SYNTHESIS OF POLYTHIAZOLES AND POLYFLUOROOLEFINS

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Abstract

This project has as its goal the synthesis of organic polymers of high thermal stability. Two approaches are being followed; namely, the condensation polymerization of a chain of aromatic nuclei joined through heterocyclic groups and the polymerization of fluoroolefins containing heterocyclics groups to give fluorocarbon polymers with pendant heterocyclic substituents.

In a preliminary study, eight model thiazole compounds with aryl substituents were prepared and compared as to thermal stability as a guide to designing polymer chains. The benzothiazole unit and 2,4-aryl-substituted thiazole structure appeared to be most stable. Two poly-(benzothiazole) products, a poly-(benzimidazole-benzothiazole) product, a poly(arylene-thiazolothiazole) product and a poly(azo-arylene-thiazole) product have been obtained in small scale reactions. All of these products were dark, infusible powders. One of the poly-(benzothiazole) products was prepared in sufficient quantity to determine certain properties. It was insoluble in all solvents tested, formed a brittle disc by compression molding at 600°F, and showed thermal stability to over 600°C by TGA.

The synthesis of perfluorocarbon polymers with pendant heterocyclic groups first requires the preparation of monomers with the structure $RCF=CF_2$, where R is a stable heterocyclic ring. Several methods designed to produce such monomers have been examined without success. The first approach involved the reaction of the lithium derivative of a heterocycle with tetra-fluoroethylene. With 2-pyridyllithium, the product obtained was 1,2-di(2-pyridyl)-1,2-difluoroethylene, instead of the desired 2-(trifluorovinyl)pyridine. A similar approach, the reaction of an organometallic with dibromotetrafluoroethylene, led to the formation of tetrafluoroethylene and a bromocyclic. Next, N-(tetrafluoroethyl)-carbazole was prepared and treated with alkaline reagents to effect dehydrofluorination. Mild alkaline treatments were ineffective and forcing conditions led to the regeneration of carbazole. Currently attempts are underway to prepare 2-(trifluorovinyl)benzazoles via condensation of the properly substituted fluoroacids with ortho-substituted anilines. The precursors, several of which have been prepared, include tetrafluoroethyl-, dihalotrifluoroethyl-, and tetrafluorocarboxyethyl-benzazoles. Attempts are underway to synthesize the monomers by dehydrofluorination, dehalogenation, or decarboxylation.

Introduction

In postulating structures for polymeric materials that would have a high degree of thermal stability, first consideration should be given to the relative stabilities of potential building units. Reference to various reports on decomposition temperatures for simple organic compounds will show that some structures, such as aromatic compounds, certain heterocyclic compounds, and fluorocarbons,

have favorably high thermal resistance. A few examples of heat stable compounds are given in Table 1:

TABLE 1

Vapor Phase Decomposition of Simple Compounds[1]

Compound	Decomposition Temperature, °F
Perfluorocyclohexane	1150-1200
Naphthalene	1150-1200
Thiophene	1100-1150
2-Phenylimidazole	1100
Benzothiazole	1025-1050
Biphenyl	950-1000
Benzimidazole	750-800
1,2,4-Triazole	800

In this contractural program, the goal is the preparation of thermally stable polymers incorporating certain of these more stable structures.

One part of this program is the preparation of polymeric chains incorporating heterocyclic rings, particularly thiazoles, with connecting arylene units. The preferred approach is the condensation of polyfunctional arylene compounds with the formation of the heterocyclic ring as the polymer-forming reaction. The polymer chain is to contain no readily removable hydrogen, as represented by an aliphatic chain or a primary amide group.

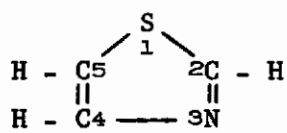
In the other part of this program, perfluoroolefin derivatives of heterocyclic compounds are to be prepared. Addition polymerization of such monomers will lead to a fluorocarbon backbone with pendant heterocyclic groups. As in the preceding program, presence of labile hydrogens is to be avoided.

I. Condensation Polymers Containing Thiazole Groups

This work can be divided into three phases. The first phase was the synthesis of a series of model compounds for a comparison of thermal stability. The other two phases are the preparation of monomers and the study of polymerization of these monomers.

A. Model Aryl-Substituted Thiazoles

A series of eight model thiazole derivatives was prepared, following standard preparative methods[2]. These compounds included various combinations of aryl substitution on the thiazole ring (formula I).



(I)

Highly purified samples of these compounds were submitted to ASD for testing in a high pressure isoteniscope. The eight model thiazole derivatives are listed,

with their decomposition temperatures, in Table 2, along with selected results for other compounds as determined by the operators of the isoteniscope[1,3]. As will be seen in the subsequent discussion of polymeric materials, correlation of relative thermal stability of a monomer structure with the thermal stability of a polymer chain of the same basic structure is not absolute. With respect to the model thiazole derivatives tested, the simple phenyl group seems to exhibit greater stability than other groups. The greater stability of compound b compared to compounds e and f suggests attachment through the 2,4-positions of the thiazole ring. The most stable of the thiazole derivatives was 2-phenylbenzothiazole, which would indicate that the fused ring system of the benzothiazole structure would produce the most heat resistant polymers.

B. Synthesis of Monomer Intermediates

Some of the simpler types of monomers have been prepared by known synthetic methods. The chief problem has now become the preparation of monomers containing heat stable connecting groups which will add flexibility to the polymer chain and impart a solubilizing effect. Some of the monomers being synthesized are indicated in the following discussion.

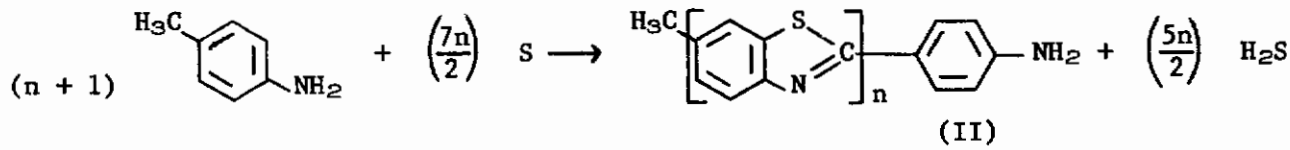
TABLE 2

Thermal Stability in a High Pressure Isoteniscope

Compound	Decomposition Temperature, °F
a. 2-Phenylbenzothiazole	943
b. 2,4-Diphenylthiazole	916
c. 2,4,5-Triphenylthiazole	897
d. 2-(1-Naphthyl)-4-phenylthiazole	876
e. 2,5-Diphenylthiazole	813
f. 4,5-Diphenylthiazole	783
g. 2-(4'-Benzamidophenyl)benzothiazole	667
h. 2-Anilino-4-phenylthiazole	613
i. Naphthalene	1053
j. Biphenyl	1010
k. Quinoline	950-1000
l. Diphenyl ether	1000
m. 1-Phenylimidazole	890
n. Diphenylmethane	850

1. Derivatives of Dehydrothio-p-toluidine

The ready availability of dehydrothio-p-toluidine (II, n = 1) from the p-toluidine-sulfur fusion reaction of dye chemistry, suggested derivatives of this



(II)

compound as polymer intermediates with a benzothiazole unit already in the monomers. Some of the intermediates obtained and their methods of synthesis are as follows:

a. 2-(4'-Acetamidophenyl)benzothiazole-6-carboxylic acid

This compound was prepared by the oxidation of the acetyl derivative of dehydrothio-p-toluidine (II) by potassium permanganate in pyridine.

b. 2-(4'-Cyanophenyl)-6-methylbenzothiazole

This compound was prepared by diazotization of II, followed by reaction with cuprous cyanide.

c. 2-Phenylbenzothiazole-4',6-dicarboxylic acid

This compound was prepared by the oxidation and hydrolysis of the preceding compound with permanganate.

d. 2-(4'-Amino-3'-mercaptophenyl)benzothiazole-6-carboxylic acid

Preparation of this compound was unsuccessfully attempted by the reaction of sulfur monochloride (the Herz reaction[4]) with 2-(4'-aminophenyl)benzothiazole-6-carboxylic acid.

2. Derivatives of Arylene Diamines

Both in this study of thiazoles and in the work of Marvel[5] with imidazoles, the formation of fused ring systems is dependent upon the reaction of a carboxylic acid group with an aryl amine, having an ortho mercapto group (to permit formation of a benzothiazole) or having an ortho amino group (to permit formation of a benzimidazole). Such intermediates as have been studied are as follows:

a. 3,3'-Dimercaptobenzidine

This compound was prepared by the reaction of benzidine with sulfur monochloride[4].

b. 3,3',4,4'-Tetraaminobiphenyl

This compound was obtained from the Chemical and Dyestuffs Division of Koppers Company, Inc.

c. Bis(4-amino-3-mercaptophenyl) ether

Preparation of this compound was unsuccessfully attempted by the reaction of oxy-dianiline with sulfur monochloride[4].

C. Polymers Prepared

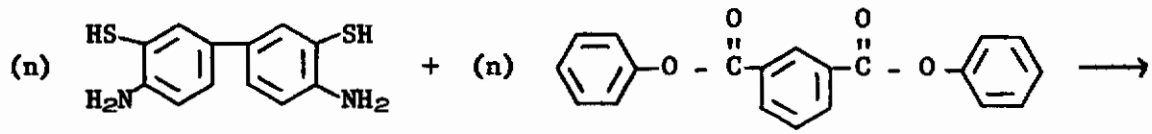
Polymeric products have been produced from some of the monomer intermediates described in the preceding section and from some other reactions of an exploratory nature. The preliminary results for polymers produced in this program thus far indicate that poly(benzothiazoles) are indeed quite thermally stable.

1. Extension of the Primuline Fusion Reaction

The old reaction of p-toluidine with a sulfur melt (as previously noted in paragraph B.1.) produces dehydrothio-p-toluidine (II, n = 1) and primuline base (II, n = 2) as the major products. The reaction could theoretically proceed to the polymer range with "n" becoming a large number, were the higher homologs more readily fusible. Use of high boiling organic solvents with p-toluidine and sulfur resulted in the same products as the melt reaction. When a mixture of anhydrous sodium tetrasulfide and potassium pentasulfide was used as a molten reaction medium, sulfur converted dehydrothio-p-toluidine (at 260° maximum reaction temperature) and primuline base (at 285° maximum reaction temperature) to apparently identical brown powders. Characterization of these products by infrared absorption analysis and by elemental analysis indicated that each was a poly(benzothiazole), probably cross-linked by sulfide bonds. This polymer was insoluble in phenol, 97% formic acid, dimethylsulfoxide, dimethylformamide and sulfuric acid. A study of the physical properties of this product will be given in a later paragraph.

2. Condensation of 3,3'-Dimercaptobenzidine with Diphenyl Isophthalate

An equimolar mixture of 3,3'-dimercaptobenzidine (III) and diphenyl isophthalate (IV) was intimately mixed and heated first to 300° under nitrogen



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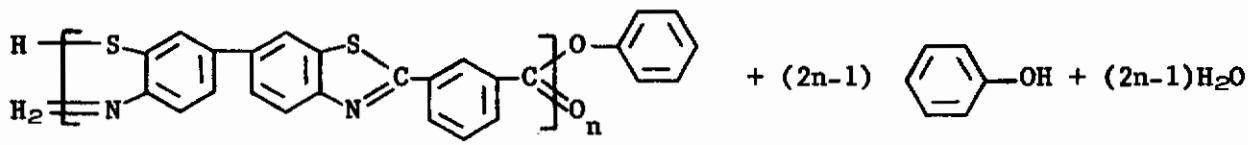
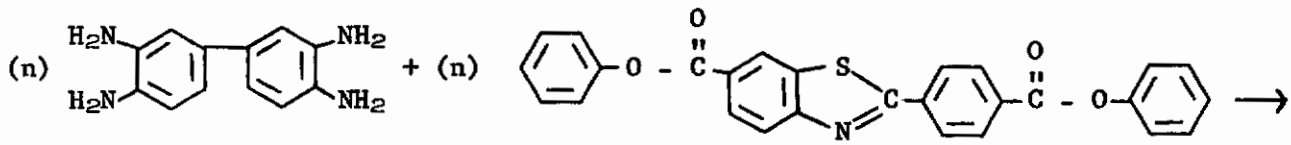


(V)

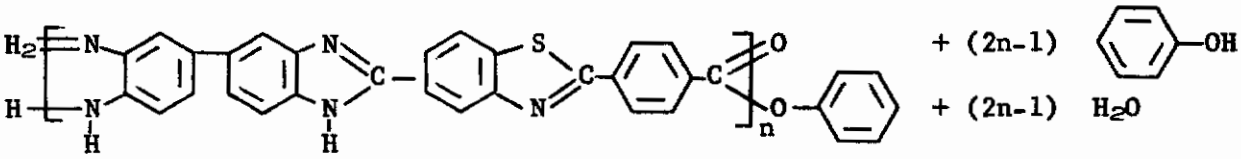
and, after pulverizing, to 400° under vacuum. The infrared absorption analysis was consistent with the proposed structure for the poly(benzothiazole) (V). The elemental analysis values for C, H, N and S were low, presumably because of incomplete combustion. This dark green solid was infusible and insoluble in the common solvents.

3. Condensation of 3,3',4,4'-Tetraaminobiphenyl with Diphenyl 2-Phenylbenzothiazole-4',6-dicarboxylate

Since the benzimidazole polymers prepared by Marvel[5] possessed such excellent thermal stability, a combined benzothiazole-benzimidazole polymer might be expected to have high thermal resistance. A mixture of 3,3',4,4'-tetraaminobiphenyl (VI) and diphenyl 2-phenylbenzothiazole-4',6-dicarboxylate (VII) was condensed by the same procedure as in the preceding paragraph. The infrared absorp-



(VI) (VII)

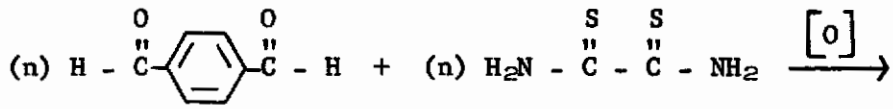


(VIII)

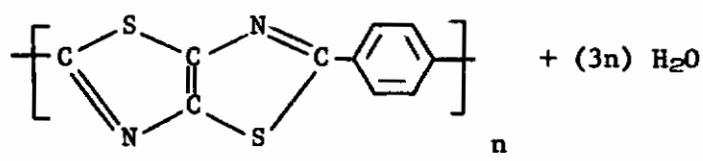
tion analysis was consistent with the proposed structure for the poly(benzimidazole-benzothiazole) (VIII). Elemental analysis values for C, H, N and S were again low, especially the values for carbon and nitrogen. The dark brown product was infusible and insoluble in common solvents.

4. Condensation of Terephthaldehyde with Rubeanic Acid

The availability of rubeanic acid (dithiooxamide) suggested this intermediate for the preparation of polymer chains with pairs of thiazole rings /condensation with bis(haloacetyl)compounds/ or with thiazolothiazole[6] units (condensation with dialdehydes). By heating a solution of terephthalaldehyde (IX) and rubeanic acid (X) in triglyme, first with air as the oxidant, and in a second



(IX) (X)

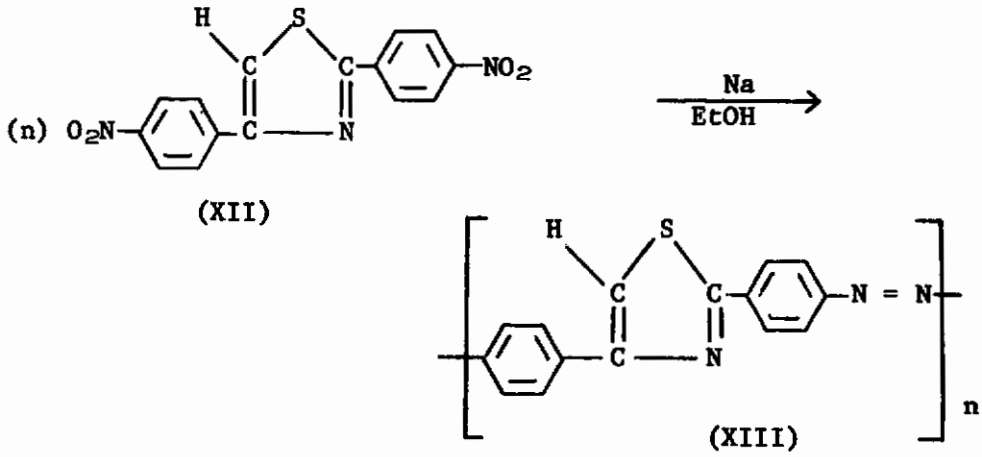


(XI)

experiment with sulfur added to the reaction mixture, a brown powder was obtained in each case. The infrared absorption analysis of the two products showed the same absorption peaks, but the presence of the thiazolothiazole group could not be confirmed. The elemental analysis for C, H, N and S was low, possibly due to incomplete combustion, relative values for nitrogen and sulfur being too low for the expected poly(phenylene-thiazolothiazole) (XI).

5. Partial Reduction of 2,4-Bis(p-nitrophenyl)benzothiazole

The favorable thermal stability of 2,4-diphenylthiazole suggested that linking units of the compound through the phenyl rings might produce thermally stable polymers. The mixed acid nitration of 2,4-diphenylthiazole produced 2,4-bis(p-nitrophenyl)thiazole (XII). The reduction of this compound over sodium amalgam gave a brown, infusible powder. Infrared absorption analysis showed absorption peaks characteristic of 1,4-phenyl substitution and of thiazoles, but the presence of an —N = N— group could not be established. The elemental analysis was too low for all elements, except hydrogen, for the expected poly(azo-phenylene-thiazole) (XIII).



II. Perfluorocarbon Polymers with Pendant Heterocyclic Groups

The first part of this phase of the project, the synthesis of monomers which will yield a polymer with a fluorocarbon backbone and pendant heterocyclic groups, $-(\underset{R}{CF}CF_2)_n$, has not been completed. The second part, polymerization of the monomers to high molecular weight materials and a study of their thermal stability, will be inaugurated when the monomers become available. The attempts to prepare the desired monomers are discussed in what follows.

A. Reaction of Organolithium Compounds with Tetrafluoroethylene (TFE)

It had been originally planned to synthesize monomers of the type $RCF=CF_2$, where R was pyridyl, carbazolyl and fluorenyl.

The first approach consisted of reacting, tetrafluoroethylene (TFE) with organolithium compounds in a manner analogous to the preparation of 1-phenyl-1,2,2-

trifluoroethylene (alpha, beta, beta-trifluorostyrene) by Dixon[7].

$$CF_2 = CF_2 + RLi \longrightarrow RCF = CF_2 + LiF$$

(XIV)

$$RCF = CF_2 + RLi \longrightarrow RCF = CFR \longrightarrow R_2C = CFR \longrightarrow R_2C = CR_2$$

(XV)

Dixon recommended using an excess of TFE and a low temperature in order to obtain XIV, where R was alkyl or phenyl. In the reaction of 2-pyridyllithium with TFE, Dixon isolated a 10% yield of XV, R = C_5H_4N. No mention was made of the isolation of the type XIV product. A reinvestigation of the reaction of 2-pyridyllithium with a three-fold excess of $CF_2 = CF_2$, at -60°C, gave no evidence that XIV, R = C_5H_4N, was obtained in the final product. Instead a high yield of crude 1:2 product, XV, R = C_5H_4N was obtained. The failure to obtain XIV, 2-(trifluorovinyl)pyridine under conditions that gave alpha, beta, beta-trifluorostyrene, was ascribed to the greater contribution of the pyridyl group to the positive nature of the terminal CF_2 group in XIV.

In a similar reaction between 9-fluorenyllithium and TFE, only 1,2-di-(9-fluorenyl)-1,2-difluoroethylene was isolated. In this case, reaction occurred only above 0°C, a temperature at which an excess of TFE could not be maintained. Thus it is possible that, if this reaction were carried out under pressure in order to maintain an excess of TFE, the desired 9-fluorenyllithium might form.

B. Reaction of Organolithium Compounds with Tetrafluorodibromoethane (TFDE)

A second approach was explored in which organolithium compounds were made to react with 1,1,2,2-tetrafluoro-1,2-dibromoethane (TFDE). It was hoped that bromotetrafluoroethyl derivatives would form, which could then be dehalogenated to trifluorovinyl compounds.

$$RLi + BrCF_2CF_2Br \longrightarrow RCF_2CF_2Br + LiBr$$

$$RCF_2CF_2Br + Zn \longrightarrow RCF = CF_2 + ZnBrF$$

Reactions occurred very readily at -50° and -30° with butyllithium and fluorenyllithium, but did not give the desired products. Instead, TFE and butyl bromide were formed in the first case, and TFE, 9-bromofluorene, and bifluorene were formed in the second case.

$$RLi + BrCF_2CF_2Br \longrightarrow RBr + LiBr + CF_2 = CF_2$$

Carbazolyllithium did not react with TFDE at 100°C. At 140°C a reaction occurred, but investigation of the reaction product showed that the desired N-(bromotetrafluoroethyl)carbazole, if formed at all, was not a major constituent of the mixture.

C. Attempted Dehydrofluorination of N-(1,1,2,2-tetrafluoroethyl)carbazole

The next approach was to attempt the preparation of a monomer, $R_2NCF = CF_2$, by dehydrofluorination of the precursor $R_2NCF_2CF_2H$ compound. For this purpose, it was decided to attempt the dehydrofluorination of N-(1,1,2,2-tetrafluoroethyl)carbazole (XVI). This compound can be prepared according to U. S. Patent 2,861,990 from carbazole and TFE under pressure in the presence of carbazolylpotassium and dimethylformamide. We have found that this reaction occurred at atmospheric pressure in dioxane, so that no special equipment was necessary. However, attempts to dehydrofluorinate XVI with potassium ethoxide in ethanol or 50% aqueous KOH at reflux gave back unchanged XVI. Heating with KOH in ethylene glycol at 190°C led to regeneration of carbazole and TFE. It is postulated that in the intermediate XVII which resulted from abstraction of a proton by the base, displacement of nitrogen rather than fluorine occurred. Thermal cracking of XVI at

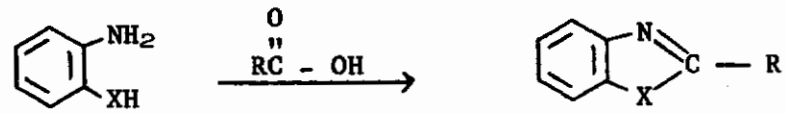
$$\underset{\text{(XVI)}}{C_{12}H_8NCF_2CF_2H} + B^{\ominus} \longrightarrow \underset{\text{(XVII)}}{C_{12}H_8NCF_2CF_2^{\ominus}} \longrightarrow C_{12}H_8N^{\ominus} + CF_2 = CF_2$$

about 260°C gave a black residue and a blue-violet sublimate which were not identified. The lack of success in the synthesis of the desired monomers by the reaction of organometallics with TFE and TFDE led to a shift to another synthetic approach which is described below.

D. Attempted Preparations of 2-(Trifluorovinyl)benzazoles

The synthetic route envisioned here is the preparation of benzimidazoles, benzothiazoles, and benzoxazoles substituted in the 2-position with a fluoroalkyl group which can subsequently be converted to the trifluorovinyl group.

2-Substituted benzimidazoles, benzoxazoles, and benzothiazoles are frequently prepared by the condensation of organic acids with the proper ortho-substituted aniline as shown below:



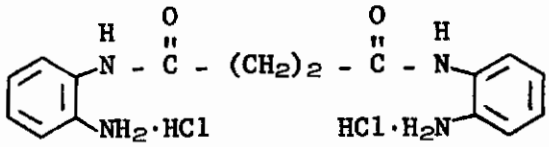
X = NH, O, S

X = NH, O, S

(XVIII)

Recently a number of 2-perfluoroalkylbenzimidazoles, (XVIII), X = NH, R = CF_3, CF_2CF_3, and $CF_2CF_2CF_3$ [8a,b,9] have been synthesized by this method.

A number of dibasic acids also have been condensed with ortho-phenylenediamine. Succinic acid when reacted in a 1:1 molar ratio with ortho-phenylenediamine in 4N hydrochloric acid[10] has been reported to give a mixture of the compounds XIX and XX. Quite recently Lane[8a] reported the formation of the heptafluoroadipobis-2-benzimidazole (XXI). It appears to us, therefore, that this general route should prove fruitful in the preparation of the desired trifluorovinyl benzazoles. By the judicious selection of the acid, a variety of monomer



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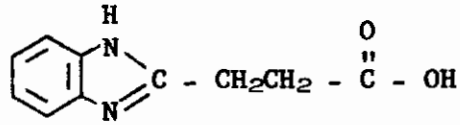

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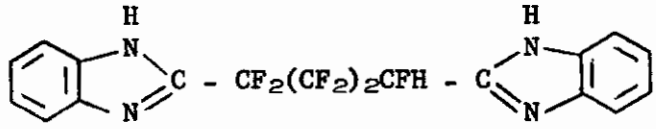


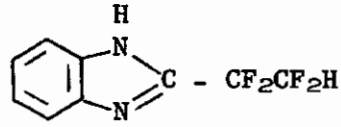
(XXI)

precursors would become available. These would enable us to investigate and to evaluate three of the general methods, dehydrohalogenation, dehalogenation and pyrolysis, for introducing the double bond in fluorocarbons.

To date, a number of 2-(perfluoroalkyl)benzimidazoles and benzothiazoles have been prepared and their attempted conversion to the desired 2-(trifluorovinyl) benzazoles have been or are currently in progress.

1. 2-(1,1,2,2-Tetrafluoroethyl)benzimidazole (TFB) and Its Attempted Dehydrofluorination

The condensation of 2,2,3,3-tetrafluoropropionic acid with ortho-phenylenediamine in 4N hydrochloric acid yielded 2-(1,1,2,2-tetrafluoroethyl)-benzimidazole (TFB) (XXII) in 46% yield. Attempts to dehydrofluorinate TFB in refluxing triethylamine, and with potassium t-butoxide in dimethylsulfoxide at



(XXII)

temperatures ranging from 35° to 130° were unsuccessful, TFB being recovered for the most part unchanged.

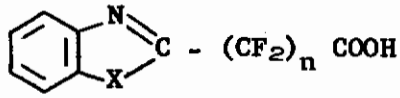
The attempted dehydrofluorination of TFB in refluxing 17% sodium hydroxide solution was unsuccessful and led to the formation of the disodium salt of oxalic acid, inorganic fluoride ion and a 60% yield of benzimidazole. Further attempts to dehydrofluorinate this compound has been temporarily suspended.

2. The Reaction of Dibasic Perfluoro-Acids with ortho-Phenylenediamine and ortho-Aminothiophenol. The Pyrolysis of 2-(1,1,2,2-Tetrafluoro-2-carboxyethyl)benzimidazole and Its Salt

The pyrolysis of the sodium salts of perfluoro-acids is a useful method for the preparation of terminal olefins[11].

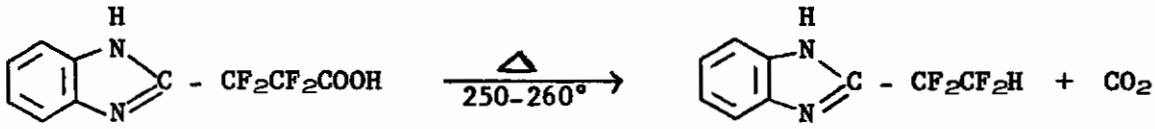
$$RCF_2CF_2COO^{\ominus}Na^{\oplus} \xrightarrow{\Delta} RCF = CF_2 + CO_2 + NaF$$

The condensation of perfluorosuccinic acid and perfluoroglutaric acid with ortho-phenylenediamine yielded the novel acids XXIII, (X = NH, n = 2), 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzimidazole, and XXIII, (X = NH, n = 3), 2-(1,1,2,2,3,3-hexafluoro-3-carboxypropyl)benzimidazole, in 60% and 46% yield respectively. In a similar fashion, the acid XXIII, (X = S, n = 2), 2-(1,1,2,2-tetrafluoro-2-carboxyethyl)benzothiazole, has been prepared in ca. 60% yield.



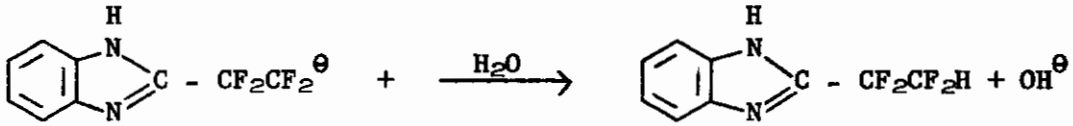
(XXIII)

Initial pyrolyses studies of the acid XXIII, (X = NH, n = 2) and its sodium salt have been carried out. This acid when heated at 250-260° decarboxylates with the formation of TFB. Likewise the decarboxylation of the moist sodium



(XXIII)

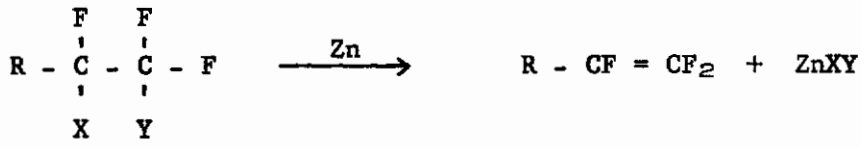
salt at 260-290° at atmospheric pressure occurs with the formation of TFB. A reasonable explanation for the formation of TFB is indicated.



However, the pyrolysis of the anhydrous sodium salt at 240-280°/0.2 mm. in a sublimation unit, yielded sublimates, which were obviously mixtures, carbon dioxide, and a residue which was predominantly inorganic fluoride. The infrared spectra of the sublimates showed new absorptions at 5.55μ, 5.65μ, and 5.82μ not present in the starting material. The trifluorovinyl group, as well as alpha-fluorocarbonyls, are known to absorb in this same general region. However, it is possible that conjugation with an aromatic system may cause a shift to shorter wavelengths. These results indicate that the reaction has proceeded to a certain extent in the desired direction. Initial efforts to separate the components of the mixture by fractional sublimation have been unsuccessful. Further efforts to separate the mixture are currently in progress.

3. 2,3,3-Trifluoro-3-bromo-2-chloropropionic Acid and 2-(1,2,2-Trifluoro-2-bromo-1-chloroethyl)benzimidazole

A third general method for preparing terminal fluoroolefins under rather mild conditions utilizes the dehalogenation of a properly substituted fluoro-compound with zinc as shown below:



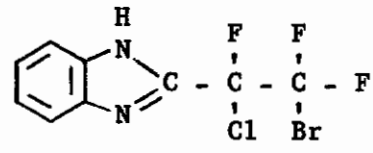
$$R - \overset{F}{\underset{X}{C}} - \overset{F}{\underset{Y}{C}} - F \xrightarrow{Zn} R - CF = CF_2 + ZnXY$$

X = Y = Cl, Br, I or any combination of these.

Efforts were therefore made to prepare a suitably substituted fluoro-acid which could be condensed to form benzazoles.

The ozonization of the olefin, 3,4,4-trifluoro-4-bromo-3-chlorobutene, followed by aqueous hydrogen peroxide oxidation, yielded a pure fluoro-acid, as determined by gas phase chromatography, having the correct neutralization equivalent for the desired acid 2,3,3-trifluoro-3-bromo-2-chloropropionic acid. However, the elemental analyses, (C,H) for this compound was very poor. An aqueous potassium permanganate oxidation of the same olefin also yielded the same acid in ca. 25-30% yield.

On the assumption that the above fluoro-acid was the desired acid, a small amount of this material (2.0 g.) was reacted with ortho-phenylenediamine to give a trace amount of a product, believed to be the desired intermediate (based on infrared spectrum, and C, H, N analyses), 2-(1,2,2-trifluoro-2-bromo-1-chloroethyl)benzimidazole (XXV). However, if the zinc dehalogenation procedure is to prove feasible, the yield of the condensation reaction must be greatly improved. Efforts in this direction are currently underway.



(XXV)

III. Characterization of Polymers

Polymers prepared under this program are to be studied for thermal stability, solubility, moldability and structural strength. Most of the reactions were first trials, being carried out on a small scale. Only the poly(benzothiazole) from the primuline fusion reaction has been obtained in sufficient quantity for testing.

1. Thermogravimetric Analysis

The ASD has requested that samples of polymers be submitted for thermogravimetric analysis and other characterizing tests. The TGA curve obtained for poly(benzothiazole), 910-W51A (the primuline fusion reaction), is shown on

Figure 1. On the figure are also plotted values for polyphenyl and "Teflon", as reported by Doyle[13]. The TGA determination of ASD and of Doyle are carried out in the same manner. Calculation of decomposition temperatures was therefore adapted from the report by Doyle. The "differential procedural decomposition temperature", DPDT, was calculated from a plot of weight loss per hour, the temperature where the loss amounted to 10% per hour being taken as the DPDT, found to be 620° for Sample 910-W51A. The "integral procedural decomposition temperature", IPDT, was calculated from the ratios of areas under the TGA curve, using Doyle's equation:

$$T_{A*K*} = 875\ A*K* + 25$$

For Sample 910-W51A, the IPDT was 690°C. Some representative values of decomposition temperatures are shown in Table 3, for comparison with the poly(benzothiazole). As was noted earlier in this report, relative stabilities of simple compounds do not necessarily predict the relative stabilities for the corresponding

TABLE 3

Thermogravimetric Analysis - Calculated Decomposition Temperatures

Polymer	IPDT, °C	DPDT, °C
Poly(benzothiazole) 910-W51A	690	620
Teflon	555	490
Polyphenyl	535	510
Silicone (SR32)	505	450
Nylon 66	420	360
Polystyrene	395	330
Plexiglass	345	280

polymer. For example, the decomposition point for biphenyl (1010°F)[a] is higher than that of 2-phenylbenzothiazole (943°F)[b], as shown in Table 2. The corresponding polymers, however, reverse the order of thermal stability, poly(benzothiazole) (620°C) showing a higher TGA value than does polyphenyl (510°C) as shown in Table 3 and Figure 1.

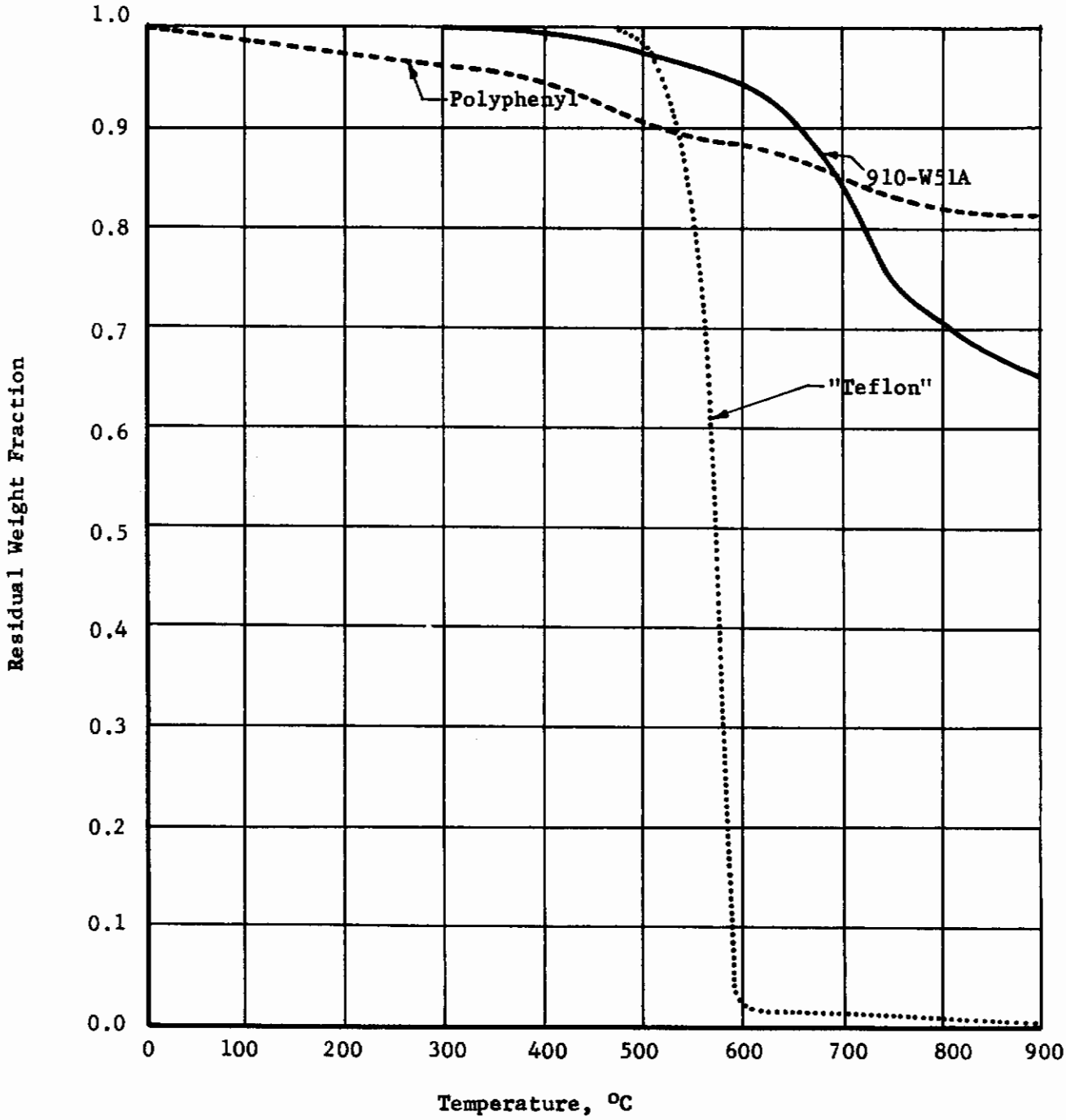
(a) 1010°F equals 543°C
(b) 943°F equals 505°C

2. Solubility Studies

The discussion of the poly(benzothiazole), 910-W51A, in an earlier paragraph noted the unsuccessful attempts to effect solution of this polymer. The range of solubility attempted was at the 1% solution level, in order to develop a means of obtaining molecular weight value. The following solvents were tested, under a nitrogen atmosphere:

Figure 1

Thermogravimetric Analysis Data[13]
(ΔT 150°C per hour, nitrogen)



Sample (g.)	Solvent (g.)	Temp. (°C)	Time (hrs.)	Residue* (g.)
0.13	Sulfolane (14.4)	235-9	2.0	0.13
0.08	Hexachlorobenzene (11.6)	235-9	2.0	0.07
0.10	N-methyl-2-pyrrolidone (14.7)	193-9	5.0	0.07
0.40	2-Phenylbenzothiazole (14.1)	255-71	2.0	0.39
0.40	Dimethylsulfoxide (32.8)	164-70	4.0	0.40

*Some residues were not recovered quantitatively, because of mechanical losses. No detectable solid separated out of any of the solvent filtrates.

Concentrated sulfuric acid was slightly colored, but a slight floc observed upon neutralization of the diluted acid filtrate was too minute to be isolated.

3. Moldability of Polymers

Since the poly(benzothiazole), 910-W51A, was infusible and insoluble, a compression molding at high temperature was attempted. A small electrically-heated mold with a 7/8" diameter cylindrical cavity was adapted to a Vicat press capable of a maximum pressure of 20 tons. A 3/16" thick disc of the polymer was produced by a temperature of 600°F at a pressure of 20 tons after a holding time of 5 minutes. This disc was hard, but rather brittle. In a statistically designed experiment, 1/16" discs were prepared at varying temperatures (400 to 600°F), varying pressures (5 to 20 tons) and varying holding times (5 to 20 minutes). Many of the discs were too fragile to remove from the mold intact, and most were too brittle to obtain a relative hardness value.

4. Structural Strength of Molded Polymers

The poly(benzothiazole) could not be tested for tensile modulus or flexural modulus, since molded shapes for these tests could not be obtained.

IV. Conclusions

Polymers containing thiazole and benzothiazole units have been shown to have high thermal stability. The major problem is the formation of polymers with structural modifications in the connecting groups which will enhance solubility and moldability without greatly reducing thermal stability.

The major problem in the preparation of fluorocarbon polymers with pendant heterocyclic groups is the synthesis of the perfluorovinylheterocyclic monomers. The benzazole derivatives of the perfluoro acids appear to be promising intermediates.

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