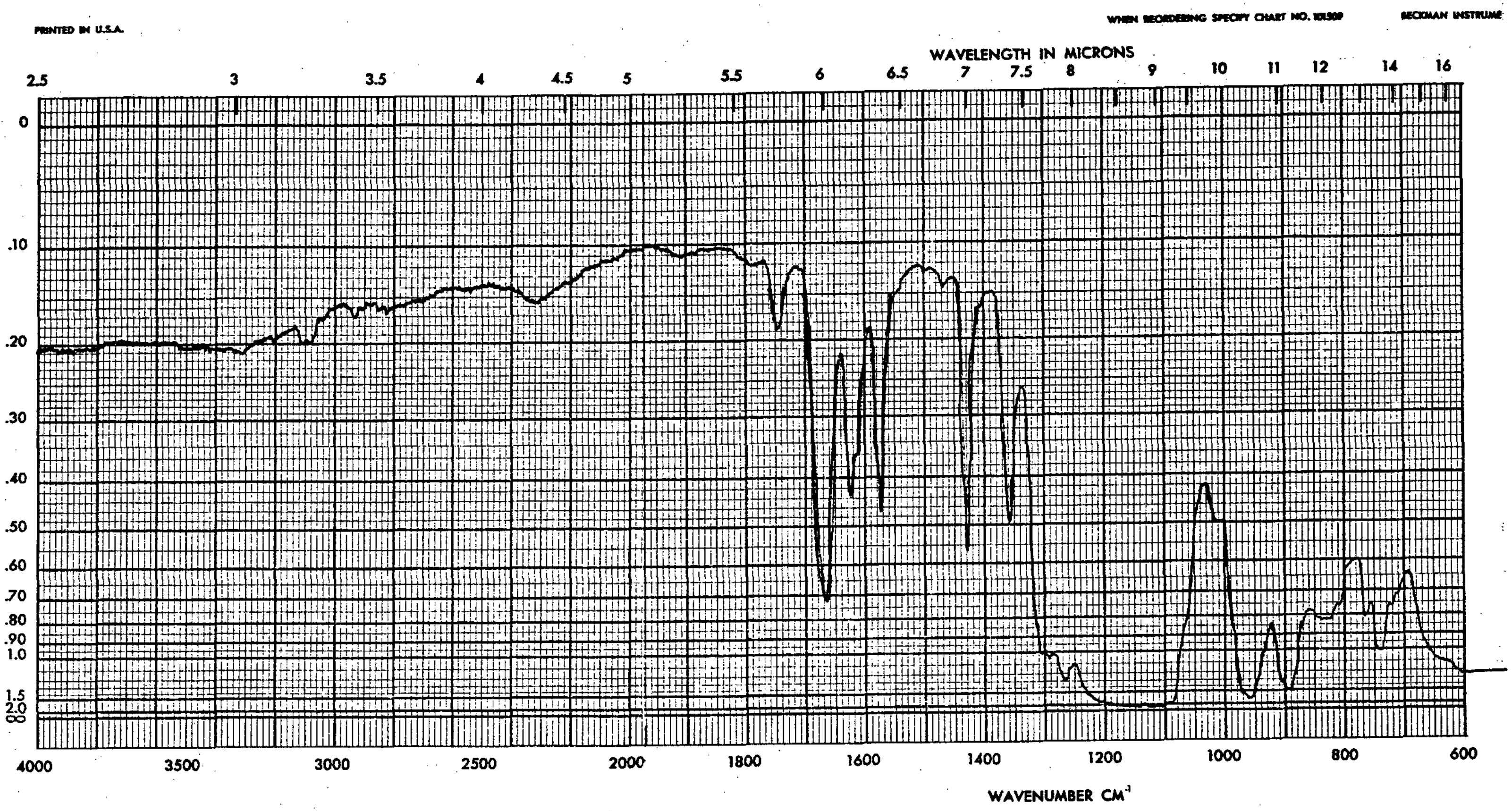


Fig. 9 - Infrared Spectrum of Methyl Perfluorosebacimidate-3,3'-diamino-4,4'-Dihydroxybenzophenone Polymer

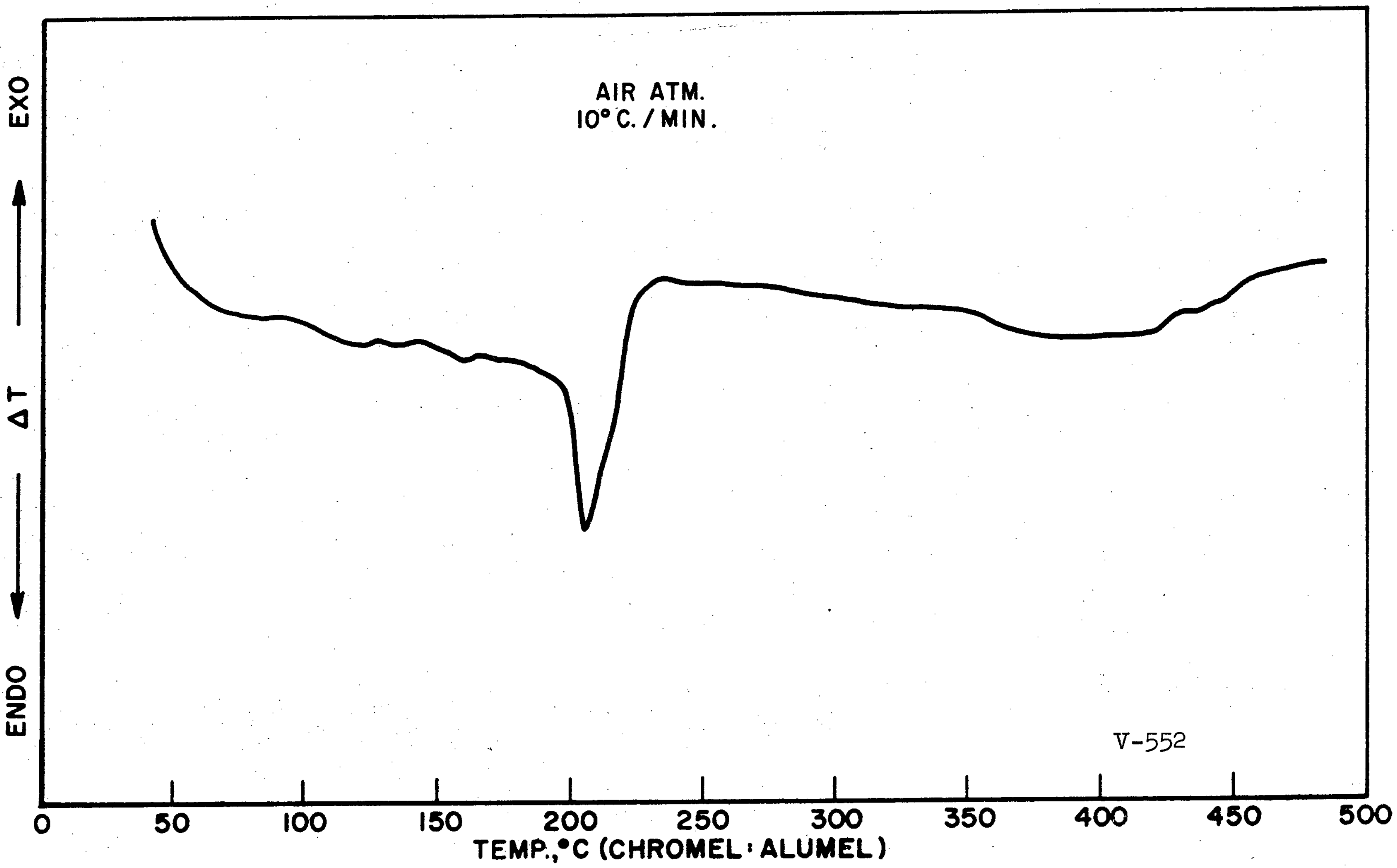


Fig. 10 - DTA of Methyl Perfluorosebacimidate-3,3'-diamino-4,4'-dihydroxybenzophenone Polymer

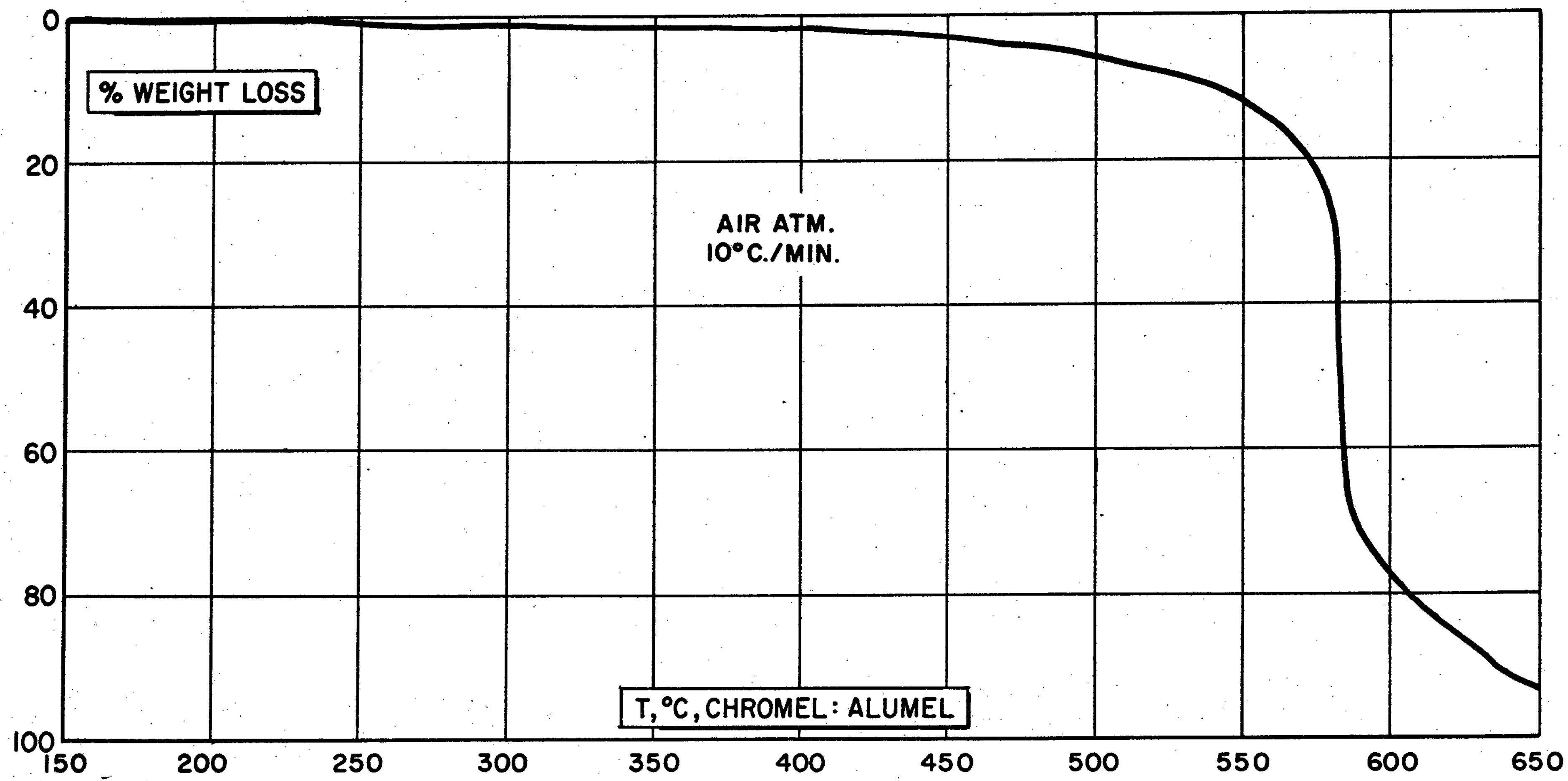
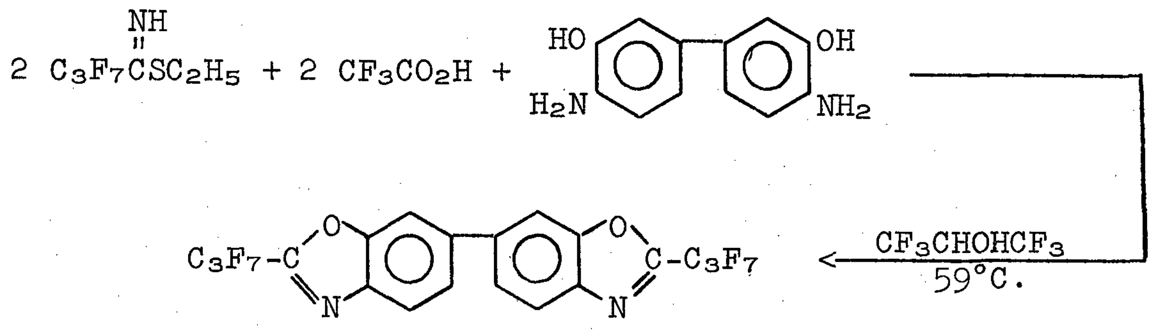


Fig. 11 - TGA of Methyl Perfluorosebacimidate-3,3'-diamino-4,4'-dihydroxybenzophenone Polymer



Model I

After two days, a 75.7% yield of Model I was obtained, but 20.6% of the dihydroxybenzidine was converted to dihydroxybenzidine bis(trifluoroacetate). The latter material formed even though the acid was neutralized with the thioimidate prior to mixing with dihydroxybenzidine. With less than the stoichiometric amount of trifluoroacetic acid, the yield of Model I increased to 83.3%, but a 13.4% yield of dihydroxybenzidine bis-(trifluoroacetate) also formed. It appears that strong acids, such as trifluoroacetic acid, cannot be used in the reaction since they deactivate the dihydroxybenzidine via stable salt formation.

In all polymerization reactions with dihydroxybenzidine, color gradually develops during the first two days and generally does not increase further during the latter stages of the reaction. To determine if the color is generated by simple decomposition, dihydroxybenzidine was subjected to the normal polymerization conditions, but in the absence of imidate ester. Initially, the solvent was water-white, but became amber within two days. After a total of seven days, the cooled mixture was filtered to recover 93% of the dihydroxybenzidine. Evaporation of the dark green filtrate left a small amount of additional dihydroxybenzidine and a brown methanol-soluble decomposition product. The infrared spectrum of this material was not well defined, but all bands characteristic of dihydroxybenzidine were present along with an additional broad band in the 1700-1770 $cm.^{-1}$ region. Thus, dihydroxybenzidine is sensitive to decomposition even in the absence of moisture and air, and it appears to be more susceptible before it has reacted sufficiently to enter into solution.

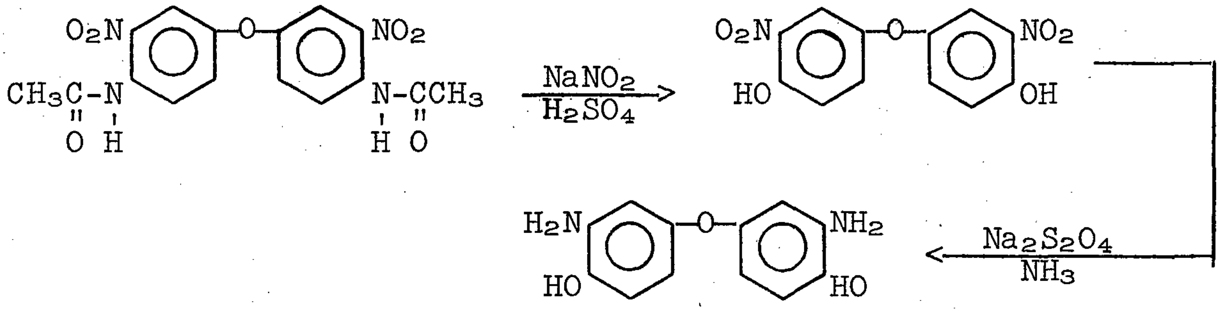
If some decomposition of dihydroxybenzidine takes place in every polymerization, then accurate stoichiometry is not attained with the bibenzoxazole polymers. However, results of the kinetic study with the perfluorosebacimidate-dihydroxybenzidine polymer suggest that high molecular weights might be obtained without the accurate stoichiometry necessary for most condensation polymerizations. To test this possibility, Polymer I, $R_f = \left(CF_2 \right)_8$, was prepared in the usual manner except that a 15% excess of dihydroxybenzidine was used. Some of the dihydroxybenzidine, which is normally solubilized in two days, remained insoluble throughout the eight-day reaction. The excess dihydroxybenzidine was quantitatively recovered by a simple filtration and identified by infrared analysis. A 96.5% yield of polymer was obtained. After the usual heat treatment at 200°C., a molecular weight value of 16,000 was measured by vapor pressure osmometry.

All polymerization reactions promoted by acetic acid have been carried out with a 2-10% excess of the promoter. To determine the minimum promoter necessary, Polymer I, $R_f = \left(CF_2\right)_8$, was prepared without excess acetic acid. With either an equivalent or one half an equivalent of acetic acid, the reaction of dihydroxybenzidine was incomplete and a thin slurry persisted. After seven days, excess acetic acid was added, but homogeneity was still not attained and as much as 6.5% of the dihydroxybenzidine was recovered. The failure of the reaction to go to completion cannot be explained and investigation of the acid requirement will continue.

The homogeneous preparation of the benzophenone polymers is much faster than the dihydroxybenzidine polymerizations and provides a system which should minimize side reactions and simplify optimization of reaction conditions.

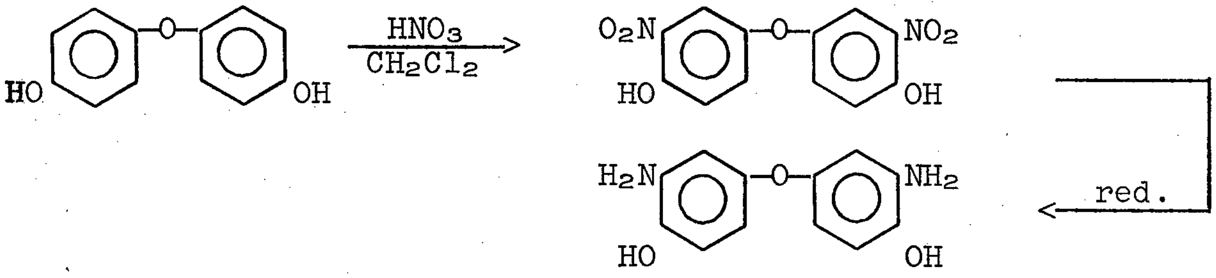
E. ATTEMPTED PREPARATION OF BIS(3-AMINO-4-HYDROXYPHENYL) ETHER

The preparation of this monomer, which should impart improved flexibility to the heterocyclic portion of the polymers, was first attempted by diazotization and reduction of commercial bis(4-acetamido-3-nitrophenyl) ether.



However, the final product was insoluble in acids, and elemental analysis indicated some coupling recurred. A step-by-step investigation revealed that hydrolysis of the diazonium salt in strong sulfuric acid was not producing the desired bis(4-hydroxy-3-nitrophenyl) ether. When the hydrolysis was subsequently carried out in very dilute acid at temperatures below 100°C., elemental analysis indicated the desired bis(4-hydroxy-3-nitrophenyl) ether had been obtained. However, ebulliometric measurements showed the molecular weight was more than five times theory, and this synthesis route was abandoned.

The preparation of the monomer by the following route was then investigated:



The nitration of 4,4'-oxydiphenol was carried out under the same conditions used successfully in the dinitration of 4,4'-biphenol. However, there is evidence of excessive nitration and milder conditions will be necessary.

SECTION III

SUMMARY

Perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers have been prepared from carefully purified monomers and the polymers purified by precipitation from hexafluoroisopropanol solution with methanol. However, intrinsic viscosities greater than 0.28 have not been attained and the infrared spectra of the polymers still exhibit the impurity carbonyl band at 1745 cm.$^{-1}$. Model compounds indicate this band cannot be attributed to a fluorinated acid nor an ester, amide or N-methyl amide of a fluorinated acid. With the corresponding perfluorosebacimidate polymer, intrinsic viscosities as high as 0.76 were obtained and the 1745 cm.$^{-1}$ carbonyl band was very small.

Two materials have been isolated from the liquors of methanol precipitations. One of these is a sublimable solid which appears to be a completely cyclized mer, and the other appears to be polymer which shows a higher concentration of the 1745 cm.$^{-1}$ carbonyl band in its infrared spectrum.

DTA measurements show the resilient perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymer has a glass transition temperature of -15°C. and the onset of thermal decomposition is 350°-400°C. in nitrogen.

Polymers have been prepared from dihydroxybenzidine and methyl perfluoro-4,9-dioxadodecanediimidate, which have intrinsic viscosities as high as 0.38. These polymers are tough leathery materials which soften at ~65°C. and have a glass transition near 21°C. [They appear to be more stable thermally than the perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers.]

A new polymer has been prepared by the reaction of 3,3'-diamino-4,4'-dihydroxybenzophenone with methyl perfluorosebacimidate. This polymer is a solid which softens at 205°C., forms films, and has excellent thermal stability. The reaction is faster than with dihydroxybenzidine since both monomers and the polymer are soluble in hexafluoroisopropanol. This homogeneous system will be examined to determine if molecular weights higher than those obtained with dihydroxybenzidine are possible. The intrinsic viscosity of the initial polymer was 0.23.

Trifluoroacetic acid cannot be used to promote the polymerization reaction since it deactivates the aminophenol monomer via stable salt formation.

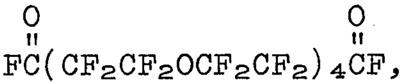
SECTION IV

EXPERIMENTAL

A. PURIFICATION OF DIHYDROXYBENZIDINE

To a 1-liter Erlenmeyer flask was charged concentrated hydrochloric acid, 50 ml., dionized water, 400 ml., and crude dihydroxybenzidine, 11.5 g. The mixture was heated on the steam bath and then filtered hot to remove the insoluble tars. The hot filtrate was treated with 1 g. Norit charcoal for 15 minutes and filtered. The charcoal treatment was repeated with 0.5 g. Norit, and the resulting filtrate was cooled in ice. The addition of concentrated hydrochloric acid, 30 ml., precipitated dihydroxybenzidine dihydrochloride which was filtered, washed with concentrated hydrochloric acid, 45 ml., and vacuum dried. The light tan product, 10.6 g., was heated on a steam bath with deionized water, 150 ml., concentrated hydrochloric acid, 3 ml., and Norit charcoal, 1.g. After 15 minutes, the mixture was filtered and charcoal treatment was repeated on the filtrate with 0.5 g. of Norit. Concentrated hydrochloric acid, 10 ml., was added to the filtrate of the second charcoal treatment and after cooling, pure white dihydroxybenzidine dihydrochloride, 7.0 g., was isolated by filtration. The dihydroxybenzidine dihydrochloride, 7.0 g., and deionized water, 160 ml., were heated on the steam bath in an Erlenmeyer flask and treated twice with 0.5 g. Norit charcoal. The filtrate from the second treatment was maintained under nitrogen and cooled to room temperature. A solution of sodium acetate, 4.4 g., in deionized water, 15 ml., was added to precipitate the dihydroxybenzidine. The slurry was pressure filtered with nitrogen through a frit, and the cake was washed with deionized water, 200 ml., ethyl alcohol, 50 ml., and finally with ethyl ether, 50 ml. The solid dihydroxybenzidine was dried on the vacuum line without heat in the absence of light and air. The yield was 4.9 g. (42.6%).

B. PREPARATION OF DIMETHYL PERFLUORO-4,9,14,19-TETRAOXADOCOSANEDIIMIDATE

Perfluoro-4,9,14,19-tetraoxadocosanediacid fluoride,

$F\overset{O}{\overset{\|}{C}}(CF_2CF_2OCF_2CF_2)_4\overset{O}{\overset{\|}{C}}F$, 24.99g., and dry diethyl ether, 250 ml., were placed in a 500 ml. flask equipped with a magnetic stirring bar, reflux condenser, and a gas inlet tube which dipped below the liquid level. To maintain anhydrous conditions, the condenser outlet was connected through a bubbler to a source of nitrogen. Anhydrous ammonia was bubbled in for three hours at 0-5°C., and then for two hours at room temperature. After stirring overnight, the mixture was filtered with nitrogen pressure through

a "frit" to remove ammonium fluoride. The ether was evaporated from the filtrate leaving 23.9 g. of a yellow solid which was identified as the diamide by infrared analysis.

The diamide, 23.9 g., and phosphorus pentoxide, 100 g., were placed in a 500 ml. flask and thoroughly mixed by hand shaking. The flask was connected to a distilling head equipped with a receiver and a source of vacuum. With the pressure reduced to about 100 mm., the flask was heated on a sand bath to about 260°C., and 17.7 g. (77% yield) of cloudy liquid was obtained which was identified by infrared analysis as the dinitrile. The dinitrile was distilled under reduced pressure and pure perfluoro-4,9,14,19-tetraoxadocosanedinitrile was collected at 110-112°C./4.5 mm.

The dinitrile, 10.6 g., dry methanol, 70 ml., and dry triethylamine, 0.9 ml., were placed in a 200 ml. flask under a dry nitrogen atmosphere and stirred at room temperature. After 0.5 hour, a homogeneous solution was formed and agitation was continued overnight. The excess methanol and triethylamine were removed under vacuum and the crude imidate ester was transferred to a small still. The imidate ester was distilled and the entire distillate was collected at 97.5-106°C./<1 μ. The once-distilled imidate ester was then fractionally distilled and pure dimethyl perfluoro-4,9,14,19-tetraoxadocosanediimidate, 9.0 g., was collected at 106-108°C./<1 μ.

C. PREPARATION OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANEDIIMIDATE - DIHYDROXYBENZIDINE POLYMERS

The reactor was a flat bottomed cylindrical glass tube (capacity about 160 ml.) tapered at the top and welded to an 8-inch small bore condenser with a female 24/40 ₮ joint at the top. A pressure equalized addition funnel with a Teflon stopcock, a male 24/40 ₮ at the bottom and a female 14/35 ₮ joint at the top, was joined to the top of the reactor condenser with a Teflon sleeve. The top of the addition funnel was connected via standard taper joints with Teflon sleeves through a gas bubbler to a source of dry nitrogen. No lubricants or greases were used and stirring was done magnetically. The equipment was dried in an oven and cooled under nitrogen. Methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate, 4.06 g. (0.004 mole), and A.C.S. grade glacial acetic acid, 0.64 g., were charged to the addition funnel in a dry nitrogen bag. Dihydroxybenzidine, 0.89 g. (0.004 mole), was charged to reactor in the dry box and both reactor and addition funnel were assembled in the hood while maintaining the nitrogen atmosphere. Dry distilled hexafluoroisopropanol, 50 ml., was added via syringe to the reactor and 10 ml. to the addition funnel. With stirring, the contents of the addition funnel were added to the reactor over a period of about five minutes. The funnel and condenser were washed down with 10 ml. additional hexafluoroisopropanol, and the white slurry was heated with an oil bath to 65°C. After 48 hours the dihydroxybenzidine had completely dissolved to produce a light amber solution. After seven days the reaction was cooled and the polymer was isolated and purified by precipitation with methanol.

D. PURIFICATION OF PERFLUORO-4,9,14,19-TETRAOXADOCOSANE-DIIMIDATE-DIHYDROXYBENZIDINE POLYMERS BY PRECIPITATION

The hexafluoroisopropanol solution of crude perfluoro,4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymer (4.55 g., theoretical yield) was filtered directly from the reactor through a glass frit to remove any solid contamination. The filtrate was then evaporated to 30-40 ml. with a stream of dry nitrogen and transferred to a small addition funnel equipped with a Teflon stopcock. The stem of the funnel was inserted through a small hole in the metal cap of a 500 ml. Waring Blendor jar. The cap was lined with Teflon to provide a good seal between the jar and the cap. Methanol, 200 ml., was placed in the jar, and with the Blendor at medium speed the polymer solution was added as rapidly as possible and chased with a small hexafluoroisopropanol wash. The liquors were decanted and the polymer, which had been deposited on the sides of the jar, was redissolved in a minimum of hexafluoroisopropanol. Trace amounts of polymer suspended in the liquors were recovered by centrifugation. The precipitation procedure was repeated twice more with methanol and the polymer was heated under vacuum to remove the hexafluoroisopropanol. Finally, the polymer was heated to 85°C./<1 μ for six hours, but infrared analysis indicated some hexafluoroisopropanol still remained. The intrinsic viscosity was 0.09. After heating at 160°C. under full vacuum for 4 hours, the intrinsic viscosity was 0.15 and hexafluoroisopropanol was not visible in the infrared spectrum.

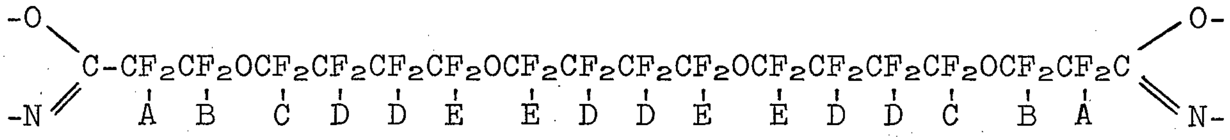
The light yellow liquors from the precipitation were distilled separately and the components in all three precipitation liquors were the same. The liquid which was distilled at atmospheric pressure was composed of methanol and hexafluoroisopropanol. The residual material was heated to 88°C./<1 μ and a white solid sublimed to the top of the flask, leaving a sticky polymeric residue. The white solid analyzed as follows:

Theory:	C, 32.8; H, 0.55; N, 2.55; F, 55.3; MW, 1098 (Mer) (Original Polymer)
Found:	C, 33.05; H, 0.99; N, 3.35; F, 53.8; MW, 1025
M. P.:	89-90°C.

Nuclear Magnetic Resonance:

Proton Spectrum - one kind of benzene ring having 1,2,4-trisubstitution. No observable OCH_3, NH or OH.

Fluorine Spectrum



Chemical Shifts in ppm, $CFCl_3$	Relative No. of Fluorines
A + 118.07	4
B + 87.98	4
C + 84.58	4
D + 126.80	12
E + 84.12	8

The total amount of solid was 0.44 g. The sticky residue had the same infrared spectrum as the original polymer except that the band at 1745 $cm.^{-1}$ was larger.

E. EXTRACTION OF DIMETHYL PERFLUORO-4,9,14,19-TETRAOXADOCOSANE-DIIMIDATE-DIHYDROXYBENZIDINE POLYMER

A sample of dihydroxybenzidine-methyl perfluoro-4,9,14,19-tetraoxadocosanediimidate copolymer in a 5 ml. beaker was placed in the extraction chamber of a Soxhlet extractor. Dimethylformamide, 100 ml., was charged to the bottom flask and heated to reflux. With the first siphon of the extraction, the solvent returning to the flask was dark. As the extraction continued over a period of 3 days, the siphoning solvent became less colored and finally was water white. The solvent remaining in the beaker was decanted and polymer was desolvated under vacuum at 150-200°C. A sample of the residual polymer when heated for three hours at 240°C. in vacuo showed no tendency to crosslink.

F. PREPARATION OF PERFLUORO-4,9-DIOXADODECANEDINITRILE

Dimethyl perfluoro-4,9-dioxadodecanedioate, 25 g., and dry ethyl ether, 100 ml., were placed in a 250 ml. flask equipped with a magnetic stirring bar, reflux condenser, and a gas inlet tube which dipped below the liquid level. A nitrogen head was maintained on the condenser outlet to insure anhydrous conditions. Anhydrous ammonia was bubbled in for five hours at 0-5°C. and the mixture was then stirred over night. The solvent was evaporated and the solid product was dissolved in 75 ml. of acetone. The product was reprecipitated by pouring into 400 ml. of distilled water. After filtration and washing, the diamide dried to 20.76 g.

The dried diamide, 20.7 g., was thoroughly mixed with phosphorus pentoxide, 100 g., in a 500 ml. flask which was then connected to a still head equipped with a reciever and a source of vacuum. The pressure was reduced to 100 mm. and the flask was heated on a sand bath to 200°C., resulting in the slow distillation of a water white liquid. Toward the end of the distillation, pressure was reduced to 15 mm. and the pot temperature increased to 250°C. The clear perfluoro-4,9-dioxadodecanedinitrile, which weighed 17.45 g. (90.5%), was identified by infrared analysis.

G. PREPARATION OF METHYL PERFLUORO-4,9-DIOXADODECANE DIIMIDATE

Perfluoro-4,9-dioxadodecanedinitrile, 17.45 g., dry methanol, 42 ml., and triethylamine, 0.5 ml. were placed in a 100 ml. flask under a dry nitrogen atmosphere and stirred at room temperature. After about 0.5 hour the mixture became homogeneous and agitation was continued overnight. The excess methanol and triethylamine were removed under vacuum and the flask with crude imidate ester was transferred to a small still. The imidate distilled at 50-55°C./ <1 μ in a yield of 18.6 g. (94%). The distillate was returned to the still and fractionally redistilled, collecting the material boiling at 53-55°C./<1 μ. The yield was about 16 g.

H. PREPARATION OF PERFLUORO-4,9-DIOXADODECANEDIIMIDATE DIHYDROXY-BENZIDINE POLYMERS

The one piece reactor described in Report Nr. PH-1Q-68 and all glassware were predried in an oven and cooled in a nitrogen atmosphere. No greases or lubricants were used and the reaction was maintained under a nitrogen atmosphere. Purified dihydrobenzidine, 1.75 g. (0.0081 mole), was charged to the reaction in a dry box. Fractionally distilled methyl perfluoro-4,9-dioxadodecanedimidate, 4.45 g. (0.0081 mole), was charged to the addition funnel in a dry nitrogen bag. The reactor and addition funnel was transferred to the hood and assembled while maintaining the nitrogen atmosphere. Dry distilled hexafluoroisopropanol, 50 ml., was added via syringe to the reactor and 10 ml. to the addition funnel. With stirring, the contents of the addition funnel were added dropwise to the reactor over a period of about five minutes. The funnel and condenser were washed down with 10 ml. additional hexafluoroisopropanol, and the white slurry was heated with an oil bath at 65°C. After 43 hours, the dihydroxybenzidine had dissolved forming a clear, light yellow solution. The reaction mixture was pressure filtered through a "frit" and most of the solvent was removed from the filtrate under vacuum at ambient temperature. Full vacuum was applied and the mass was gradually heated. At 65°C., white crystals, 0.83 g., sublimed to the top of the tube. These crystals melted at 66°C. and appeared to be ammonium hydrogen acetate. The remaining polymer was heated to 200°C. for two hours and a very small amount of sublimate collected in the cool end of the tube. The infrared spectra of the sublimate and residual polymer were similar. The sublimate weighted 0.1 g. and the polymer weighed 5.1 g. The intrinsic viscosity was 0.29.

I. PREPARATION OF 3,3'-DIAMINO-4,4'-DIHYDROXYBENZOPHENONE

4,4'-Dihydroxy-3,3'-dinitrobenzophenone, 20.75 g., and water, 182 ml., were charged to a 1-liter, 3-neck flask equipped with a stirrer, condenser, thermometer and an addition tube. Aqueous 28% ammonia. 68 ml., was added to the flask to produce a yellow slurry. Sodium dithionite, 79.5 g., was added in small portions over a period of 30 minutes, during which time the reaction exothermed to 61°C. The contents of the flask were heated to 99°C. on a steam bath for 50 minutes and cooled to 50°C. The pH was adjusted to 5.0 with acetic acid and the flask was cooled in ice. The solids were filtered by vacuum, washed with 200 ml. water, and vacuum dried at 50°C. The yellow product weighed 9.24 g. (55.4%).

Crude 3,3'-diamino-4,4'-dihydroxybenzophenone, 9.2 g., was added to a mixture of concentrated hydrochloric acid, 35.5 ml., and deionized water, 284 ml. This mixture was heated on a steam bath and treated four times with 0.5 g. of Norit charcoal, the charcoal being removed on a heated filter after each treatment. The light yellow solution was treated with concentrated hydrochloric acid, 21.5 ml., and cooled in ice.

The first crop of 3,3'-diamino-4,4'-dihydroxybenzophenone dihydrochloride crystals was filtered off and redissolved in 100 ml. deionized water. The 3,3'-diamino-4,4'-dihydroxybenzophenone was precipitated by the addition of 16 ml. of 25% sodium acetate solution which raised the pH to 5. The cake was pressure filtered under nitrogen, washed with deionized water and ethyl ether, and dried under vacuum. The purification yield was 5.449 g. (59%) although more of the dihydrodichloride salt was recovered by concentration of mother liquors. The purified 3,3'-diamino-4,4'-dihydroxybenzophenone melted at 245-247°C. with decomposition.

Analysis:

Theory: C, 63.93; H, 4.92; N, 11.48

Found: C, 63.85; H, 5.28; N, 11.1

J. PREPARATION OF 3,3'-DIAMINO-4,4'-DIHYDROXYBENZOPHENONE-PERFLUOROSEBACIMIDATE POLYMERS

The one-piece reactor described in Report Nr. PH-1Q-68 and all glassware were predried in an oven and cooled in a nitrogen atmosphere. No greases or lubricants were used and the reaction was maintained under a nitrogen atmosphere. Purified 3,3'-diamino-4,4'-dihydroxybenzophenone, 2.02 g. (0.0083 mole), was charged to the reactor in a dry box. Methyl perfluorosebacimidate, 4.27 g. (0.0083 mole), and ACS grade glacial acetic acid, 1.23 g. (0.0205 mole), were charged to the addition funnel in a dry nitrogen bag. The reactor and addition tube were assembled in the hood while maintaining the nitrogen atmosphere. Dry, distilled hexafluoroisopropanol, 50 ml., was added via syringe to the reactor and 10 ml. to the addition funnel. With stirring, the contents of the addition funnel were added dropwise to the reactor over a period of about five minutes. The funnel and condenser were washed down with 10 ml. additional hexafluoroisopropanol, and the mixture was heated with an oil bath. As the bath temperature reached 65°C., the last pieces of 3,3'-diamino-4,4'-dihydroxybenzophenone dissolved leaving a clear amber solution. After 48 hours at 65°C. , the solution was cooled and poured into 300 ml. of methanol to precipitate the polymer. The solid polymer was filtered, washed with methanol and vacuum dried. The yield of pale yellow polymer was 5.38 g. (98%). The intrinsic viscosity was 0.19. After heating for two hours at 190°C., the intrinsic viscosity was 0.23.

K. PREPARATION OF MODEL I

The reactor (Report Nr. PH-1Q-68) and all glassware were predried in an oven and cooled in a nitrogen atmosphere. Purified dihydroxybenzidine, 2.0 g. (0.00925 mole), and hexafluoroisopropanol, 40 ml., were charged to the reactor. Ethyl perfluorobutyrthioimidate, 5.31 g. (0.0206 mole), trifluoroacetic acid, 2.35 g. (0.0206 mole), and hexafluoroisopropanol, 10 ml., were placed in the addition funnel. The contents of the funnel very gradually added to the reactor and then chased with 5 ml. more hexafluoroisopropanol. The resulting slurry was agitated for 5 days, but there appeared to be no reaction. The reactor was then heated in an oil bath at 65°C. for two dyas. After cooling, the reaction mixture was filtered and 0.85 g. of dihydroxybenzidine bis(trifluoroacetate) was obtained. The filtrate was poured into 400 ml. of deionized water and the precipitated Model I was filtered, washed with water and vacuum dried. The yield of Model I was 4.01 g. (75.7%). The product without further purification melted 147-148°C.

L. PREPARATION OF POLYMER IN THE PRESENCE OF EXCESS DIHYDROXYBENZIDINE

A one piece reactor described in report Nr. PH-1Q-68 without greases or lubricants was used and the reaction was maintained under a nitrogen atmosphere. Purified dihydroxybenzidine, 1.91 g. (0.0088 mole), was charged to the reactor in a dry box. Distilled methyl perfluorosebacimidate, 3.98 g. (0.0077 mole), and A.C.S. grade glacial acetic acid, 0.97 g. (0.016 mole), were charged to the addition funnel in a dry nitrogen bag. The reactor and addition funnel were transferred to a hood and assembled while maintaining the nitrogen atmosphere. Dry distilled hexafluoroisopropanol, 50 ml., was added via syringe to the reactor and 10 ml. to the addition funnel. With stirring, the contents of the addition funnel were added dropwise to the reactor over a period of about five minutes. The funnel and condenser were washed down with 2-5 ml. portions of hexafluoroisopropanol and the slurry was heated to reflux (59°C.) with an oil bath. The dihydroxybenzidine did not completely dissolve during the eight-day reaction and the 15% excess, 0.25 g., was quantitatively recovered and identified by infrared analysis. The polymer was precipitated with 300 ml. of water, washed with methanol and water, and finally vacuum dried to 4.71 g. (96.5% yield). The molecular weight of the polymer measured by membrane osmometry was 5,800. A Soxhlet extraction of samples of this polymer with dimethylformamide was carried out for three days, filtered, washed well with methanol and vacuum dried. The molecular weight by osmometry of this sample was 8,900. A second sample of the original polymer was heated to 200°-205°C. for two hours. The molecular weight of this sample was 16,000.

M. ATTEMPTED PREPARATION OF BIS(3-AMINO-4-HYDROXYPHENYL) ETHER

Concentrated hydrochloric acid, 25 ml., bis(4-acetamido-3-nitrophenyl) ether, 11.5 g., and water, 225 ml., were placed in a 500 ml. 3-neck flask equipped with thermometer, stirrer and reflux condenser. The mixture was refluxed with stirring for 30 hours, periodically adding small portions of concentrated hydrochloric acid. After cooling, the red crystalline solid was filtered, water washed and vacuum dried to 8.6 g.

Theory:	C, 49.7; H, 3.45; N, 19.3
Found:	C, 49.55; H, 3.42; N, 19.3
M.P.:	173°-174°C.

This bis(4-amino-3-nitrophenyl) ether, 7.9 g., was dissolved in a mixture of concentrated sulfuric acid, 12 ml., water, 16 ml., and ice, 29 g., contained in a 600 ml. beaker equipped with a magnetic stirring bar. Keeping the temperature at 0°-5°C., a solution of sodium nitrite, 3.8 g., in water, 9 ml., was gradually added below the surface of the mixture in the beaker. The resulting yellow slurry was stirred for 10-15 minutes after the addition was complete and then decomposed by dropwise addition to 70% sulfuric acid, 55 ml., which was maintained at 160°C. the last portions of the diazotization slurry were washed in with 50% sulfuric acid. After addition was complete, the sulfuric acid solution was held at 160°C. for 30 minutes and cooled overnight. The slurry was filtered on a fritted funnel and washed several times with water. The dried product, 7.31 g., was black, and efforts to recrystallize the solid were unsuccessful.

The above crude product, which should be bis(4-hydroxy-3-nitrophenyl) ether, 5.9 g., was placed in a small flask with water, 54 ml., and 28% ammonium hydroxide, 20 ml. Sodium dithionite, 23.5 g., was gradually added in small portions, but the exotherm increased the temperature to only 37°C. The mixture was heated to 100°C. for one hour, cooled, filtered at pH 5.0, and vacuum dried. The dark solid, 7.6 g., was insoluble in dilute hydrochloric acid.

Analysis:

Theory: C, 62.1; H, 5.17; N, 12.08
Found: C, 40.6; H, 3.13; N, 7.23

N. DIAZOTIZATION OF BIS(4-AMINO-3-NITROPHENYL) ETHER

bis(4-Amino-3-nitrophenyl) ether, 9.1 g., sulfuric acid, 13.9 ml., water, 19 ml., and ice, 33.5 g., were placed in a 600 ml. beaker equipped with a magnetic stirrer. At 0°-5°C., a solution of sodium nitrite, 4.4 g., in water, 10.5 ml., was gradually fed to the bottom of the beaker. After the addition was completed, stirring was continued for 10 minutes and the diazotization slurry was poured into 130 ml. water. After stirring for 15 minutes the solution was filtered through a frit to remove unreacted bis(4-amino-3-nitrophenyl) ether, 1.75 g. The filtrate was heated on a steam bath for twenty hours, cooled, filtered, and the cake was washed with water. The bis(4-hydroxy-3-nitrophenyl) ether dried to 6.0 g.

Analysis:

Theory: C, 49.32; H, 2.74; N, 9.59; Mol. wt., 292
Found: C, 49.17; H, 2.74; N, 10.04; Mol. wt., 1667

O. NITRATION OF 4,4'-OXYDIPHENOL

Methylene chloride, 191 ml., and 4,4'-oxydiphenol, 26.2 g., were charged to a 500 ml., 3-neck flask equipped with an addition funnel, thermometer, and agitator. Maintaining the temperature at -10° to -5°C. with a salt and ice bath, 70% nitric acid, 66 ml., was added dropwise from the addition funnel over a period of 3.25 hours. After stirring 0.5 hour longer at -10°C., the temperature was raised to 0°C. and slurry was diluted with 192 ml. of water. The slurry was filtered at room temperature, and the solid yellow product was thoroughly washed with water. After vacuum drying at 55°C., a yield of 29.9 g. (79%) was obtained.

Analysis:

Theory: C, 49.3; H, 2.74; N, 9.59 [bis(4-hydroxy-3-nitrophenyl) ether]
Found: C, 39.8; H, 1.73; N, 14.55
M.P.: 181.5°C.

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1. ORIGINATING ACTIVITY *(Corporate author)*
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2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE
Synthesis and Characterization of Perfluoroalkyl Heterocyclic Elastomers

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Technical Report - 1 September 1968 to 1 September 1969

5. AUTHOR(S) *(Last name, first name, initial)*
Madison, Norman L.; Burton, Charles D.

6. REPORT DATE 1969	7a. TOTAL NO. OF PAGES 40	7b. NO. OF REFS 1

8a. CONTRACT OR GRANT NO.
F33615-68-C-1120

b. PROJECT NO.
7340

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
PH(2)-1F-69

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
AFML-TR-67-261, Pt. III

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Perfluoro-4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers have been prepared from carefully purified monomers DTA measurements show the glass transition temperature is -15°C. and the onset of thermal decomposition occurs at 350°-400°C. in nitrogen. The highest intrinsic viscosity attained was 0.28.

Polymers prepared from dihydroxybenzidine and methyl perfluoro-4,9-dioxadodecanediimidate soften at $\sim$65°C. with a T_g near 21°C. Thermal decomposition takes place above 400°C., and intrinsic viscosities to 0.38 have been attained.

A new polymer has been prepared from the reaction of 3,3'-diamino-4,4'-dihydroxybenzophenone with methyl perfluorosebacimidate. The polymer softens at 205°C., forms films and has excellent thermal stability. Whereas the reactions with dihydroxybenzidine are heterogeneous, this polymerization reaction is completely homogeneous since the polymer and both monomers are soluble in hexafluoroisopropanol. The parameters of this faster reaction are being investigated to determine if molecular weights higher than those attained with the bibenzoxazoles are possible. The intrinsic viscosity of the initial polymer as 0.23.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Thermal stable elastomers						
Perfluoroalkyl heterocyclics						
Perfluoroalkyl bibenzoxazole polymers						
Methyl perfluorosebacimidate - dihydroxybenzidine polymers						
Methyl perfluoro,4,9,14,19-tetraoxadocosanediimidate-dihydroxybenzidine polymers						
Methyl perfluoro-4,9-dioxadodecanediimidate-dihydroxybenzidine polymers						
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