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SYNTHESIS AND CHARACTERIZATION OF PERFLUOROALKYL HETEROCYCLIC ELASTOMERS

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

TECHNICAL REPORT AFML-TR-67-261, PART 1

September 1967

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SYNTHESIS AND CHARACTERIZATION OF
PERFLUOROALKYL HETEROCYCLIC ELASTOMERS

N. L. Madison and C. D. Burton

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FOREWORD

This report was prepared by The Dow Chemical Company, Midland, Michigan, on Air Force Contract Nr. AF 33(615)-5268. The contract was initiated under Project Number 7340, Task Nr. 734004, "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. Richard L. Van Deusen, MANP, as Project Engineer.

This report represents the work performed on this contract for the period 1 May 1966 to 1 May 1967, and is being submitted as the Annual Technical Report as part of the contract commitment by the authors in June, 1967. It is Dow Report Nr. PH-1Q-67.

Management direction at Dow is under Dr. R. P. Ruh, Laboratory Director of the Scientific Projects Laboratory, and supervised by Dr. D. A. Rausch, Assistant Laboratory Director. Dr. N. L. Madison and Mr. C. D. Burton are the principal investigators, and were assisted by Mr. C. E. Schultz.

This technical report has been reviewed and is approved.

W. E. Gibbs

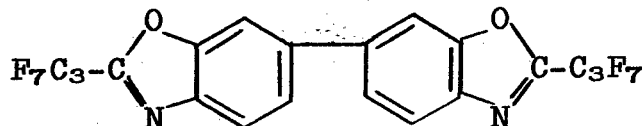
W. E. GIBBS

Chief, Polymer Branch

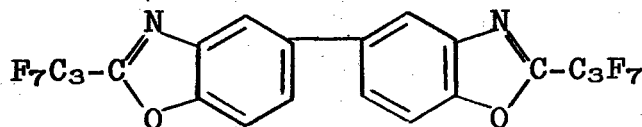
Nonmetallic Materials Division

ABSTRACT

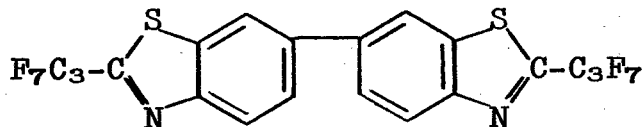
To determine if thermally stable elastomeric polymers can be obtained from perfluoroalkyl heterocyclic backbones derived from benzoxazoles and benzothiazoles, a study of related models (I, II, and III) was undertaken.



(I) 2,2'-bis(heptafluoropropyl)-6,6'-bibenzoxazole



(II) 2,2'-bis(heptafluoropropyl)-5,5'-bibenzoxazole



(III) 2,2'-bis(heptafluoropropyl)-6,6'-bibenzothiazole

These models were synthesized and fully characterized. Chemical reactivity studies indicated the models to be resistant to strong acid hydrolysis and to attack by secondary and tertiary amines. Models I and III are stable at 350°C., while Model II begins to decompose at 250°C.

Procedures for preparing the models were optimized, and polymers congeneric to Models I and III have been prepared which have a $(\text{CF}_2)_8$ between the heterocyclic rings.

Each transmittal of this abstract outside the Department of Defense must have prior approval of the Polymer Branch, MANP, Non-metallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.

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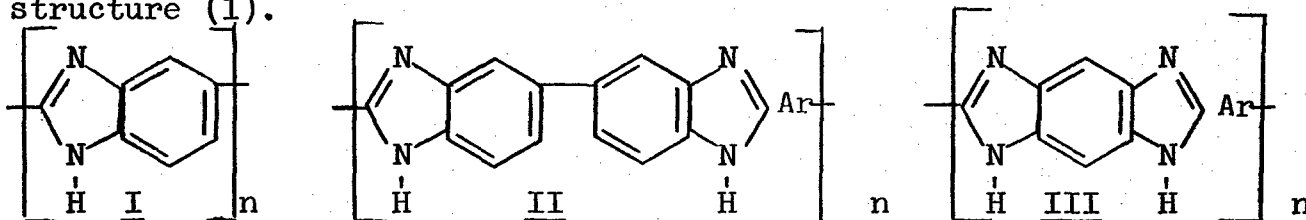
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SECTION I

INTRODUCTION

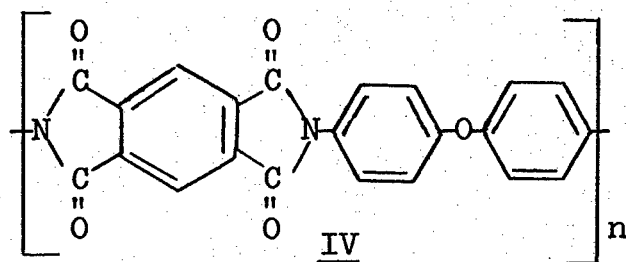
The purpose of this research is to synthesize heterocyclic fluorine-containing polymers for use as high temperature elastomers. Specifically, the program involves the synthesis of selected perfluoroalkyl heterocyclic model compounds and the determination of their relative stabilities. Polymers congeneric with the most attractive of these models are then prepared and evaluated as elastomers.

The general area of research in thermally stable organic materials has been dominated by the synthesis of polymers containing aromatic heterocyclic rings formed by polycondensation reactions. This area has been the subject of many recent reviews (1, 2) and has been the subject of discussion at various conferences on thermally stable materials (3, 4). Pioneers in this field have been Dr. Carl Marvel and his co-workers, at the University of Arizona, who have synthesized three groups of polymers (I, II, III) which are based on the benzimidazole structure (1).

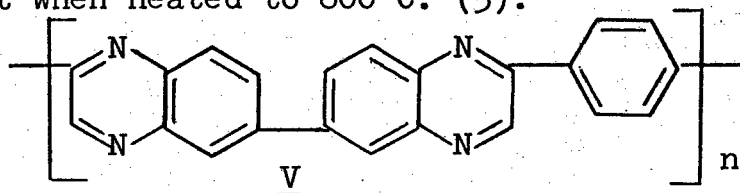


These polymers were prepared by the condensation of diphenyl esters of aromatic diacids with aromatic tetramines (1). The polymerization, which is a thermal reaction, normally gave clean polymers of molecular weights between 50,000 and 100,000. Very few of these polymers, however, showed a melting point, and above 400°C. they became insoluble in all solvents, indicating that crosslinking had occurred before the polymer melted. Before this heat treatment, the polymers were quite soluble in dimethylformamide (DMF), dimethylsulfoxide (DMSO), and other dipolar aprotic solvents. When cast from DMSO, these polymers gave quite remarkably stable films and fibers. It is notable that, when analyzed thermogravimetrically in nitrogen, these polymers were stable to 500°C. The oxidative stability of these materials was also excellent, based on the very little difference in their behavior in air or nitrogen at temperatures to about 550°C.

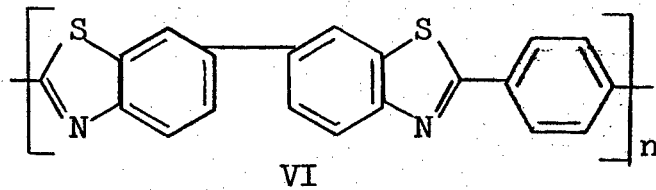
Prior to and concurrent with the polybenzimidazole research, there have been several other aromatic heterocyclic polymers prepared with similar thermal and oxidative properties. Polypyromellitimides have been prepared by du Pont (5), and marketed as "H-film", which is based on the following aromatic structure (IV).



Polyquinoxalines (V), prepared by polycondensation of diaminobenzidines and 1,4-diglyoxalbenzene at the State University of Iowa, are stable in air at 500°C., and lose less than 20% of their weight when heated to 800°C. (5).



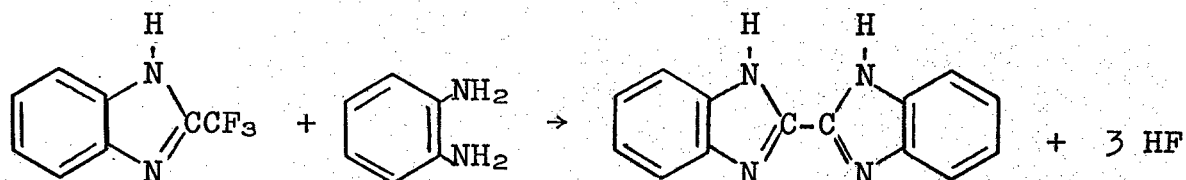
Polybenzothiazoles (VI) have been prepared by several investigators at Narmco Research and Development Laboratories (5).



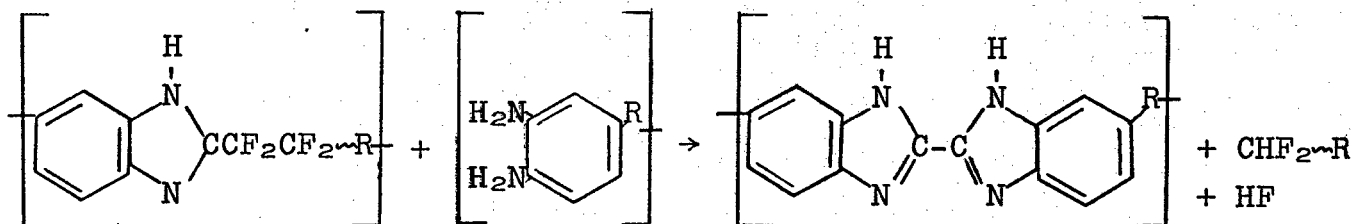
Thermogravimetric analysis confirms that these polymers are also very thermally stable.

A recent Russian review article presented a thorough picture of the many new heterocyclic polymers (2). However, as with the polybenzimidazoles, the most stable members of the various types of heterocyclic polymers were those with aromatic linkages between the heterocyclic rings, thereby limiting these materials to use in non-resilient systems.

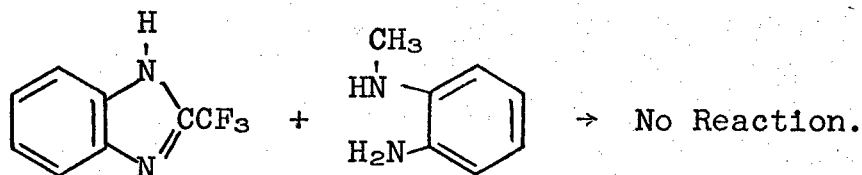
To improve the mechanical properties of these polymers, Marvel prepared polybenzimidazoles with flexible, aliphatic groups connecting the benzimidazole rings. This modification, however, considerably reduced the thermal and oxidative stability of the polymers as compared to those with aromatic groups connecting the heterocyclic rings. To improve the oxidative and thermal stability, Marvel then prepared polybenzimidazole polymers with $-C_2F_4-$ and $-C_4F_8-$ groups connecting the heterocyclic rings. Both of the polymers were not very thermally stable; however, these stabilities may not be representative, since both were low molecular weight polymers (3). These low molecular weights may have resulted from a complicating reaction reported by Lane (6), as indicated on the following page.



This reaction, which also occurs with the $-\text{C}_2\text{F}_5$ derivative, could reduce the molecular weight of a polymer chain by fission or by disturbing the stoichiometry of the polymerization reaction.

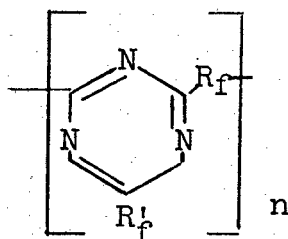


Lane has reported that this reaction does not occur with N-methyl or N-phenyl substituted amines.



Marvel, however, has not reported an investigation of this approach to obtain higher molecular weights.

Using a similar ring condensation polymerization approach, H. C. Brown (7) has prepared perfluoroalkyl triazine polymers of the general structure:



These triazine polymers were stable at temperatures from 350°C . to 410°C ., and retained their properties after being heated in refluxing fuming nitric acid for 24 hours. This work clearly establishes that thermal and oxidative stability combined with improved flexibility, as compared to the heterocyclic polymers connected with an aromatic linkage, can be obtained by incorporating a perfluoroalkyl group between heterocyclic rings.

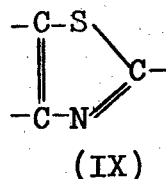
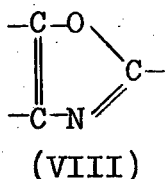
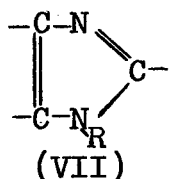
More recently, Brown (3) and his co-workers have been conducting work on the synthesis of models and polymers of perfluoroalkyl oxadiazoles, pyrazoles, and triazoles.

Thus, polymeric structures containing heterocyclic groups connected by aromatic groups are among the most thermally stable polymers known. Furthermore, it had been shown that aliphatic fluorocarbon segments between triazine rings had good stability and led to flexible polymers. However, this approach to the synthesis of flexible polymers had been studied to only a limited extent. For example, the effect on the resulting polymer properties of the variation of the type and size of the heterocyclic group and the linking fluorocarbon segment had not been investigated in any detail.

Although it seemed possible from this approach that resilient materials with good mechanical, thermal, and chemical properties might be obtained, many problems had to be satisfactorily solved. These included determining the most desirable heterocyclic rings and the fluorocarbon segment with the best properties, and preparing polymers with sufficient molecular weight for good mechanical properties.

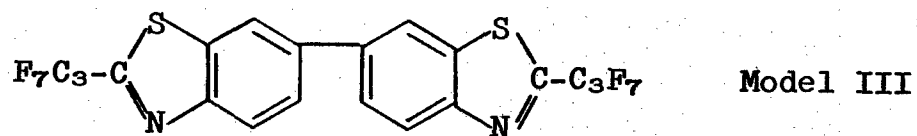
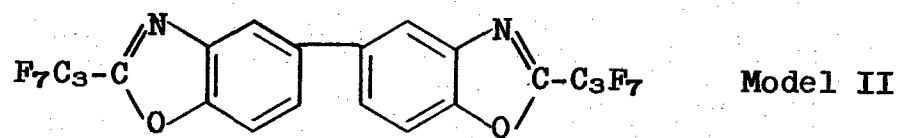
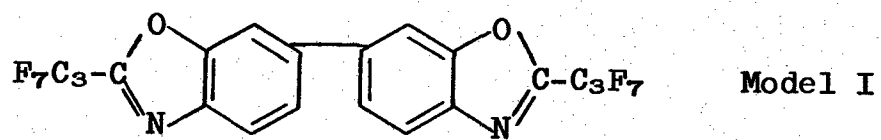
In the preparation of thermally stable heterocyclic polymers there were two criteria which had to be met which limited the number of heterocyclic rings for investigation. First, the heterocyclic ring had to have good thermal and oxidative stability, and, secondly, the type of heterocyclic ring was limited by the fluorocarbon derivatives capable of undergoing ring-forming polycondensation reactions.

Heterocyclic rings which seemed to meet these requirements, excluding triazoles, triazines, oxadiazoles and thiadiazoles, were imidazoles (VII), oxazoles (VIII), thiazoles (IX), and the benz derivatives of each of these simple rings.



In the past, the type and length of the fluorocarbon segment has been rather limited, since the only dibasic perfluoroacids readily available had been $(CF_2)_n(CO_2H)_2$, where $n = 2$ to 4 . However, more recently, limited quantities of longer chain dibasic perfluoroacids have been made available.

Our approach was to select two or three of the six proposed systems from the model compounds, and, after evaluating the models, optimize reaction conditions and prepare the congeneric polymers. Two bibenzoxazoles and one bibenzothiazole were selected as the initial systems and the following three models were chosen for study.



SECTION II

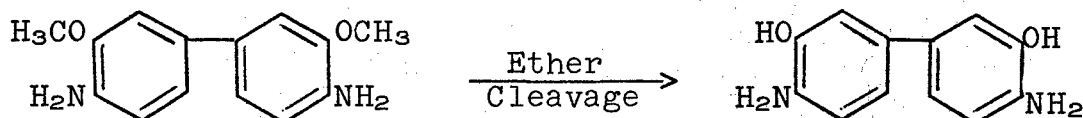
DISCUSSION

The synthesis of the models (I, II, and III) and polymers by proposed methods required the preparation of three intermediates, dihydroxybenzidine, diaminobiphenol and dimercapto-benzidine.

A. PREPARATION OF INTERMEDIATES

1. Dihydroxybenzidine

The following route was selected to prepare dihydroxybenzidines:

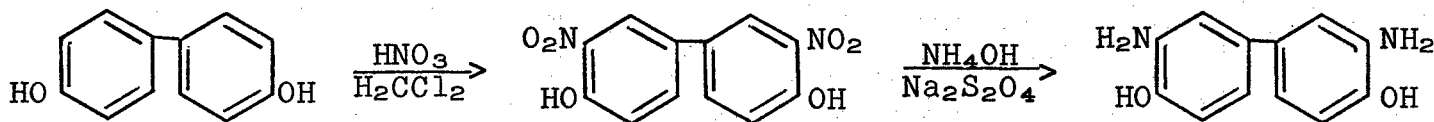


The starting material, o-dianisidine, is commercially available as the free base and was converted to the dihydrochloride (hydrogen sulfide was liberated during this operation, indicating that the dianisidine was prepared by sulfide reduction and the sulfide was incompletely removed).

Initial attempts were made to cleave the ether linkage by hydrolysis with hydrogen iodide by the method of Burkhardt and Wood (8). The product was a black, tarry material from which dihydroxybenzidine was isolated as a dark powder in only about 13% yield. Repeating the procedure, but removing the excess hydrogen iodide by decanting rather than by distillation, resulted in only a partially cleaved product (even after 48 hours of refluxing at 127°C.). This method was abandoned in favor of a modification of a patented procedure (9) which involved cleavage of o-dianisidine dihydrochloride with aluminum chloride in toluene. This procedure gave a white powder with the proper elemental analysis.

2. Diaminobiphenol

The scheme used to prepare 3,3'-diaminobiphenol, the positional isomer of dihydroxybenzidine, is as follows:

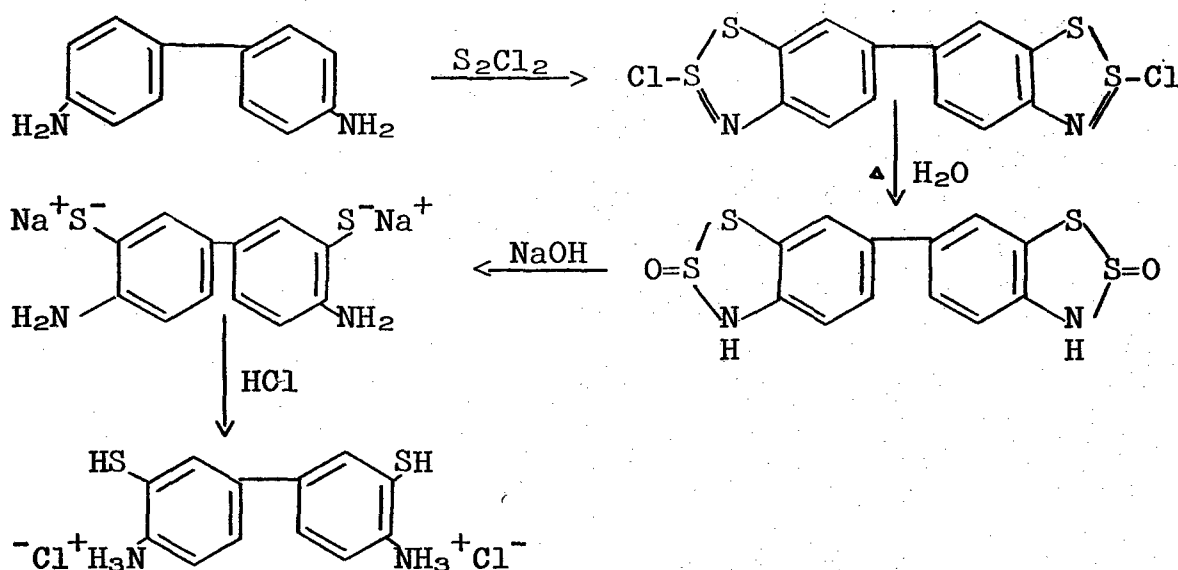


The biphenol was purchased from Dow and nitrated as received with either nitric acid in acetic acid or with nitric acid in methylene chloride. Both methods gave a solid which melted near the reported literature values; however, the yield using the methylene chloride procedure was nearly quantitative. Recrystallization of the product from acetic acid proved to be tedious and was not undertaken on large samples. The melting points and the product color changed insignificantly upon recrystallization. The elemental analysis was in good agreement with the theoretical value.

Subsequent reduction to the amine was to be carried out catalytically with hydrogen; however, the insolubility of the dinitro compound in solvents suitable for the hydrogenation made this route impractical. Reduction with sodium dithionite gave a 90% crude yield of the 3,3'-diaminobiphenol. This product was purified by preparing the dihydrochloride and reprecipitation from an aqueous solution by the addition of gaseous HCl to the mixture. (The dihydrochloride was fairly insoluble in concentrated aqueous HCl.) The free base was prepared by the addition of sodium acetate to an aqueous solution of the dihydrochloride.

3. Dimercaptobenzidine

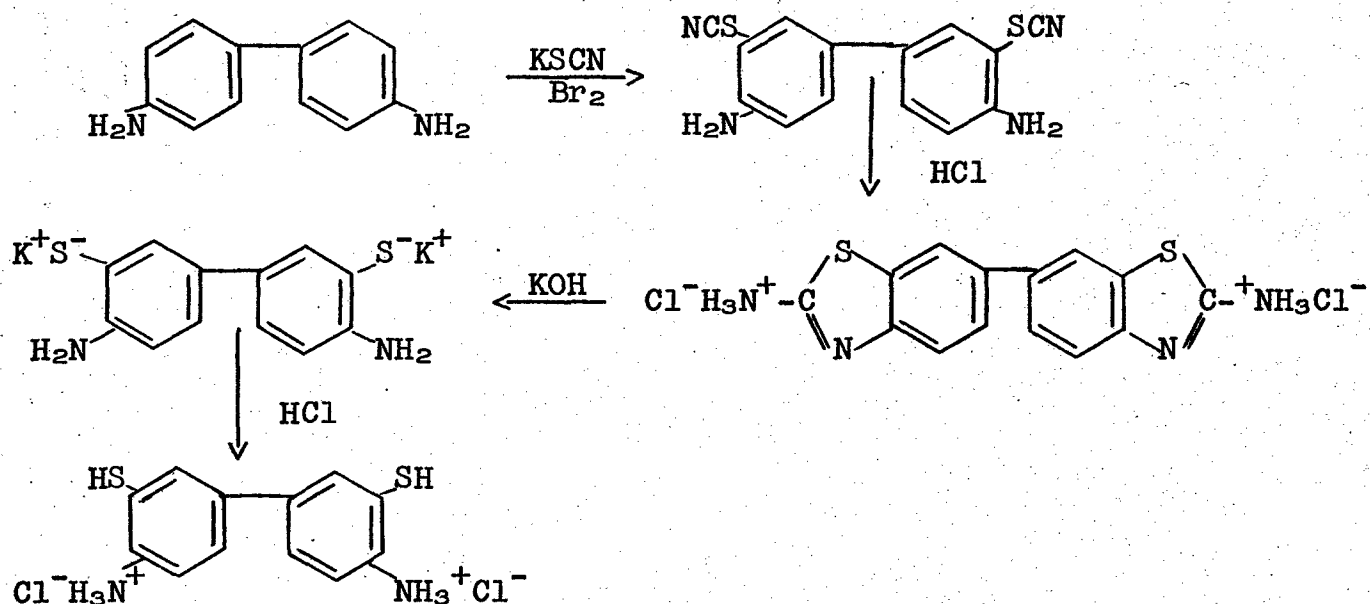
The required intermediate for preparing Model III is dimercaptobenzidine (or its dihydrochloride). There are two reported methods of preparation (10, 11) of this material, but superficially the earlier one reported appeared to be more convenient, since it did not require handling cumbersome quantities of solvent. This procedure, which was therefore used with only minor modification, is outlined below:



Unfortunately, this method gave an impure product, which was mostly in the form of a sulfide rather than the free mercaptan, indicating that oxidation occurs at some stage of the process. Workers at Koppers (12) believed that this oxidation occurred after treatment of the metal salt with acid, suggesting that the final product was very sensitive to air oxidation. However, a re-examination of the reaction scheme established that the intermediates, thiazolium chloride and thiazolium dioxide, were deficient in sulfur, pointing to the possibility of coupling to form the sulfide by loss of sulfur-containing species before the last step of this reaction was carried out. The work at Koppers suggested that they were able to prevent the oxidation from occurring after and during neutralization "by a process outside the scope of this study." Although none of the Koppers' process was disclosed, it is evident that it does not prevent oxidation, but actually involves a reduction of the sulfide to the mercaptan.

When this procedure was carried to completion, the infrared spectrum of the benzidine dihydrochloride did not show a mercaptan band at 3.9μ .

Evidence that the oxidation did not occur after reaction of the mercaptide with hydrochloric acid was obtained from the preparation of the benzidine dihydrochloride by a second, less convenient route:



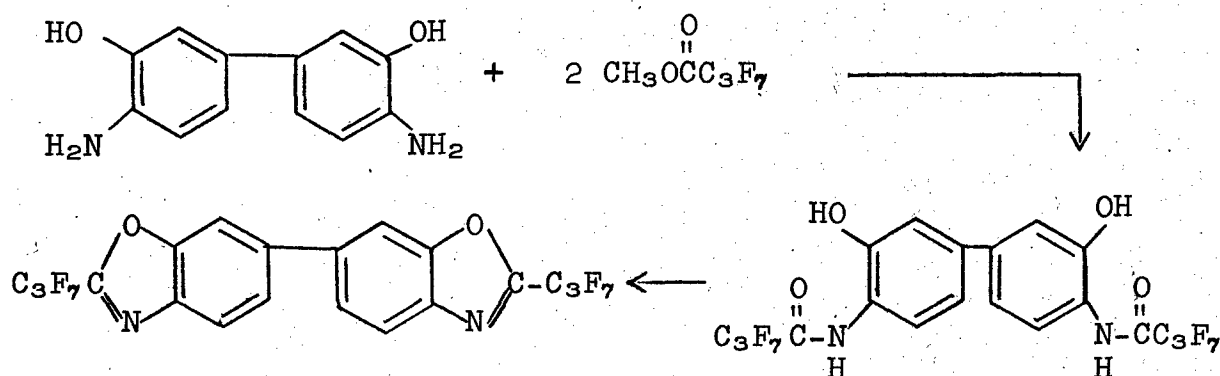
These reactions all proceeded smoothly, although several filtration operations were slow and very time-consuming. The final product of this scheme was dimercaptobenzidine dihydrochloride, as evidenced by the strong infrared band at 3.9μ .

There was no evidence that this material oxidizes very rapidly to the sulfide. However, for long-term storage the mercaptobenzidine was kept in the form of the dipotassium salt. After several months, about 3% of the material was water insoluble and was identified as dimercaptobenzidine disulfide. The free base dimercaptobenzidine was readily obtained by dissolving the dipotassium salt in water, filtering to remove the disulfide, and treating the filtrate with acetic acid.

B. PREPARATION OF MODEL COMPOUNDS

1. Two-Step Synthesis with Esters of Perfluorobutyric Acid

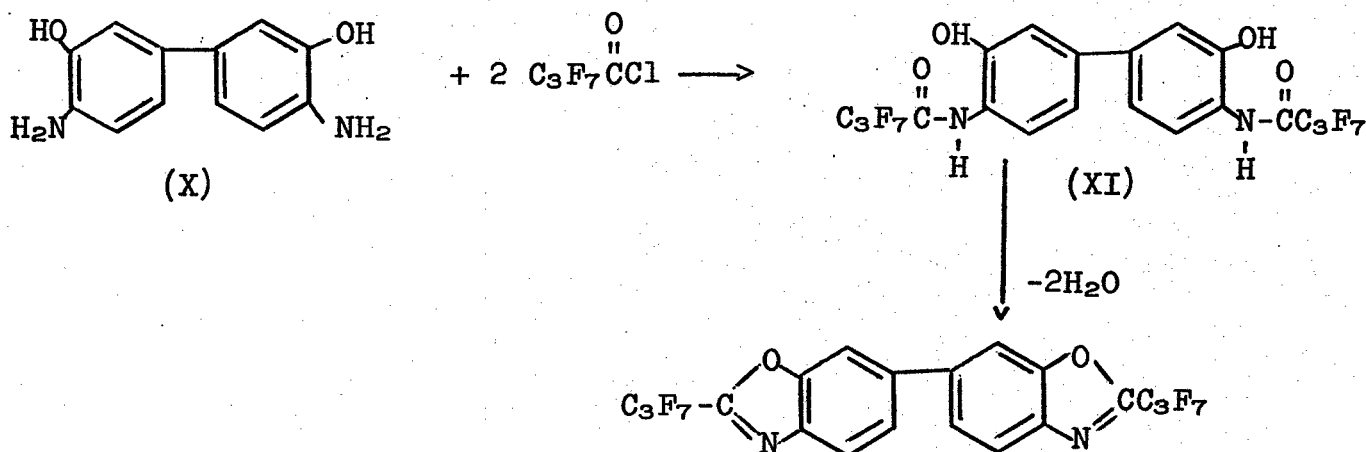
The following reaction scheme was chosen to synthesize Model I:



An attempt was made to prepare the fluorinated bis(butyramide) from methyl perfluorobutyrate at room temperature, but the isolated product was the starting free base. Another attempt to prepare the amide by heating an identical mixture at 100°C. for 24 hours resulted in an entirely water-soluble product. At temperatures above 100°C., an unworkable black tar was obtained. Although the reaction of methyl esters with amines is the standard method of preparing perfluoroacylamides, none of the desired product could be found in any of the reactions. This reaction was repeated at 120°C. in polyphosphoric acid, but there was no apparent reaction of the ester, only a tarry residue of dihydroxybenzidine.

2. Two-Step Synthesis with Perfluorobutyryl Chloride

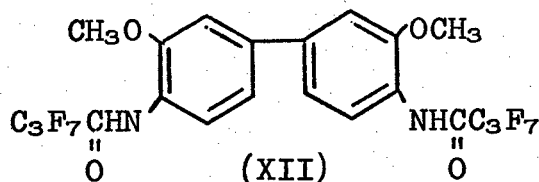
Since the attempts to form the bis(butyramide) from methyl perfluorobutyrate were unsuccessful, the acid chloride was substituted for the ester.



Model I

By using the acid chloride, the amide was prepared and, although several products are theoretically possible (ester as well as amide can form), the major product with either dihydroxybenzidine or diaminobiphenol was the corresponding diamide.

The preparation of the amide (XI) was most successfully carried out by mixing a stoichiometric quantity of (X) with the acid chloride in pyridine. The purple product appeared to be two materials (from infrared analysis). When separation was effected by extraction with benzene or methylene chloride, one of the products was found to be a bis-ether resulting from o-dianisidine in the starting material, (XII),

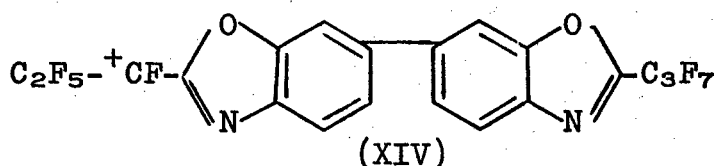
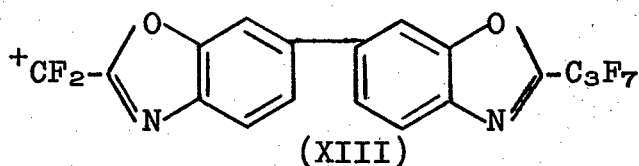


and the other, the desired diamide (XI). The diamide, however, retained the deep purple color. Upon heating, the color disappeared and the amide was then readily purified by recrystallization. Attempts were made to prepare (XI) either in DMAC, or triethylamine and, although the purple color was absent, the yields were considerably lower.

The diamide from diaminobiphenol was prepared in the same manner, but it appeared to be a single product. It was purified by either sublimation or recrystallization from acetone. The elemental analyses and the infrared spectrum were in agreement with the proposed amide structure.

An attempt was made to prepare a perfluorobutyramide from dimercaptobenzidine dihydrochloride, but this reaction was unsuccessful.

To effect cyclodehydration, each of the amides was heated with an excess of polyphosphoric acid at 200°C. Model I was initially obtained in low yield as a white fuzz, which sublimed from the acid. Infrared analysis showed that -C=O , -O-H , and the -N-H peaks which were present in the amide were all absent, as expected, in the model. In addition, a sharp characteristic -N=C- band appeared at $6.23\ \mu$ and the strong -C-F bands at $\sim 8.3\ \mu$ were still present. Mass spectral analysis (Table I) showed the principal ion to be the parent, 572. This ion was slightly more intense than the second most intense ion, 453 (the parent minus a C_2F_5 group). The parent is also greater than five times the intensity of the third most intense peak, 553, (or the parent minus fluorine). These results indicated that rupture takes place initially to give a stable carbonium ion, such as (XIII) or (XIV), as a result of scission along the side chain in preference to cleavage of the ring.



Olah (13) has reported that fluorobenzyl carbonium ions such as O^+CF_2 and $\text{O}^+\text{CF}-\text{O}$ are very stable species. This may also be true of the benzoxazole carbonium ions (XIII) and (XIV) in which the ring is strongly aromatic.

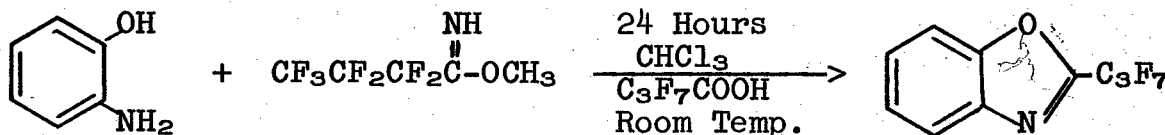
An improved preparation involved use of a horizontal sublimation apparatus which resulted in a crude yield of 59% of Model I. An attempt to effect the cyclodehydration with sodium methoxide in methanol yielded tars.

Cyclodehydration to give Model II was carried out in the same manner at 200°C. and crude yields of 72% were obtained. The infrared spectrum of Model II had essentially the same peaks as did Model I; the -C=N- peak was shifted to slightly higher wavelengths ($6.39\ \mu$). Both models were white, crystalline solids which were readily soluble in acetone and could be recrystallized from an acetone-water mixture or from methanol. Small amounts of colored impurities were removed with charcoal, but much of the model is apparently absorbed by this treatment.

The benzothiazole model was not prepared by this method due to the lack of the required intermediate amide.

3. One-Step Synthesis with Methyl Perfluorobutyrimidate

G. I. Braz et al. (14) have reported the preparation of benzoxazoles from the reaction of o-aminophenols and imidate esters. From the reaction of o-aminophenol with methyl perfluorobutyrimidate, Braz obtained a 55% yield of the corresponding benzoxazole.



Although, without optimization, the yields were not sufficiently high to apply this reaction to the preparation of the corresponding condensation polymers, it offered the possibility of utilizing a one-step procedure for making either the model or the corresponding polymer.

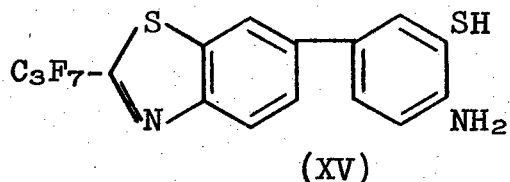
The methyl perfluorobutyrimidate was prepared conveniently from the reaction of perfluorobutyronitrile and methanol in the presence of trimethylamine in a Fischer-Porter reactor.

To prepare Model I, the general procedure of Braz was followed, but only a very poor yield of the model was obtained. The perfluorobutyric acid, used in the reaction, was added to a slurry of the dihydroxybenzidine, the imidate ester, and chloroform. The main product was a water-soluble salt. The procedure was modified by adding a mixture of the imidate and the acid to a chloroform slurry of the dihydroxybenzidine. Although this procedure improved the yield (from 12% to about 25%), the yields were too low to be of synthesis value.

When dioxane was used as a solvent and the reaction was carried out at 60°-80°C., a crude yield (all one product by infrared analysis) of Model I of greater than 90% was obtained. In addition, it was found that the same high yield of relatively pure model could be attained by using trifluoroacetic acid instead of perfluorobutyric acid. Braz carried out his cyclization reactions using perfluoro acids which were derivatives of the imidates employed. This procedure would be very wasteful in polymer preparation, where expensive diacids would be consumed without incorporation into the polymer. A low molecular weight salt would be desirable, since ammonium salts of the acids are co-products of the reaction and can be readily sublimed from the polymer. Ammonium perfluorobutyrate sublimes readily and was

recovered in this manner from one preparation of the model. Model II was prepared by this modified procedure in a crude yield of greater than 86%, and it thus appears that this procedure was directly applicable to synthesis of the polymers.

When methyl perfluorobutyrimidate was treated with dimer-captobenzidine following the procedure described above, Model III was isolated in 67% yield along with a compound, believed to be the half-reacted mercaptan, (XV), in 11% yield.



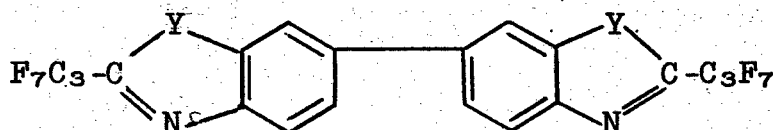
Although the analysis for this material (XV) is excellent, the absence of an S-H band in the infrared spectrum casts some doubt on the proposed structure.

The structure of the model was fully supported by the elemental analysis, the infrared spectrum, and NMR. It is a white solid which is readily recrystallized from acetone. It is also soluble in hot methanol and in hot benzene. The mass spectral cracking pattern of Model II was essentially the same as Model I and, while Model III gave the same general pattern, it showed a greater susceptibility for the central biphenyl bond to scission. In all three cases, rupture of the side chains occurs in preference to ring cleavage. However, the parent peak is the most intense, indicating the high stability of these materials (Table I).

4. Optimization of Model Yields

To insure good yields, high purity, and high molecular weights for the proposed polymers, the imidate ester-dihydroxybenzidine reaction was further studied via the preparation of Model I. When this reaction was run at the reflux temperature of dioxane for 5 hours, the crude yield was only 46% and some dihydroxybenzidine was recovered. Infrared analysis of the crude material indicated other impurities were also present. When the reaction was repeated at 48-59°C. for 24 hours, a quantitative crude yield of the model was obtained, and, although the infrared analysis substantiated the structure, the material was colored. Reprecipitation from a sulfuric acid solution, followed by recrystallization from hexane, gave nearly pure Model I. The hexane-insoluble material was a black tar which showed some carbonyl function by infrared analysis and had the odor of perfluorobutyric acid. The substitution of tetrahydrofuran for dioxane in a 50°C. reaction resulted in a much darker reaction mixture which produced a rather dark, crude product in 77% yield. This material did not dry as easily as previous materials and the infrared spectrum contained bands characteristic of tetrahydrofuran along with the expected Model I.

Table I
Comparison of Model Mass Spectra^(a)



Ion	Relative Intensity	
	Model I (Y=O) ^(b)	Model III (Y=S)
Parent	100.00	100.00
Parent Minus CF ₂ CF ₃	84.17	82.05
Parent Minus F	20.42	13.56
1/2 Parent Minus CF ₂ CF ₃	13.16	30.45
Parent Minus 2 CF ₂ CF ₃	6.99	16.47

^aFive most intensive peaks.

^bModel II essentially identical with Model I.

G. I. Braz et al. (14) also reported the preparation of benzoxazoles by reaction of o-aminophenols with imidate esters in the free base form using hot dioxane as the reaction medium. This technique was applied to the preparation of Model I and the reaction was carried out at 80°C. for 72 hours. The crude yield was 98%, but major impurities were shown to be present by infrared analysis. Reprecipitation of this material from concentrated sulfuric acid gave a dark green product which appeared to be some type of organic ammonium salt. There was no recovered model, possibly indicating that ring closure occurred on only one side and sulfuric acid decomposed the resulting material.

C. CHEMICAL STABILITY OF THE MODELS

All three models were insoluble and unchanged after boiling in water for 24 hours. A refluxing ether-triethylamine solution dissolved the models, but they were recovered unchanged. When Model I was refluxed 4 hours in diethylamine, there was no apparent reaction.

Concentrated sulfuric acid at 25°C. or 100°C. dissolved all three models, but dilution of the solution with water quantitatively reprecipitated Models I and III. Most of Model II was also recovered in a pure state by this procedure, but there was

some weight loss, indicating slight decomposition to water-soluble products. Model III was not affected by refluxing with concentrated hydrochloric acid, but all three were completely decomposed to water-soluble products with 70% nitric acid at 100°C. In most strong aqueous acids, the models, particularly I and III, appear to be resistant to hydrolysis. The decomposition in hot nitric acid may be due to nitration or oxidation rather than hydrolysis.

D. THERMAL STABILITY OF THE MODELS

As a guide in selecting which of the three heterocyclic systems might be stable as polymer units, the stability of each of the three models was determined. Unfortunately, all three materials are volatile and TGA analysis could not be used; therefore, samples were heated in evacuated, sealed glass ampoules.

Initially, the three models were heated for 24 hours at 250°C., but there was no change in the melting points or infrared spectra. Although Model II was darkened slightly in the melt, upon resolidification it resumed its original color. (It appeared to contain a small amount of charcoal, so subsequent studies have been performed on a clarified sample.) There were trace amounts of volatile products from the two benzoxazoles, one of which was identified as methanol and another as acetone, which indicates that residual recrystallization solvents still remained. However, the heated and devolatilized samples did not differ in weight by more than 0.3% from the original samples.

Samples of the three models were heated for seven days at 250°C. There was darkening in the two benzoxazole models and no apparent change in the benzothiazole. The melting points changed slightly, but there was no discernible change in the infrared spectra. There were still only traces of volatiles and insignificant weight changes in all cases.

The two benzoxazoles were heated for 12 days at 250°C. and for one day at 350°C. Model I had a slightly lowered melting range, but exhibited no change in the infrared spectrum. There was only a trace of volatile product which was entirely $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$. Under the same conditions, Model II degraded more severely, darkening considerably and forming volatile products (CO_2 , SiF_4 , and $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$). However, in spite of the darkened appearance and some apparent charring, the melting point was not severely lowered (see Table II).

The benzothiazole was heated for seven days at 250°C. and then for one day at 350°C. There was only a slight graying of the model and no apparent gassing. The melting point was not depressed and the infrared spectrum was unaltered. The models thus appear to have good stability. The stability order appears to be: (III) > (I) > (II). Therefore, polymer systems based on Models III and I were chosen for further study and those based on Model II were excluded from further investigation.

Table II

Stability of Models I, II, and III (Heated in Sealed Tubes)^a

Run No.	Model	Time, days	Temp., °C.	Wt. Change, %	M. Range, Before Heating, °C.	M. Range, After Heating, °C.	Volatiles
1	I	1	250	~0.3	147.5-148.0	147.5-148.0	MeOH
2	I	7	250	~0.8	---	146.8-148.0	MeOH
3	I	12	250	---	---	145.0-147.1	MeOH
		1	350				CF ₃ CF ₂ H
4	II	1	250	~0.3	94.8-95.2	94.8-95.2	MeOH
5	II	7	250	~0.3	---	94.0-95.0	MeOH
6	II	12	250	~2	---	91.0-92.5	SiF ₄ , CO ₂
		1	350				CF ₃ CF ₂ CF ₂ H
7	III	1	250	None	157.5-160.8	157.5-160.8	Acetone
8	III	7	250	None	157.5-160.8	157.5-161.0	Acetone
9	III	7	250	---	---	158.0-160.8	Acetone
		1	350				
10	II	3	350	~7	---	---	SiF ₄ , CO ₂ ^b
							CF ₃ CF ₂ CF ₂ H

^aThere were no infrared spectral changes in any of the models after heating.^bThe weight loss was determined by the weight of volatile material removed.

E. PREPARATION OF MONOMER INTERMEDIATES

In order to prepare polymers congeneric to the model compounds I and III, it was necessary to synthesize several derivatives of available difunctional perfluoroalkyl compounds.

1. Preparation of Perfluorosebaconitrile

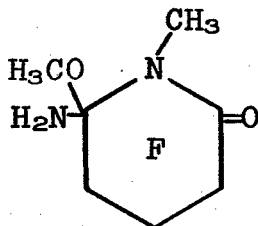
Impure perfluorosebacamide, as received from the Project Engineer, was initially hydrolyzed with hydrochloric acid and then treated with permanganate. This produced a white, hygroscopic product which was then recrystallized from water. Without further purification, the acid was converted to the methyl ester in an overall yield from crude diamide of 66%.

The pure diamide was prepared in quantitative yield from the ester with ammonia. Dehydration of the diamide with phosphorus pentoxide, P_2O_5 , gave an excellent yield of very pure perfluorosebaconitrile.

2. Preparation of Derivatives of Perfluoroglutaric and Perfluoroadipic Acids

The first few reactions to prepare the polymer of Model I indicated that the preparation of polymers would be much more difficult than the preparations of the model compounds and it was felt that optimization of the yields should be carried out on a polymer system. Because of the limited supply of perfluorosebacic acid, the more available perfluoroadipic and perfluoroglutaric acids were chosen for this study.

A recently patented procedure (15) was used to prepare perfluoroglutaronitrile, which involved heating the diamide with bis-1,4-trichloromethylbenzene in trichlorobenzene. This method is reported to avoid cyclization of the amide to the imide; however, the yields were found to be poor. In attempting to vacuum distill the methyl perfluoroglutarimide, prepared from the dinitrile, the principal product obtained was identified as the lactam,

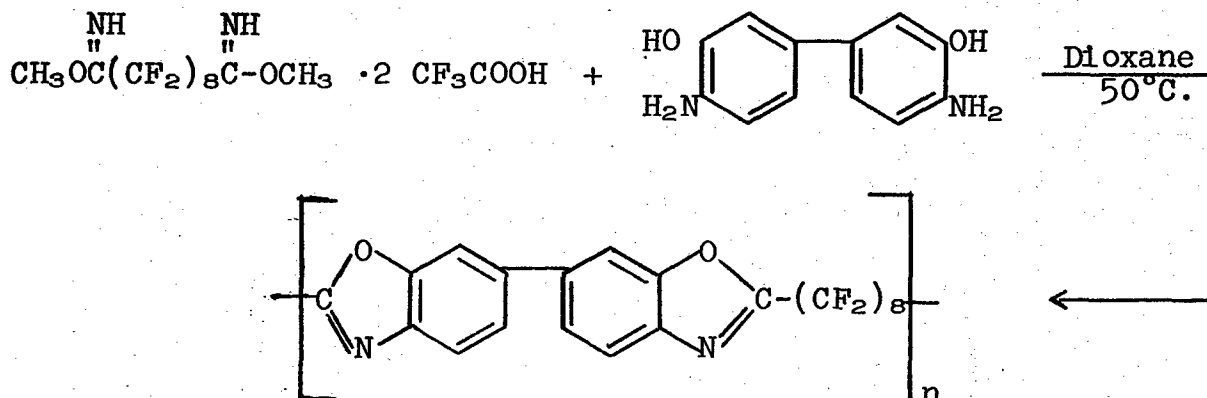


From NMR and infrared analysis, none of the imide was observed. Perfluoroadipic acid was prepared by oxidation of perfluorocyclohexene with potassium permanganate in aqueous acetone, and esterified by reaction with ethanol in the presence of sulfuric acid to produce diethyl perfluoroadipate in 66% yield. The ester was converted to the amide with ammonia and then dehydrated with P_2O_5 to obtain a 65% yield of perfluoroadiponitrile. Methyl perfluoroadipimide was prepared by reaction of the nitrile

with methanol in the presence of triethylamine and purified by distillation. The yield was 78% based on perfluoroadiponitrile.

F. PREPARATION OF BIBENZOXAZOLE POLYMERS

Polymers were first prepared by reaction of the bis(trifluoroacetic acid) salt of dimethyl perfluorosebacimide with dihydroxybenzidine at 50°C.



The imide ester was prepared by reaction of perfluorosebaconitrile with methanol in the presence of triethylamine and isolated by vacuum stripping the excess methanol and triethylamine. It was used without further purification, since most higher molecular weight imide esters are unstable at their boiling points.

The first polymer was synthesized with a slight excess of the imide ester salt and the rest were made using stoichiometric quantities of the reactants, but all products were essentially identical. The polymers had similar infrared spectra containing carbonyl bands and broad absorption indicative of organic amine salts in the 3-4 μ range. Heating the polymers in stages to 380°C. did not change the infrared spectra. A sample of polymer was recrystallized from tetrahydrofuran, but there was no change in the color, softening point, or infrared characteristics. Heating the polymers beyond the softening point (232°C.) and cooling resulted in somewhat brittle masses. Sulfuric acid solutions of the polymer were dark red and, after precipitation with water, both the broad absorbance in the 3-4 μ region and the carbonyl bands had increased. In addition, sulfuric acid treatment reduced the percent carbon, fluorine and nitrogen, increased the percent hydrogen, and left residual sulfur in the polymer.

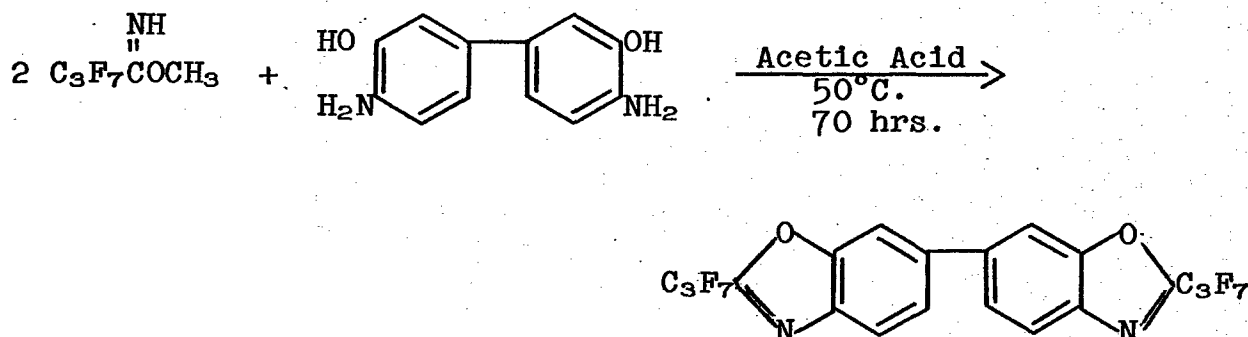
Although the elemental analyses would not support the presence of a large number of end groups, since they were close to theoretical, the brittle nature of these materials and the infrared characteristics were indicative of low molecular weight polymers.

To determine why the polymer molecular weights were apparently low, whereas the models were formed in good yield, the physical and chemical characteristics of the imidate esters were investigated. A small amount of dimethyl perfluorosebacimidate was prepared and excess reagents were stripped. The neat material was then heated under vacuum at 120°C. for several hours. There was no discoloration and no apparent decomposition, although a trace of methanol was detected in the gases above the sample. The neat material was then heated further to 140°C., where some reflux was noted but no decomposition. Elemental analysis of the residual material was excellent for pure imidate ester.

Since the imidate ester was stable at the temperatures required for cyclization, the salt was prepared for investigation by adding a slight excess of trifluoroacetic acid to the dimethyl perfluorosebacimidate. Within a few minutes, the mixture turned solid and the resulting products were found to be methyl trifluoroacetate and perfluorosebacamide. In contrast, the reaction of trifluoroacetic acid and methyl perfluorobutyrimidate was much slower, but precipitation of the perfluorobutyramide began after one hour at room temperature.

Thus, both polymer formation and model formation are accompanied by the competing reaction to form perfluoroacyl amides. Since the models were produced in good yields, it was expected that polymers of high molecular weight could be achieved. However, when the polymer synthesis was carried out, early precipitation was noted which probably slowed the polymerization process. This could allow the competing amide formation reaction to dominate and, thus, result in low molecular weight polymers.

Brown and Wetzel (16) noted that perfluoroimideate hydrochlorides also readily decomposed to give perfluoroamides and alkyl chlorides, but no mention was made of salts of imidate esters and weaker acids. When acetic acid was mixed with methyl perfluorobutyrimidate at 25°C., there was neither salt nor amide formation after 24 hours. Consequently, the following reaction was carried out to determine if the interaction of acetic acid and the imidate was sufficiently strong to promote the formation of Model I:



Model I was obtained in 94% yield as a light tan solid, M.P., 146-147.5°C. (pure M.P. 147.5-148.0°C.). Infrared analysis showed no extraneous absorbance and the product could be recovered unchanged from sulfuric acid solution in essentially theoretical yield. Thus, it appeared that acetic acid would be useful for polymer preparation.

The bibenzoxazole polymer was prepared with methyl perfluorosebacimide in acetic acid at 50°C. for 24 hours, after which the temperature was raised to 70°C. for another 24 hours. The product was a grey solid obtained in quantitative yield, but the resolidified melt was again brittle. A small carbonyl peak was detected by infrared analysis, but there was no infrared absorption other than C-H in the 3-4 μ range. Elemental analysis was in good agreement with the proposed polymer, but, as with previous polymers, there was some decomposition after reprecipitation from sulfuric acid solution.

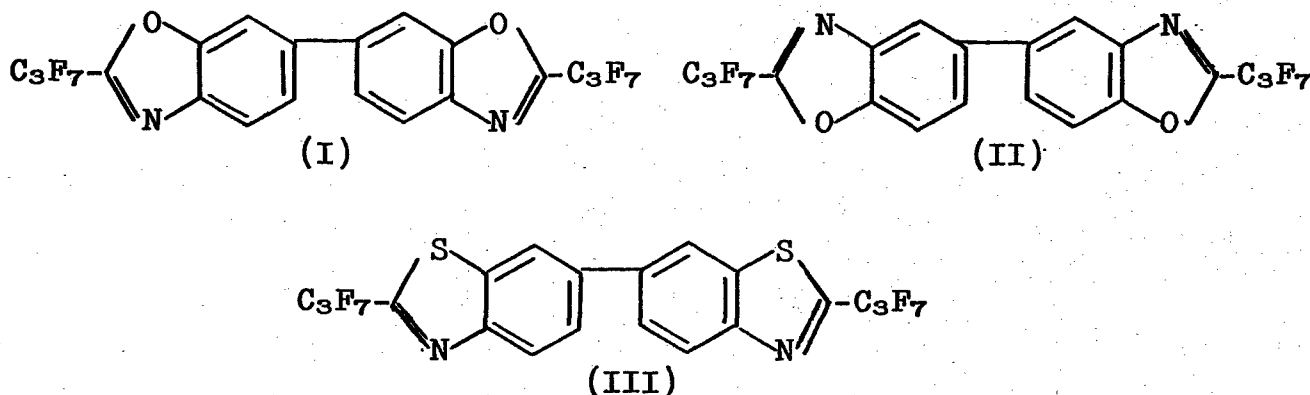
From the appearance of the reaction, it is assumed that there is a solubility problem which impedes the growth of the polymer and results in short chains. To overcome this, the polymerization was carried out in refluxing acetic acid (118°C.) for 48 hours.

Again the reaction mixture was not homogeneous and the resulting grey solid, M.P. 220-225°C., contained carbonyl bands in its infrared spectrum. All of the bibenzoxazole polymers prepared appear to be only moderate molecular weight materials, and no solvent has yet been found which will give a homogeneous reaction mixture. However, regardless of the method used, acetic acid or trifluoroacetic acid, the elemental analyses correspond to a polymer containing a 1:1 ratio of perfluoroalkyl chain to bibenzoxazole group and the infrared analysis establishes that benzoxazole rings are present.

SECTION III

SUMMARY

Three selected model compounds, I, II, and III, which are representative of proposed polymeric elastomers have been prepared in fair yield by a two-step process by cyclodehydration of an intermediate bisanilide,

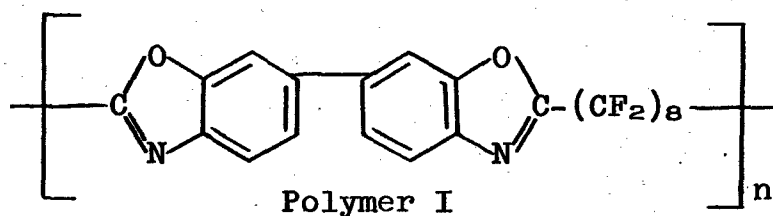


and in good yield by a one-step process from the reaction of imide esters with properly substituted biphenyls.

Thermal degradation studies indicated that all three models are very stable in the absence of air at 250°C. and that Models I and III are stable at 350°C., showing no weight loss and only a slightly depressed melting point. Oxidative stability has not been determined due to the volatile nature of the models.

All three compounds were very resistant to strong acid, such as concentrated sulfuric acid or concentrated hydrochloric acid, and unreactive toward secondary and tertiary amines. The thermal and chemical stability studies indicated that polymers based on structures congeneric with Models I and III should be sufficiently stable and unreactive for high temperature applications.

Polymers based on Model I were prepared by reaction of dihydroxybenzidine with methyl perfluorosebacimide in the presence of either trifluoroacetic acid or acetic acid. Although trifluoroacetic acid promotes a side reaction resulting in the formation of perfluorosebacamide, polymers prepared by this system were essentially identical to those prepared with acetic acid. The proposed structure:



was established by elemental and infrared analysis. These polymers were somewhat brittle; and modifications, which may be necessary to obtain elastomeric properties, will be undertaken when it has been established that high molecular weights can be or have been achieved.

Bibenzothiazole polymers based on Model III were prepared by the same reaction with dimercaptobenzidine using dimethylacetamide as the solvent. In this solvent, the polymerization reactions were homogeneous, but polydimercaptobenzidine disulfide was formed as a byproduct.

In addition, analyses indicate that a considerable amount of degradation took place during the polymerization resulting in a non-homogeneous product.

SECTION IV

EXPERIMENTAL

A. PREPARATION OF 3,3'-DINITROBIPHENOL

Biphenol, 94 g., and methylene chloride, 750 ml., were charged to a 2-l. resin flask equipped with a stirrer, thermometer, and dropping funnel. The resulting slurry was cooled to $-10^{\circ}\text{C}.$, and 70% nitric acid, 260 ml., was gradually added at this temperature over a period of 3.5 hours. The reaction mixture was stirred at $-10^{\circ}\text{C}.$ for 0.5 hour longer and the temperature was allowed to rise to $0^{\circ}\text{C}.$ Approximately 750 ml. of water was added and the reaction stirred overnight with the top open to evaporate the methylene chloride. The product was filtered on a Buchner funnel and vacuum dried at $65^{\circ}\text{C}.$ overnight. Yield was 131.5 g. (94.3%). The product was a yellow solid, M.P. $270.5^{\circ}\text{C}.$ (Lit. M.P. $272^{\circ}\text{C}.$).

Analysis: Theory - C, 52.19%; H, 2.89%; N, 10.14%

Actual - C, 52.0%; H, 2.78%; N, 9.86%

Recrystallization from acetic acid did not improve the purity of the product.

B. REDUCTION OF 3,3'-DINITROBIPHENOL

3,3'-Dinitrobiphenol, 118.5 g., water, 1145 ml., and 28% aqueous ammonia, 430 ml., were charged to a 3-l., 3-neck flask equipped with a stirrer, thermometer, and reflux condenser. Sodium dithionite, 500 g., was added in small portions over a period of 0.5 hour and the reaction exothermed to $90^{\circ}\text{C}.$ The mixture was heated at $100^{\circ}\text{C}.$ for one hour, cooled to $50^{\circ}\text{C}.$ and treated with acetic acid to a pH of 4.6. After cooling to $20^{\circ}\text{C}.$, the dark brown solid was filtered off by suction and air dried (84 g.). Crude 3,3'-diaminobiphenol, 83 g., water, 2500 ml. and 28% HCl, 86 g., were charged to a 3-l. flask and heated to $85^{\circ}\text{C}.$ where solution was essentially complete. Norit charcoal, 6.5 g., was added and the mixture was refluxed for one hour, filtered hot to remove the charcoal and transferred to a 5-l. flask where a nitrogen atmosphere was maintained. After cooling to $50^{\circ}\text{C}.$, a solution of 82 g. sodium acetate in 150 cc. of water was added to precipitate the 3,3'-diaminobiphenol. The contents of the flask were cooled to $15^{\circ}\text{C}.$ filtered on a Buchner funnel, washed with water and sucked as dry as possible using a rubber dam. The wet cake, 228 g., was vacuum dried to 52.7 g. of a grey solid which darkened rapidly in light. M.P. $>300^{\circ}\text{C}.$

Analysis: Theory - C, 66.7%; H, 5.56%; N, 12.95%

Actual - C, 63.4%; H, 5.6%; N, 12.1%

The hydrochloride and free base were insoluble in other solvents.

C. PREPARATION OF o-DIANISIDINE DIHYDROCHLORIDE

o-Dianisidine, 400 g., was slurried with 1.5-l. of concentrated hydrochloric acid on a steam bath for one hour. The excess acid was filtered off with a Buchner funnel and the product was vacuum dried.

D. PREPARATION OF DIHYDROXYBENZIDINE

Method 1

o-Dianisidine dihydrochloride (0.1 mole), 350 ml. of toluene and one mole of aluminum chloride were placed in a 1-liter flask. The mixture was refluxed with stirring for 25 min., cooled to 80°C., whereupon 0.05 mole of additional dianisidine dihydrochloride was added. After additional refluxing of 20 minutes, another 0.05 mole of the dihydrochloride was added and the entire mixture was then refluxed for two hours. The toluene was decanted and the black solid was mixed with ice. Concentrated hydrochloric acid, 400 ml., was added to the slurry and the entire mass was filtered. The filter cake was washed with 200 ml. of concentrated hydrochloric acid and the product was vacuum dried overnight.

The pulverized product was dissolved in 3-l. of water, Norit charcoal was added, and the mixture was heated for 30 min. at 80°-90°C., and then filtered. To the clear filtrate was added 60 g. of sodium acetate in 150 ml. of water. The white solid product was removed by filtration, vacuum oven dried and analyzed. M.P. > 300°C.

Analysis: Theory - C, 66.6%; H, 5.60%; N, 12.94%

Actual - C, 66.8%; H, 5.96%; N, 12.55%

Method 2

A slurry of 500 ml. of 57% hydriodic acid and o-dianisidine was heated at 110°C. for 20 hours. The excess acid was vacuum distilled and the residue extracted with one liter of water, leaving a black, insoluble tar. The aqueous extract was filtered, treated with Norit charcoal and then neutralized with 30 g. of sodium acetate. The pink solid was recovered by filtration and dried in air, turning grey and then black upon standing. Only 12 g. of product was recovered in this manner.

This procedure was repeated by refluxing for 48 hours rather than 20 hours and the excess hydriodic acid was decanted. The product was dissolved in 4 l. of water and sufficient sodium acetate added to precipitate the free base. Infrared analysis indicated that cleavage was incomplete.

E. PREPARATION OF 3,3'-DIMERCAPTOBENZIDINE DIHYDROCHLORIDE

Method 1

Benzidine, 74 g., and acetic acid, 1000 ml., were charged to a 3-l., 3-neck flask, equipped with a stirrer and a dropping funnel. Ammonium thiocyanate, 240 g., was added with agitation to form a very thick slurry which gradually thinned out. A solution of bromine, 48 ml., in acetic acid, 480 ml., was added via the dropping funnel over a period of 4.66 hours, forming a very thick, yellow slurry which was extremely difficult to filter. The filtered yellow paste, 970 g., was divided into three parts, each of which was refluxed for 2 hours in 3 l. of a 1% HCl solution. The cooled portions were filtered and the combined wet cakes were refluxed for 3 hours with a solution of potassium hydroxide in 550 ml. of water. Upon cooling, the dipotassium salt of 3,3'-dimercaptobenzidine precipitated as yellow needles. This salt was filtered, air dried, and slurried with 350 ml. of ethanol for one hour. The slurry was filtered and the cake washed six times with alcohol. After air drying, the yield of dipotassium benzidine 3,3'-dimercaptide was 129.7 g.

Analysis: Theory - C, 44.4%; H, 3.1%; N, 8.63%; S, 19.75%; K, 24.1%
Actual - C, 36.2%; H, 3.84%; N, 7.13%; S, 16.2%; K, 19.8%

The carbon, nitrogen, sulfur and potassium ratios are, respectively, 5.96:1:1:1, indicating that water is present in the analyzed samples.

Dipotassium benzidine 3,3'-dimercaptide, 12 g., was dissolved in water, 176 ml., and the insoluble material, 0.8 g., was removed by filtration. One half of this solution was poured with stirring into 28% HCl, 25 ml., and vacuum dried at 50°C. to 5.8 g. Infrared analysis clearly showed the presence of the S-H bond at 3.9 μ .

Dimercaptobenzidine as the free base was obtained by dissolving the dipotassium salt of 3,3'-dimercaptobenzidine, 40 g., in deionized water, 588 ml., and filtering to remove 2.88 g. of insoluble material. The filtrate was then poured into a solution of glacial acetic acid, 19.68 g., in deionized water, 19.7 ml., and cooled to 0°C. The light tan solid was filtered, washed with deionized water, and dried at 50°C. The yield based on soluble potassium salt was 20.39 g. (72%).

Method 2 (Hertz Method)

Sulfur monochloride, 700 g., was charged to a 1-liter, 3-neck flask equipped with a stirrer, a tube for adding solids, and a reflux condenser connected through a drying tube to vent over the surface of a sodium hydroxide solution. With agitation, benzidine, 40.5 g., was gradually added over a period of 0.5 hour, but there was no indication of reaction. The reaction was warmed and a steady evolution of hydrogen chloride began at 102°C. Heating was continued at 119°C. for 22 hours, at which time hydrogen chloride evolution had ceased. After cooling to 80°C., benzene 400 ml., was added and the mixture was cooled to 20°C. The material was filtered with nitrogen pressure through a "frit" and the cake was washed with several portions of benzene. The dark solid was dried in a nitrogen stream to 87 g. of 6,6'-bi(benzodithiazol-2-ium) chloride. Heating this material and water, 800 ml., to 50°-60°C. for several hours gradually changed the color of the solid to green. The mixture was cooled, filtered, washed with water and vacuum dried to yield 72 g. of 6,6'-bi(benzodithiazole)-2,2'-dioxide. However, the elemental analysis indicated that this product was low in sulfur.

Analysis: Theory - C, 42.35%; H, 2.35%; N, 8.25%; S, 37.65%

Actual - C, 40.8%; H, 2.77%; N, 7.8%; S, 26.57%

The 6,6'-bi(benzodithiazole)-2,2'-dioxide, 34 g., and water 50 ml., were charged to a 500 ml., 3-neck flask and treated with a solution of sodium hydroxide, 17 g., sodium dithionite, 20 g., and water, 33 g. The reaction was exothermic to 50°C. and the mixture was heated at this temperature for 2 hours. After cooling, a solution of 50 g. sodium hydroxide in 400 ml. of water, was added and the reaction continued under a nitrogen atmosphere. The mixture was heated to 80°C., filtered hot and cooled in an ice bath. Acetic acid, 75 ml., was added gradually to a pH of 6.8 and the solids were removed by filtration with a fritted pressure filter and blown as dry as possible. The 3,3'-dimercaptobenzidine was vacuum dried to 28 g. However, infrared analysis showed no S-H bond at 3.9 μ .

F. PREPARATION OF METHYL PERFLUOROBUTYRATE

Perfluorobutyric acid, 165 g., and methanol, 80 g., were placed in a 500 ml. flask. The flask was cooled in ice and concentrated sulfuric acid, 110 g., was added over a period of 3 or 4 min. with agitation. After standing overnight, the lower layer was separated and distilled, collecting the fraction boiling at 79°-80°C. The yield was essentially quantitative.

G. PREPARATION OF PERFLUOROBUTYRYL CHLORIDE

Phosphorus pentachloride, 450 g., was charged to a 1-liter, 3-neck flask equipped with a stirrer, dropping funnel and a take-off distillation column. Perfluorobutyric acid was added from a dropping funnel while stirring and heating the flask at 50°-60°C.

The perfluorobutyryl chloride distilled as it formed and was collected in the receiver. Heating was continued at 50°-60°C. for one hour after the addition of acid had been completed. The crude perfluorobutyryl chloride was redistilled twice, collecting the fraction boiling at 39°-41°C. The yield was about 70% based on perfluorobutyric acid.

H. PREPARATION OF METHYL PERFLUOROBUTYRIMIDATE

Anhydrous methanol, 50 ml., and triethylamine, 1 ml., were charged to a 6 oz. Fischer-Porter bottle containing a magnetic stirring bar. After cooling to -78°C., the bottle was evacuated and heptafluorobutyronitrile, 100 g., was condensed into it. The closed reactor was then allowed to warm gradually and stirring; initiated as soon as the reactants became liquid, was continued until the vapor pressure was equal to that expected of methanol. The reaction mixture was washed with ice water, separated, and distilled, collecting the fraction boiling at 72.5°C. The water-white liquid weighed 102.85 g. (88%).

I. PREPARATION OF MODELS - TWO-STEP REACTION - PERFLUOROBUTYRYL CHLORIDE

1. Benzoxazole Model I

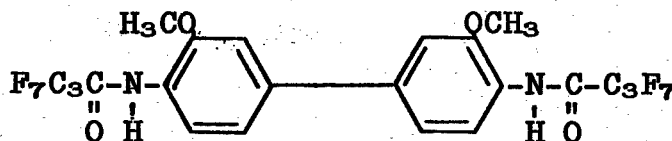
a. Preparation of bis(Perfluoroamide)

3,3'-Dihydroxybenzidine, 1.95 g., and pyridine, 25 ml., were charged to a 50 ml. flask equipped with an adapter containing a stopcock. The contents of the flask were cooled to -196°C., and the flask was evacuated to <10 μ on the vacuum line. Perfluorobutyryl chloride, 4.34 g., was measured by expansion in the vacuum line and condensed into the cold reaction flask. The flask was closed and allowed to warm to room temperature overnight. The resulting purple slurry was stirred for 2 hours and poured into 150 ml. of deionized water. The solid was filtered, washed with water and vacuum dried at 50°C. The yield of purple solid was 5.2 g. (95%), M.P. 270°-277°C.

Analysis Theory - C, 39.5%; H, 1.65%; F, 43.75%; N, 4.6%

Actual - C, 40.4%; H, 1.67%; F, 43.15%; N, 4.6%

Infrared analysis indicated the presence of two compounds. The purple solid was extracted with hot benzene in a Soxhlet extractor to remove one of the components, identified as:



The remaining material was heated to 200°C. to remove the purple color and recrystallized from acetone to obtain the desired bis(perfluoroamide).

b. Cyclodehydration to Model I

The purified bis(perfluoroamide), 1.7 g., and about 10 g. of commercial polyphosphoric acid were charged to a horizontal sublimator and heated under a nitrogen atmosphere to 200°C. for 20 hours. Large white crystals slowly collected in the cooling chamber and the polyphosphoric acid turned black. The yield was 1.09 g. (59%) and the infrared spectrum was identical to the same model prepared by the one-step process.

2. Benzoxazole Model II

a. Preparation of bis(Perfluoroamide)

3,3'-Diaminobiphenol, 2.05 g., and pyridine, 25 ml., were charged to a 50 ml. flask equipped with an adapter containing a stopcock. The flask was cooled to -196°C. and evacuated to <10 μ on the vacuum line. Perfluorobutyryl chloride, 4.6 g., was condensed in via the vacuum line and the closed flask was allowed to warm gradually. Stirring was initiated as soon as possible and continued overnight. The dark slurry was poured into 150 ml. of deionized water and the precipitate was filtered. After washing and vacuum drying at 50°C., there was obtained 5.28 g. (91%) of light tan powder which melted at 256°-258°C. Infrared and NMR analyses verified the structure and indicated only trace amounts of impurities.

b. Cyclodehydration to Model II

The above bis(perfluoroamide), 5.0 g., and about 10 g. of commercial polyphosphoric acid were charged to the horizontal sublimator and heated under a nitrogen atmosphere at 200°C. for 18 hours. The sublimed product was a yellow solid weighing 3.4 g. (72% yield) and infrared analysis indicated high purity. This material was combined with material prepared (see below) by the one-step process for purification. As with Model I, the polyphosphoric acid residue was very dark and dilution with water produced no additional product.

J. PREPARATION OF MODELS, ONE-STEP REACTION

1. Benzoxazole Model I

3,3'-Dihydroxybenzidine, 10.5 g., and dioxane, 200 ml., were charged to a 500 ml., 3-neck flask equipped with an addition tube, reflux condenser and stirrer. To this stirred mixture was added dropwise a mixture of perfluorobutyric acid, 21.5 g., and methyl perfluorobutyrimidate, 25 g. The contents of the flask were heated at 70°C. for 0.5 hour, at 80°C. for 3.25 hours, and 91°C. for 0.25 hour with a nitrogen atmosphere being maintained throughout the

reaction. Most of the solids dissolved after the first 15 minutes of heating and the mixture darkened considerably. After stirring overnight at room temperature, the condenser was replaced by a still head and 100 ml. were distilled. This distillate contained only dioxane. The reaction flask was cooled to 20°C. and the solids were separated by filtration. After washing with water, the solids were vacuum dried at 50°C. to give 15.95 g. of light yellow material. The filtrate was poured into 300 ml. of deionized water and the precipitate was filtered, washed, and vacuum dried at 50°C. The product was darker and weighed 10.56 g. The total crude yield was 26.51 g. (95%) and the melting point of the first crop was 145°C. The infrared spectrum contained no C=O, OH, or N-H absorption. Crude benzoxazole, 13.7 g., and acetone, 220 ml., were charged to a 500 ml. Erlenmeyer flask and heated on the steam bath to give a clear amber solution. Norit charcoal, 3.4 g., was added and the mixture was warmed for 15 minutes. The hot mixture was filtered twice to insure removal of the charcoal, and deionized water, 34 ml., was added to the boiling filtrate. After cooling to room temperature, the crystals were filtered, washed with cold 80% acetone, and vacuum dried at 50°C. The product was a white solid, M.P., 147.5-148.0°C.

Analysis: Theory - C, 41.6; H, 1.04; F, 46.4; N, 4.84

Actual - C, 41.5; H, 0.99; F, 46.1; N, 4.74

Infrared, NMR, and mass spectral analyses confirmed the structure. The largest ion detected by the last technique was 572. (MW of benzoxazole I, 572).

2. Benzoxazole Model II

3,3'-Diaminobiphenol, 10.5 g., and dioxane, 200 ml., were charged to a 500 ml., 3-neck flask equipped with a stirrer, addition tube and reflux condenser. A mixture of perfluorobutyric acid, 22.2 g., and methyl perfluorobutyrimidate, 25 g., was added dropwise to the contents of the flask and the resulting slurry was heated to 80°C. for 5.5 hours under nitrogen. After stirring at room temperature overnight, 100 ml. of the solvent were removed by distillation. After cooling the residual liquid, the solids were filtered off, washed with water and vacuum dried at 50°C. to give 9.35 g. of product. The filtrate was poured into 300 ml. deionized water and the precipitate was filtered, washed, and vacuum dried. The second crop, 14.51 g., was dark brown, but the infrared spectra of the two materials were essentially the same. Total crude yield was 23.66 g. (86%). The model was dissolved in boiling benzene and separated from a small amount of tar. The benzene was evaporated and the solid was recrystallized from methanol and decoloring Norit charcoal. The solid was redissolved in acetone and filtered to remove traces of charcoal. Evaporation of the acetone gave a pure product, M.P. 94.5-95.1°C.

Analysis: Theory - C, 41.9; H, 1.06; F, 46.5; N, 4.89

Found - C, 41.6; H, 1.04; F, 46.4; N, 4.84

Infrared and NMR analyses confirm the proposed structure.

3. Benzothiazole Model III

3,3'-Dimercaptobenzidine, 12.08 g., and dioxane, 200 ml., were charged to a 500 ml., 3-neck flask equipped with stirrer, addition tube, and reflux condenser. A mixture of perfluorobutyric acid, 21.5 g., and methyl perfluorobutyrimidate, 25 g., was added dropwise with stirring, resulting in a mild exotherm and slight discoloration of the reaction mixture. The contents of the flask were heated under nitrogen at 70°C. for 0.75 hour, 80°C. for 4.5 hours, and 90°C. for 0.25 hour. Shortly after heating was initiated, all of the solids went into solution, and, after three hours, solids began to precipitate. After stirring overnight at room temperature, the solid material was filtered, washed with a little dioxane and vacuum dried at 50°C. for two hours. This grey solid weighed 12.7 g. Approximately 100 ml. of the solvent were distilled from the filtrate and the cooled residual mixture was poured into 300 ml. of deionized water. The precipitate was filtered, washed with water, and vacuum dried at 50°C. for two hours. The yellow product weighed 13.65 g., giving a total crude weight of 25.35 g. (86%). The two crops were recrystallized separately using 90 ml. of methanol for 2 g. of the benzothiazole and re-using the mother liquor for the succeeding recrystallization. No charcoal was used. In this way, 11.15 g. of pale yellow benzothiazole was obtained from the first crop and 8.95 g. of a more intense yellow solid from the second crop. The melting points of the two crystallized batches were the same, 157.5°-160.5°C. Another yellow solid, 3.4 g., which had the following analysis, was also isolated from the second crop:

Analysis:

Theory - C, 44.6; H, 2.13; F, 31.3; N, 6.5

Found - C, 45.2; H, 2.12; F, 31.2; N, 6.58

The pure benzothiazole was obtained by a second recrystallization from acetone using Norit charcoal. The crystals were white plates, M.P. 157.5°-160.8°C.

Analysis: Theory - C, 39.75; H, 0.99; F, 44.1; N, 4.63; S, 10.6

Found - C, 39.7; H, 0.94; F, 44.1; N, 4.6; S, 10.09

The structure is supported by infrared analysis.

K. THERMAL DEGRADATION OF THE MODELS

Approximately one gram (accurately weighed) of each model was sealed into a 5 ml. pyrex ampoule under high vacuum (<5 μ). The ampoules were then placed in a muffle furnace for the prescribed length of time (see Discussion). The ampoules were cooled to -196°C. and opened under nitrogen. The gases in the ampoule were then expanded into a vacuum line and a gas infrared cell. The solid residues were next accurately weighed and the and the melting points recorded.

At 250°C., none of the samples lost more than 3 mg. (~0.3%) of their original weight.

At 350°C., only Model II had a significant weight loss due to volatilization of degradation and reaction products. At 350°C. for twenty-four hours (after 12 days at 250°C.), it lost ~16 mg. (1.6%), and at 350°C. for three days, it lost 71 mg. (6.5%) of its original weight. The volatile products, as identified by infrared analysis, were SiF_4 , CO_2 , and $\text{CF}_3\text{CF}_2\text{CF}_2\text{H}$. It was noted that the ampoules were slightly etched when Model II was heated to 350°C.

Model III has a peculiarly large melting range, indicating that there are two or more crystalline forms of the material which melt close together. The melting range of the pure model is 157.5°-160.8°C. However, upon melting and rapid resolidification, the melting range is 159.5°-160.5°C. In studying the thermal decomposition of the benzothiazole, the samples, after heating and slow cooling, still exhibited this dual melting range.

L. PURIFICATION OF CRUDE PERFLUOROSEBACAMIDE

Perfluorosebacamide, 200 g., concentrated hydrochloric acid, 400 ml., and water, 400 ml., were placed in a 2-liter, 2-neck flask equipped with a stirrer and reflux condenser. The mixture was refluxed for three days and, after cooling, the water was decanted. More water, 400 ml., was added and the mixture was refluxed for three more hours. The cooled mixture was filtered by suction and the filter cake was returned to the 2-liter flask. Water, 400 ml., sodium hydroxide, 40 g., and potassium permanganate, ~15 g., were added and the contents of the flask were refluxed, the purple color gradually becoming brown. More potassium permanganate was added in small increments with refluxing for two days until the purple color persisted. After cooling, sodium bisulfite was added until the purple color disappeared and the manganese dioxide was removed by filtration. The cake washes were added to the filtrate and an excess of hydrochloric acid was added to precipitate the perfluorosebacic acid. After drying and recrystallization from water, there was obtained ~120 g. of perfluorosebacic acid. The melting range, 90-250°C., indicated some salt was also present.

The perfluorosebacic acid, 120 g., was dissolved in dry methanol, ~100 ml., in a 500-ml. flask and treated with ~100 ml. of concentrated sulfuric acid. After stirring for two hours, the material was transferred to a separatory funnel and allowed to stratify overnight. The lower layer was washed with an equal volume of water, separated and vacuum distilled, collecting the fraction boiling at 129-145°C. (12 mm.). The water-white dimethyl perfluorosebacate weighed 112 g. (89.5%) and was 99% pure by V.P.C. analysis.

Dimethyl perfluorosebacate, 110 g., was dissolved in dry ether, 500 ml., in a one-liter flask and ammonia was bubbled in with stirring. The reaction was stirred overnight, filtered and washed with ~150 ml. of ether to yield 109 g. (99%) perfluorosebacamide, M.P. 240-241.5°C. The overall purification yield was 55.5%.

M. PREPARATION OF PERFLUOROSEBACONITRILE

Pulverized perfluorosebacamide, 74 g., and phosphorus pentoxide, 210 g., were charged to a 500 ml. round bottom flask and thoroughly shaken to obtain an intimate blend. The flask was then connected to a distilling head equipped with a downward condenser and a receiving flask and the system was maintained under a nitrogen blanket. The flask was heated for nine hours to 250°C. and perfluorosebaconitrile slowly distilled. There was obtained ~56 g. (82%) of water-white product which was combined with several other runs for redistillation. The boiling point of pure perfluorosebaconitrile was 105°C.

N. PREPARATION OF METHYL PERFLUOROSEBACIMIDATE

Perfluorosebaconitrile, 5 g., was charged to a 3 oz. Fischer-Porter aerosol bottle and cooled to -78°C. The bottle was evacuated and then flushed with dry nitrogen. Anhydrous methanol, 22 ml., and triethylamine, 0.5 ml., were added with a syringe and the tube was evacuated at -78°C. The reaction mixture was allowed to warm and at 0-25°C. the remaining solids dissolved to form a clear, water-white solution. After stirring overnight, the volatile materials were removed under vacuum at room temperature, and white, solid methyl perfluorosebacimide crystallized. Heating to 120-140°C. under full vacuum caused the liquefied product to reflux, but only a trace of methanol was removed. Manipulations of the temperature indicated the melting point to be in the range of 25-28°C.

Analysis: Theory - C, 27.9; H, 1.6; N, 5.4; F, 58.9

Found - C, 28.1; H, 1.7; N, 5.45; F, 59.0

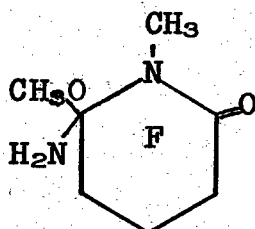
The structure is supported by infrared analysis.

O. ATTEMPTED PREPARATION OF DIMETHYL PERFLUOROGLUTARIMIDATE

bis-(1,4-Trichloromethyl)benzene, 500 g., zinc chloride, 4 g., and trichlorobenzene, 400 ml., were charged to a 2-liter, 3-neck flask equipped with a mechanical stirrer, dropping funnel and a reflux condenser leading to a series of three traps cooled to -78°C. A nitrogen atmosphere was maintained throughout the reaction to keep the system dry. The flask was heated to 145°C. and a slurry of perfluoroglutaramide, 76 g., in 200 ml. of trichlorobenzene was added over a period of 2.5 hours while increasing the temperature to 210°C. Stirring and heating were continued for 0.5 hour after the addition was complete. Most of the product condensed in the first trap. This material was transferred to a

small still and fractionated, collecting the fraction boiling at 38-40°C. The water-white perfluoroglutaronitrile weighed 19.8 g. (31%).

Dry methanol, 35 ml., and triethylamine, 0.75 ml., were charged to a 6 oz. Fischer-Porter aerosol bottle and cooled to -196°C. Perfluoroglutaronitrile, 27.5 g., was transferred by vacuum to the bottle which was then sealed and allowed to warm to room temperature overnight. The resulting colorless solution was washed twice with 100 ml. portions of water and dried over magnesium sulfate. Infrared analysis was indicative of dimethyl perfluoroglutarimide. However, vacuum distillation with the pot temperature no higher than 70°C. caused the material to cyclize to



Analysis: Theory - C, 31.6; H, 3.0; N, 10.5; F, 42.8

Found - C, 31.75; H, 2.97; N, 10.2; F, 42.7

The cyclic structure was confirmed by NMR and infrared analyses.

P. PREPARATION OF DIETHYL PERFLUOROADIPATE

Potassium permanganate, 125 g., acetone, 1.5 liters, and water, 150 ml., were charged to a 3-liter, 3-neck flask equipped with a stirrer, reflux condenser and dropping funnel. Perfluorocyclohexene, 175 g., was gradually added to this stirred mixture at a rate which did not raise the temperature above 35°C. Some external cooling was applied and the addition required ~2 hours. Stirring was continued for 0.5 hour after the addition was complete and the mixture was then filtered to give a clear filtrate and a dark filter cake. The filtrate was evaporated on a steam bath to remove the acetone and cooled. Concentrated sulfuric acid, 75 ml., was then added to the remaining solution and the resulting slurry was extracted twice with 250 ml. portions of ether. After drying with magnesium sulfate, the ether was removed by evaporation on a steam bath to give perfluoroadipic acid which was rather slushy.

The perfluoroadipic acid was dissolved in ethanol, 125 ml., and the solution was treated with a sulfuric acid, 200 ml., resulting in the formation of two layers. The lower layer was water washed, extracted four times with ether, and dried over magnesium sulfate. Evaporation of the ether left 152 g. (66%) of crude diethyl perfluoroadipate which still showed some free hydroxyl groups by infrared analysis. Another 10 g. of perfluoroadipic acid was recovered from the manganese dioxide filter cake by acidification and ether extraction.

Q. PREPARATION OF DIMETHYL PERFLUOROADIPIMIDATE

A mixture of methyl and ethyl perfluoroadipate, 172 g., was dissolved in one liter of ether contained in a 2-liter, 3-neck flask equipped with a stirrer, condenser, and a gas addition tube which dipped slightly below the surface of the liquid. Dry ammonia gas was bubbled through the solution with stirring for 4 hours, during which time a white solid gradually precipitated. The slurry was stirred for 2.5 days before the solid was removed by filtration and vacuum dried for 2 hours at 50°C. The yield of pure white perfluoroadipamide was 144 g., 91%, M.P. 236.6-237°C.

Perfluoroadipamide, 47 g., and phosphorus pentoxide, 22 g., were intimately mixed in a 500 ml. flask. The flask was attached to a distilling head and heated to 250°C. with an oil bath until no more material distilled. The product, perfluoroadiponitrile, B.P. 61-62°C., was obtained as a water-white liquid in 84% yield.

Perfluoroadiponitrile, 26.9 g., and methanol, 25 ml., were placed in a Fischer-Porter aerosol bottle under nitrogen and cooled in ice water. Triethylamine, 1 ml., was added via syringe and the two layer system was stirred under a nitrogen atmosphere. As the mixture warmed to room temperature, a homogeneous solution was formed, and the reaction was stirred overnight. The methanol and triethylamine were removed under vacuum and the dimethyl perfluoroadipimide was vacuum distilled at 52-54°C. (1 mm.). The water-white product was obtained in 78% yield.

R. POLYMERIZATION OF METHYL PERFLUOROSEBACIMIDATE WITH DI-HYDROXYBENZIDINE

At -78°C., dioxane, 40 ml., trifluoroacetic acid, 1.45 ml., and dihydroxybenzidine, 2.39 gm., were added to the methyl perfluorosebacimide in the above Fischer-Porter reactor. The mixture was allowed to warm to room temperature and stirred overnight. This thick slurry was then heated at 50°C. for four days, poured into 400 ml. of deionized water, and the precipitated solids were recovered by filtration. The yellow solid was vacuum dried at 50°C. to 7.0 g. (100% yield).

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4

Found - C, 39.0; H, 1.27; F, 47.85; N, 4.64

One gram of the polymer was dissolved in sulfuric acid, 20 ml., to form a dark solution. The polymer was reprecipitated by pouring the sulfuric acid solution into 300 ml. of water. After filtration, the solid was vacuum dried to obtain 0.95 g. of darker material.

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4

Found - C, 35.0; H, 1.45; F, 44.7; N, 3.77, S, 2.05

When the polymer was prepared by the same procedure but with a slight excess of methyl perfluorosebacimide, the results were as follows:

Analysis: Theory - C, 41.7; H, 0.95; F, 47.9; N, 4.4

Found - C, 40.2; H, 1.03; F, 48.15; N, 4.6

After the polymer was treated with H_2SO_4 , the following analysis of the product was obtained:

Found - C, 35.9; H, 1.44; F, 42.9; N, 3.97; S, 2.32

S. POLYMERIZATION OF METHYL PERFLUOROADIPIMIDATE WITH DIMER-CAPTOBENZIDINE

Dimercaptobenzidine, 2.0 g., was dissolved in dimethyl acetamide, 50 ml., contained in a 100 cc. Mini-lab reactor which was fitted with a stirrer, thermometer, addition tube and a reflux condenser. The condenser outlet was connected to dry nitrogen via a gas bubbler. Dimethyl perfluoroadipimide, 2.56 g., was added to acetic acid, 0.97 g., and the mixture was charged to the addition tube. With a nitrogen atmosphere and stirring, the imide ester salt was added to the flask and the solution was heated to 50°C. for 1 hour. The temperature was then raised to 103°C. and held for 20 hours. After cooling, one half of the solution was slowly added to 300 ml. of water, but the resultant colloidal system could not be filtered. This mixture was then transferred to a centrifuge where separation was successful. The clear liquid was decanted and the solids were dried in the vacuum oven at 50°C. The polymer was a tacky, yellow-brown solid.

Analysis: Theory - C, 46.4; H, 1.29; F, 32.6; N, 6.02; S, 13.75

Found - C, 47.7; H, 3.53; F, 19.2; N, 9.40; S, 15.87

The other half of the reaction mixture was placed in a still and the solvent was removed at 32-36°C. (2 mm.). The residual material was dissolved in acetone and filtered to remove a small amount of solids which were identified as dimercaptobenzidine disulfide. The acetone was evaporated from the product which was then dried in the vacuum oven at 50°C. The product was a tacky, black solid.

Analysis: Theory - C, 46.4; H, 1.29; F, 32.6; N, 6.02; S, 13.75

Found - C, 43.23; H, 3.32; F, 28.7; N, 8.65; S, 9.76

T. HEAT TREATMENT OF BIBENZOTHAZOLE POLYMER

One batch of polymer, prepared in the same manner as the previous example, was placed in a cap bottle equipped with a stop-cock and connected to the vacuum line. Under full vacuum (1 μ),

the bottle was heated in an oil bath to 165°C. for two hours.
A white sublimate and a crisp black residue were obtained.

Analysis: Theory - C, 46.4; H, 1.29; F, 32.6; N, 6.02; S, 13.75

Found for

Original Polymer:

C, 44.26; H, 3.43; F, 25.1; N, 9.16; S, 10.17

White Sublimate:

C, 47.68; H, 3.20; F, 22.7; N, 9.06; S, 12.75

Black Residue:

C, 44.5; H, 3.1; F, 25.8; N, 8.65; S, 10.65

Infrared analysis showed little difference in the three materials.

SECTION V

APPENDIX

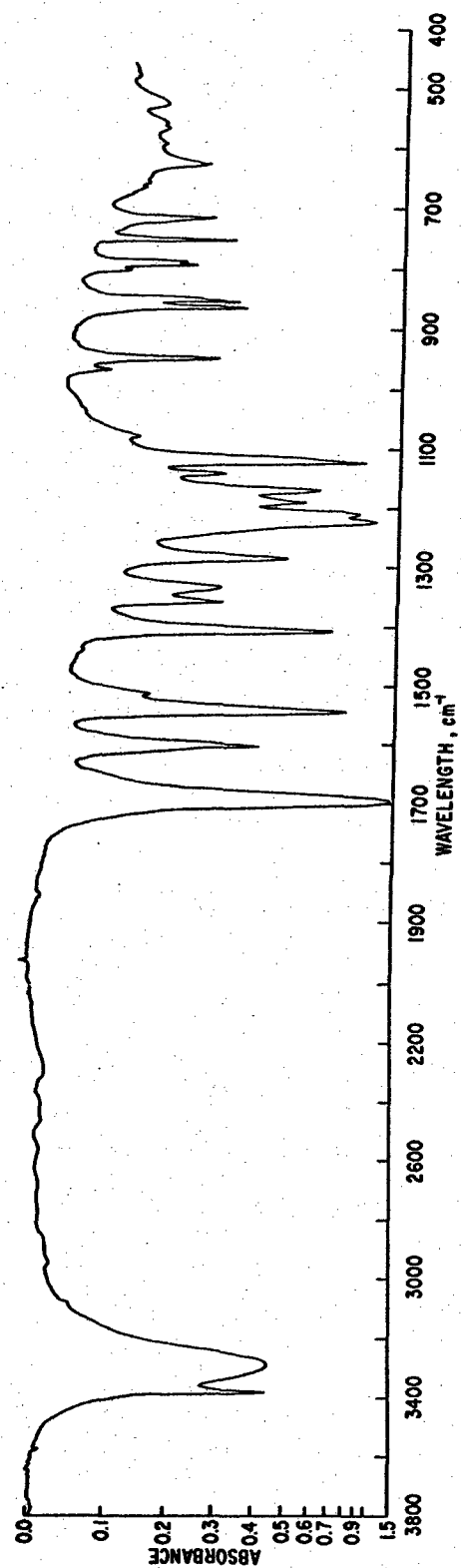


Fig. 1 - Infrared Spectrum of 4,4'-bis(Heptafluorobutyramide)-
3,3'-Dihydroxybiphenyl (Split Mull)

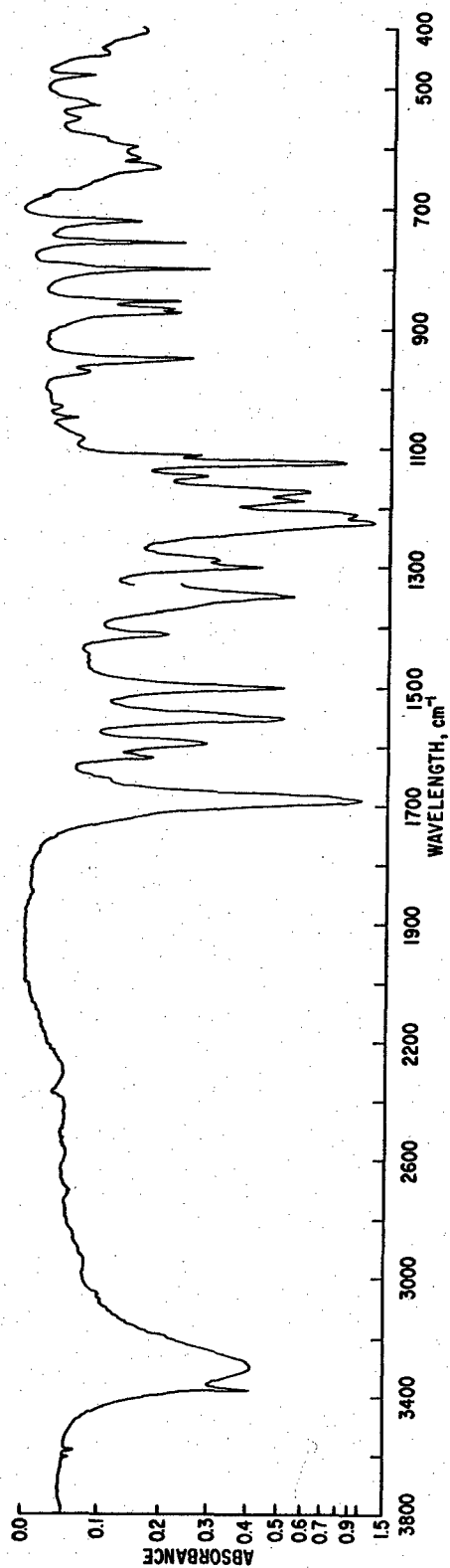


Fig. 2 - Infrared Spectrum of 3,3'-bis(Heptafluorobutyramide)-
4,4'-Dihydroxybiphenyl (Split Mull)

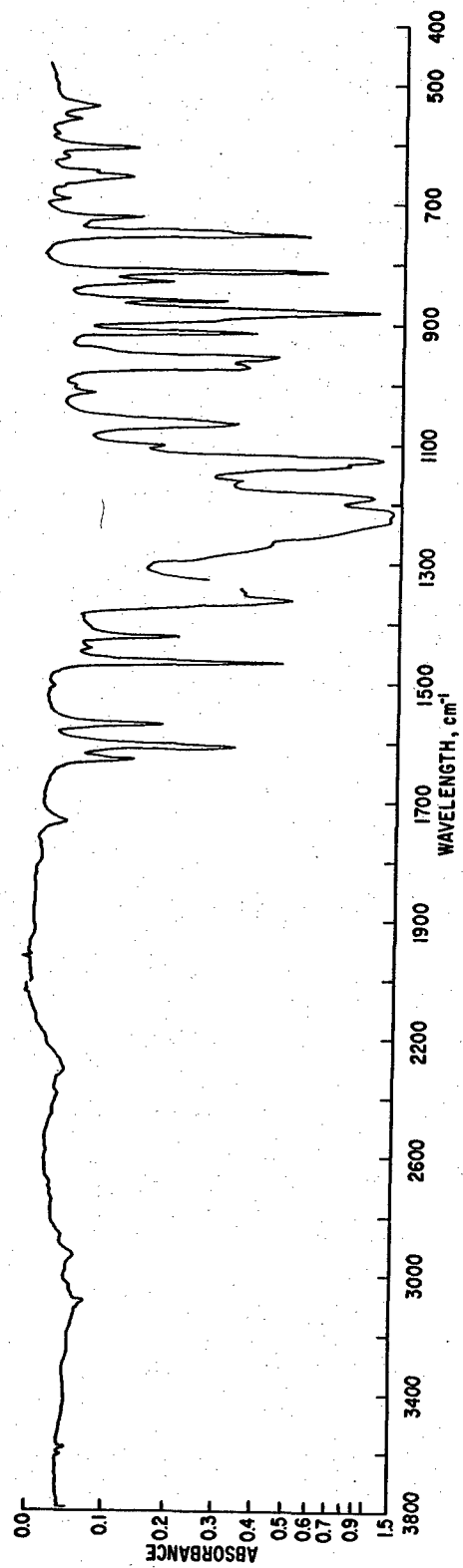


Fig. 3 - Infrared Spectrum of Model I (Split Mull)

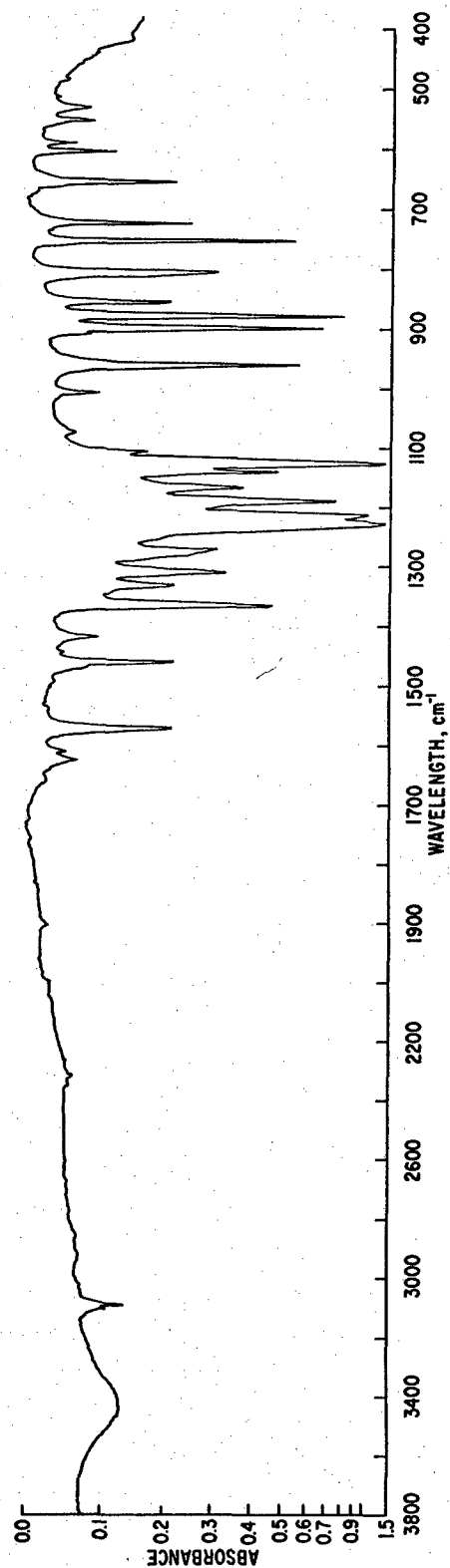


Fig. 4 - Infrared Spectrum of Model II (Split Mull)

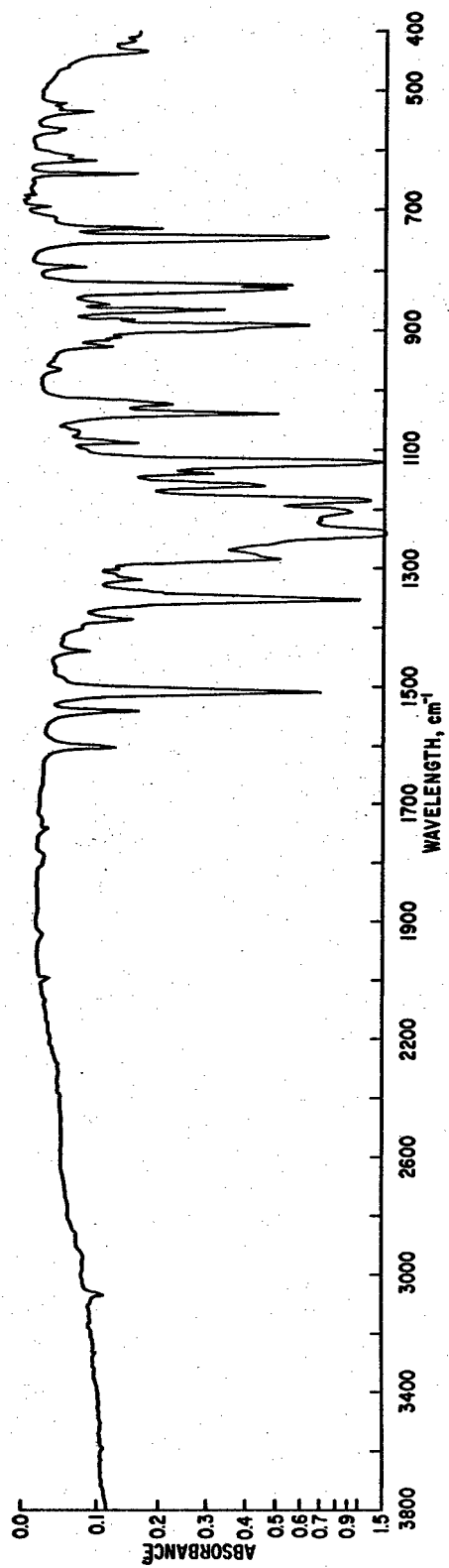


Fig. 5 - Infrared Spectrum of Model III (Split Mull)

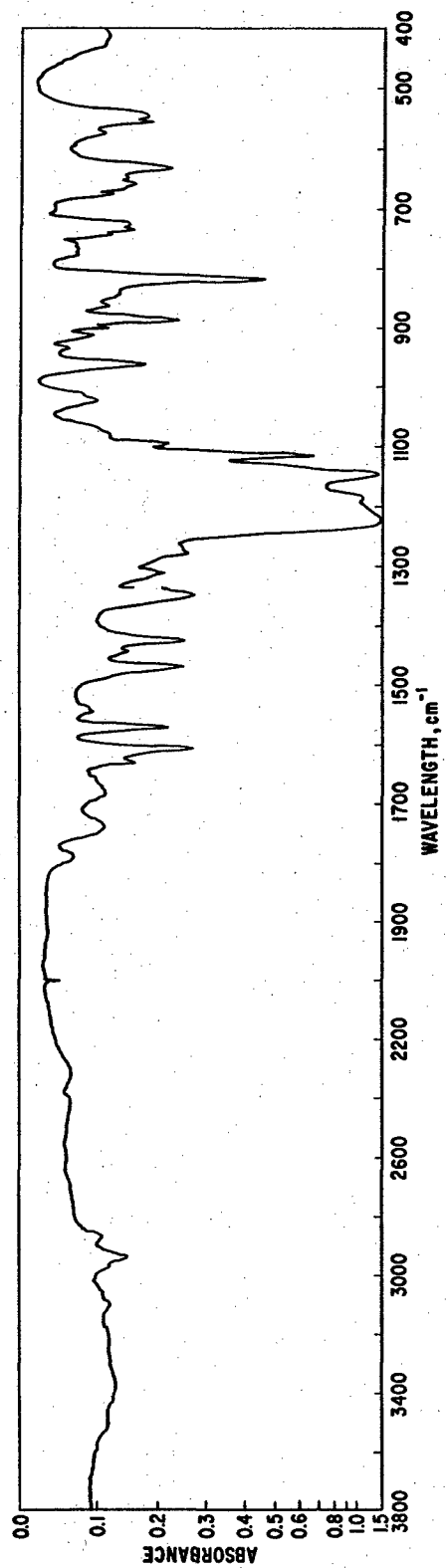


Fig. 6 - Infrared Spectrum of Bibenzoxazole Polymer I

SECTION VI

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10. AVAILABILITY/LIMITATION NOTICES Each transmittal of this abstract outside the Department of Defense must have prior approval of the Polymer Branch, MANP, Non-metallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.			
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13. ABSTRACT To determine if thermally stable elastomeric polymers can be obtained from perfluoroalkyl heterocyclic backbones derived from benzoxazoles and benzothiazoles, a study of related models (I) 2,2'-bis(heptafluoropropyl)-6,6'-bibenzoxazole, (II) 2,2'-bis(heptafluoropropyl)-5,5'-bibenzoxazole, and (III) 2,2'-bis(heptafluoropropyl)-6,6'-bibenzothiazole were made. These models were synthesized and fully characterized. They are resistant to strong acid hydrolysis and to attack by secondary and tertiary amines. Models I and III are stable at 350°C., while Model II begins to decompose at 250°C. Procedures for preparing the models were optimized, and polymers congeneric to Models I and III have been prepared which have a $(CF_2)_8$ between the heterocyclic rings. Each transmittal of this abstract outside the Department of Defense must have prior approval of the Polymer Branch, MANP, Non-metallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433.			

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