

AROMATIC POLYMERS FOR THERMALLY STABLE FIBERS AND FILMS

- I) POLYBENZIMIDAZOLES
- II) POLY(1,3,4-OXADIAZOLES)

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ABSTRACT

Dimethylacetamide and dimethylsulfoxide have been successfully employed as dry-spinning solvents for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole. The physical properties of both fibers appear to be comparable. Since dimethylacetamide produces a lighter colored yarn and in general lends itself to easier solvent removal, it emerges as the more desirable solvent for dry-spinning operations.

The fibers exhibit remarkably high resistance to hydrolysis and thermal ageing, although under the more realistic condition of air ageing the thermal properties are not nearly as impressive as under nitrogen. The N-H bond in polybenzimidazoles is suspect as the weak link leading to degradation in the hot oven. To test this hypothesis N-substituted polymers were prepared via the methylation of N-sodio polybenzimidazoles.

Oriented and crystalline polyhydrazide fibers can be converted by a unique cyclodehydration reaction into oriented and crystalline fibers of poly(1,3,4-oxadiazoles). Conversion of fibers (T/E/M₁ = 5/24/94) of the polyhydrazide derived from equimolar amounts of isophthalic dihydrazide and terephthaloyl chloride (OIoT) gave fibers (T/E/M₁ = 2.6/3.1/124) of poly(1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole), PODZ-I/T, which have excellent retention of their fiber structure even when exposed to temperatures up to 400°C. for prolonged periods of time. Such heat treatments afford a final polyoxadiazole fiber (T/E/M₁ = 1.2/1.2/90). The chemical structure of model compounds containing up to 13 alternating rings consisting of 2,5-(1,3,4-oxadiazole), m-, and p-phenylene moieties

was found to be stable up to 400-450°C. This is in agreement with observed stabilities of the corresponding polymer towards thermal degradation.

INTRODUCTION

The preparation of high molecular weight highly aromatic polymers has been a long-standing goal of polymer chemists. Such polymers would be expected to have the high degree of thermal and chemical inertness displayed by simple model systems, combined with new dimensions in mechanical properties.

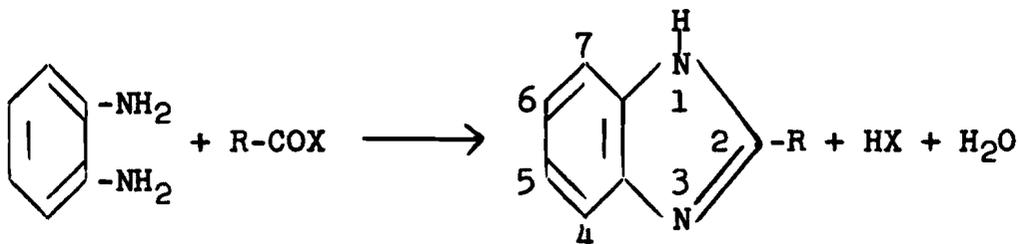
Two such highly aromatic polymeric systems which appear to meet the above specifications - the polybenzimidazoles and the poly(1,3,4-oxadiazoles) - have been the subject of the following research effort.

I. Polybenzimidazoles - James J. Kane

Discussion

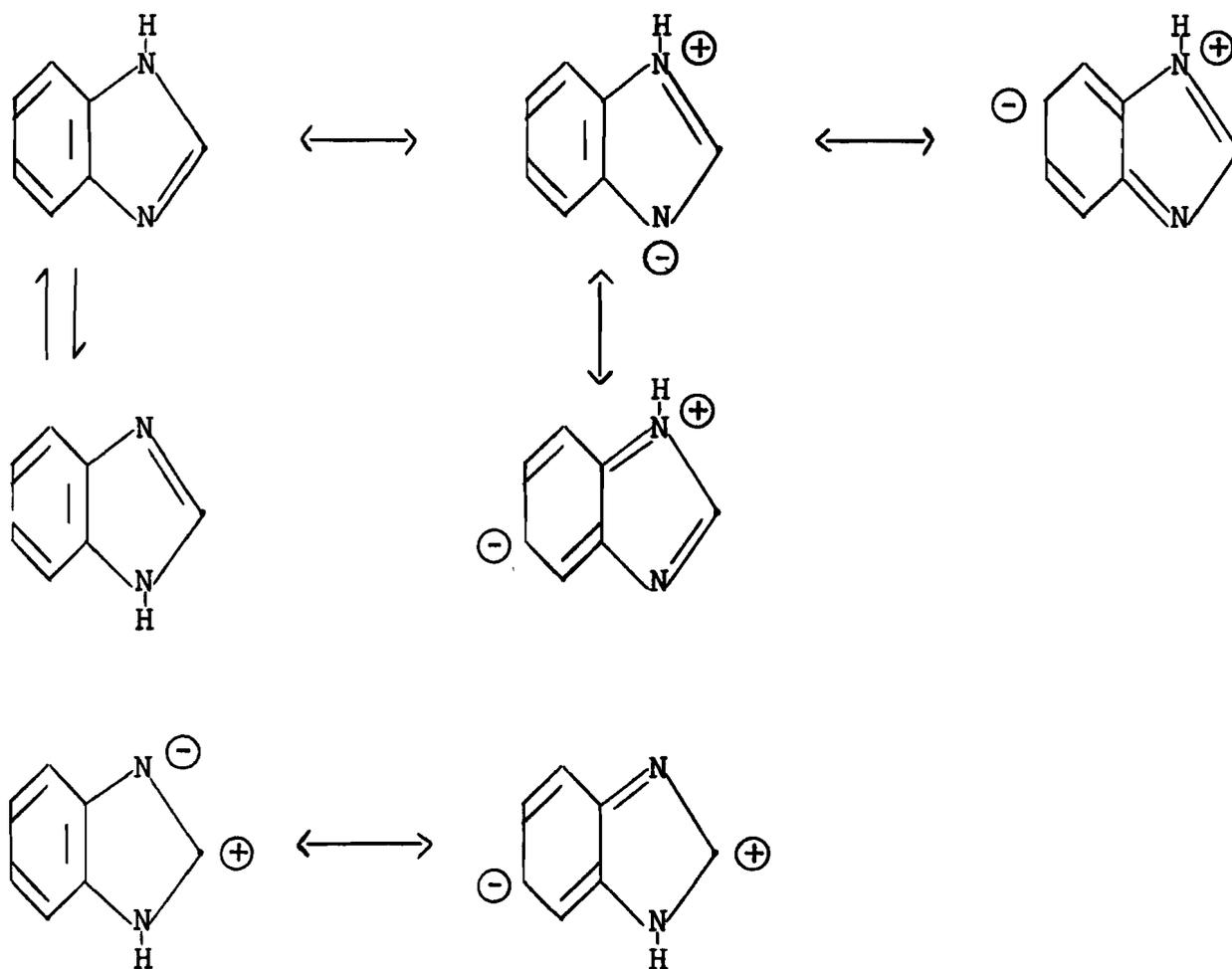
Benzimidazoles

Benzimidazole derivatives are synthesized from o-phenylenediamine and carboxylic acids or their derivatives:



The benzimidazole products are generally high melting crystalline solids possessing both acid and basic characteristics. They exhibit unusual chemical resistance to acidic, basic, and oxidizing reagents. The tautomeric nature of the benzimidazole system unsubstituted in the 1-position is a well known phenomenon rendering both nitrogens in the heterocyclic system equivalent.

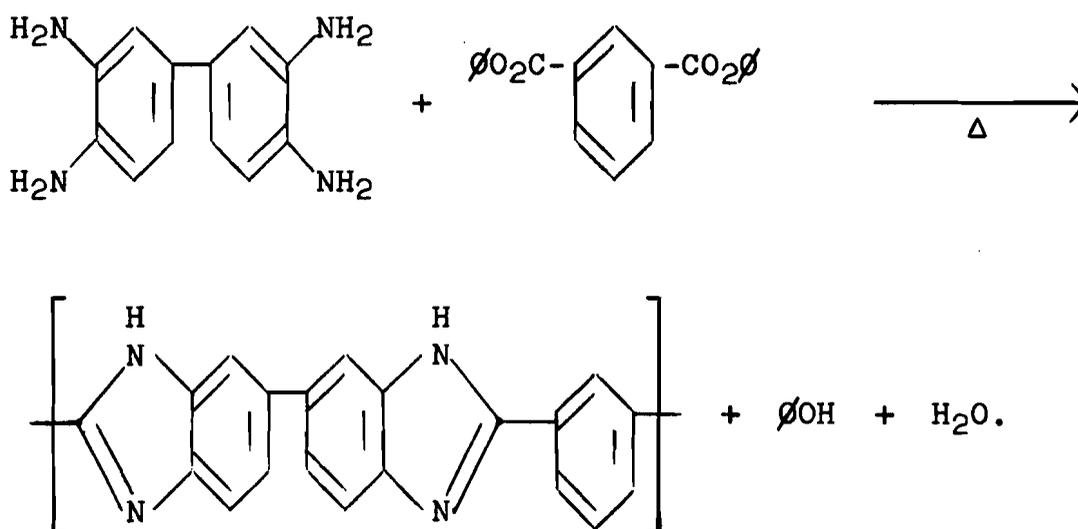
Similarly, hydrogen bonding in benzimidazoles unsubstituted in the 1-position has been demonstrated and appears to be due to association via hydrogen bonds between the imino grouping and the tertiary nitrogen in the amidine-like structure. The chemical inertness of benzimidazoles is explicable in terms of the aromatic nature of the system which derives delocalization energy from overlapping of the sextet of π electrons available to both the benzene and heterocyclic rings as described by the classical structures:



The high melting characteristics displayed by the benzimidazoles are especially pronounced in derivatives unsubstituted in the 1-position, a prerequisite necessary for association via hydrogen bonding.

Polybenzimidazoles

Application of the general synthetic route to benzimidazoles to include bifunctional materials was first accomplished by Brinker and Robinson (1) through their discovery that bis-o-diamines and aliphatic dioic acids or their derivatives react to form linear condensation polymers designated as polybenzimidazoles. A modification of this procedure resulting in the preparation of polybenzimidazoles containing recurring aromatic units was developed by Marvel and Vogel (2) through the melt polymerization of bis-o-diamines and diphenyl esters of aromatic dicarboxylic acids:



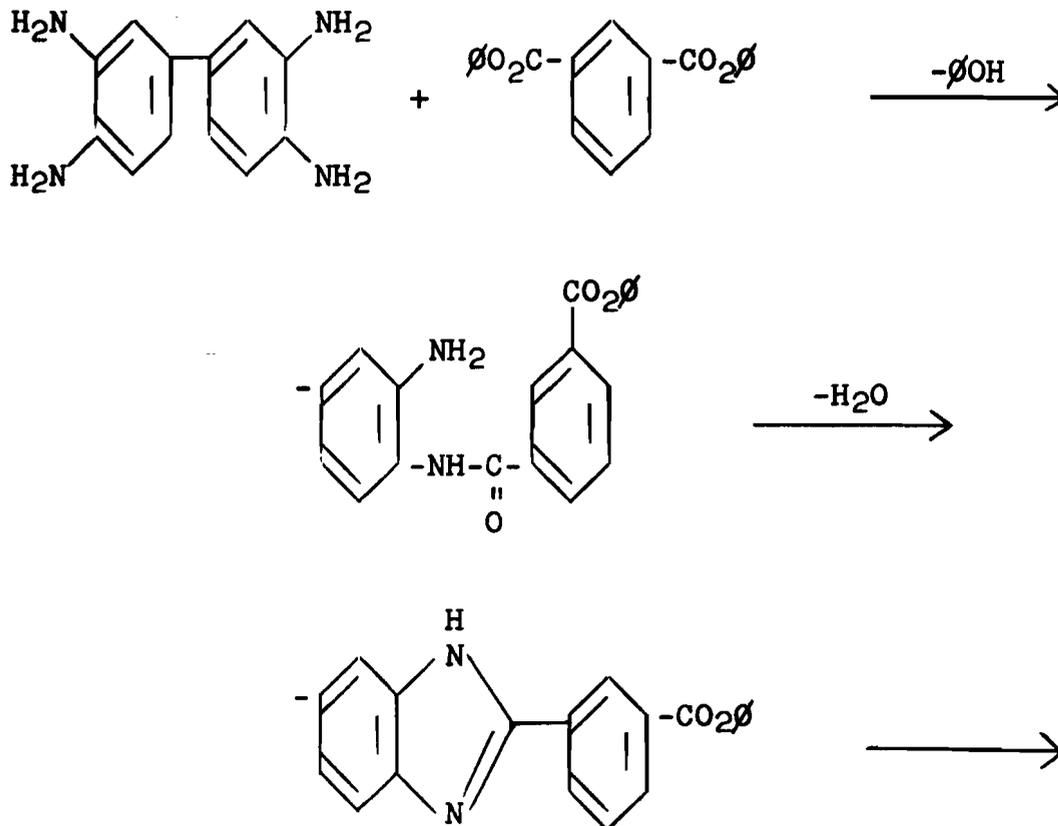
Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole

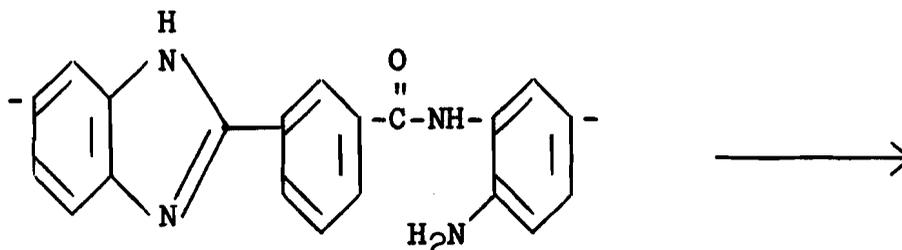
The polymers prepared by Marvel and Vogel were based on the tetraamines, 3,3'-diaminobenzidine and 1,3,4,6-tetraaminobenzene and the dioic acid moieties employed were phthalic, isophthalic, terephthalic, 2,2'-biphenyl, and 3,5-pyridyl. In general, the condensation polymers have been high melting, or infusible materials exhibiting, as anticipated, high thermal and chemical resistivities.

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, based on 3,3'-diaminobenzidine and diphenylisophthalate was chosen as the most attractive polymer for large-scale preparation and spinning operations because of the commercial availability of the tetraamine salt 3,3'-diaminobenzidine tetrahydrochloride.

The free base, 3,3'-diaminobenzidine, is liberated from the hydrochloride salt with a 4% sodium hydroxide solution. Purification is accomplished by repeated recrystallizations from methanol. Polymerization of 3,3'-diaminobenzidine and diphenylisophthalate is accomplished by heating a mixture of the two reactants in the melt at 260-290° to effect the polycondensation which is accompanied by phenol and water evolution.

The reaction mechanism appears to be straightforward and is outlined below.





Since both water and phenol appear to be evolved at the same rate it is probably safe to assume that ring formation occurs as the polymer chain grows rather than by the alternative process of preliminary poly-o-aminoamide formation and subsequent elimination of water with ring closure to form the heterocyclic portion of the repeating unit. The driving force for ring closure would be expected to be great because of the resulting delocalization energy derived by the now aromatic system. Thus, at the temperature employed, amide formation and imidazole formation might be expected to occur at similar rates.

The polymerization reaction is carried out by immersing a flask containing the solid reactants under a nitrogen atmosphere in a 260° bath. After melting, reaction commences at about 260° as evidenced by rapid evolution of phenol and water. The reaction mass soon sets up as a glassy solid of inherent viscosity of 0.3-0.4 (DMSO) which must be removed from the flask, ground, and reheated at temperatures ranging from 260-400° over a 9-12 hour period under 0.05 mm Hg pressure. During this treatment, the remainder of the phenol is removed. The polymer obtained, a bright yellow solid, has an inherent viscosity of 0.8 (DMSO). The polybenzimidazole does not melt up to 500°C. and is soluble in DMSO, formic acid, sulfuric acid, N-methylpyrrolidone, DMAc, and DMF. Insoluble portions, apparently crosslinked polymer, account for about 10% of the weight of final product. After reprecipitation from DMSO, DMAc, or DMF with water, the polymer is obtained as a tan powder. Infrared spectra of films cast from DMAc are typical of benzimidazoles.

Polybenzimidazole Fibers

Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole has been dry-spun from DMSO and from DMAc. After spinning, the yarn was extracted with water for two days and drawn 1.7X in 5 lbs. steam pressure. The yarn was then redrawn over a hot pin at the following temperatures and draw ratios: 400°, 1.1X; 350°, 1.6X; 350°, 1.3X; 350°, 1.1X; 300°, 1.2X. The redrawn fiber was highly oriented but amorphous. Treatment of the fiber with a solvent mixture of formic acid:water (50:50 by volume) induced a slight degree of crystallinity but destroyed orientation. In Table I are compiled the physical testing data for all the samples of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole.

For comparison, data describing the tensile properties for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole dry-spun from DMSO, drawn 1.8X in 12 lbs. steam pressure and 1.2X over a 360° hot pin are also tabulated in Table I. In general, the two yarns are comparable and the data strongly suggest that the difference in spinning solvents (DMSO and DMAc) has no effect on the tensile properties of the fibers. The differences in transverse properties is probably a reflection of the fact that lower molecular weight polymer was used in the DMAc spin (η_{inh} of 0.6 vs. η_{inh} of 0.8 for the dimethyl sulfoxide spin). Dimethylacetamide, then, emerges as the more desirable of the two solvents since it does not involve as bothersome solvent removal problems as DMSO. In addition, the yarn obtained by spinning from DMAc is lighter in color (straw-yellow) than that obtained from DMSO (dark brown).

Thermal stability and hydrolytic tests have been conducted on the fibers spun from DMSO and are tabulated in Tables II and III. These tests have not been repeated on fibers obtained from DMAc, but the limits of air ageing temperatures seem to be the same for both fibers since samples of the latter material had virtually no strength after 24 hours in a 400° oven and after 15 min. in a 500° oven. Hydrolytic stability of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole is unusually good as shown by the data in Table III.

TABLE I

1) POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE SPUN FROM DMAc
FIBER PROPERTIES

A. Drawn 1.65 times at 5# steam

| | <u>T^a</u> | <u>E^b</u> | <u>M₁^c</u> | <u>TR %^d</u> | | | <u>WR %^e</u> | | |
|----------|----------------------|----------------------|----------------------------------|-------------------------|----------|-----------|-------------------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 2.19 | 21.4 | 73.6 | 86 | 66 | 33 | 57 | 34 | 13 |
| Loop | 1.53 | 5.1 | - | | | | | | |
| Knot | 2.26 | 27.7 | 47.0 | | | | | | |
| Hot-Wet | 1.27 | 47.8 | 28.0 | | | | | | |

B. Drawn 1.65 times at 5# steam
and redrawn 1.1 times at 400°C.

| | <u>T</u> | <u>E</u> | <u>M₁</u> | <u>TR %</u> | | | <u>WR %</u> | | |
|----------|----------|----------|----------------------|-------------|----------|-----------|-------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 3.26 | 41.2 | 76.7 | 85 | 59 | 30 | 60 | 31 | 12 |
| Loop | 1.56 | 4.2 | - | | | | | | |
| Knot | 2.38 | 24.0 | 50.1 | | | | | | |
| Hot-Wet | 1.93 | 51.2 | 25.5 | | | | | | |

C. Drawn 1.65 times at 5# steam
and redrawn 1.6 times at 350°C.

| | <u>T</u> | <u>E</u> | <u>M₁</u> | <u>TR %</u> | | | <u>WR %</u> | | |
|----------|----------|----------|----------------------|-------------|----------|-----------|-------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 4.33 | 10.8 | 110 | 75 | 58 | 41 | 48 | 31 | 18 |
| Loop | 0.64 | 1.8 | - | | | | | | |
| Knot | 0.67 | 2.2 | 30.3 | | | | | | |
| Hot-Wet | 1.94 | 18.1 | 47.0 | | | | | | |

D. Drawn 1.65 times at 5# steam
and redrawn 1.1 times at 350°C.

| | <u>T</u> | <u>E</u> | <u>M₁</u> | <u>TR %</u> | | | <u>WR %</u> | | |
|----------|----------|----------|----------------------|-------------|----------|-----------|-------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 2.99 | 17.8 | 92.7 | 77 | 54 | 30 | 50 | 27 | 12 |
| Loop | 1.38 | 3.2 | - | | | | | | |
| Knot | 1.97 | 8.4 | 5.1 | | | | | | |
| Hot-Wet | 1.52 | 41.4 | 40.0 | | | | | | |

TABLE I (CONT'D.)

E. Drawn 1.65 times at 5# steam and redrawn 1.2 times at 300°C.

| | <u>T</u> | <u>E</u> | <u>M₁</u> | <u>TR %</u> | | | <u>WR %</u> | | |
|----------|----------|----------|----------------------|-------------|----------|-----------|-------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 3.43 | 10.0 | 119.7 | 81 | 57 | - | 52 | 28 | - |
| Loop | 0.40 | 1.6 | - | | | | | | |
| Knot | 0.81 | 5.3 | 20.6 | | | | | | |
| Hot-Wet | 1.70 | 31.2 | 40.3 | | | | | | |

2) POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE SPUN FROM DMSO
FIBER PROPERTIES

A. Drawn 1.8 times at 12# steam and redrawn 1.2 times at 360°C.

| | <u>T</u> | <u>E</u> | <u>M₁</u> | <u>TR %</u> | | | <u>WR %</u> | | |
|----------|----------|----------|----------------------|-------------|----------|-----------|-------------|----------|-----------|
| | | | | <u>3</u> | <u>5</u> | <u>10</u> | <u>3</u> | <u>5</u> | <u>10</u> |
| Straight | 4.16 | 6.9 | 121 | 88 | 68 | - | 62 | 36 | - |
| Loop | 1.60 | 1.5 | 104 | | | | | | |
| Knot | 2.80 | 4.0 | 67 | | | | | | |
| Hot-Wet | 2.40 | 23.4 | 74 | | | | | | |

-
- a) - T = Tenacity (gr./denier)
 - b) - E = % Elongation at Break
 - c) - M₁ = Initial Modulus (gr./denier)
 - d) - TR = % Tensile Recovery at 3, 5, 10% Elongation
 - e) - WR = % Work Recovery at 3, 5, 10% Elongation

TABLE II

1) THERMAL STABILITY OF POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE FIBERS

| <u>T (in air)</u> °C. | <u>Time (hours)</u> | <u>T/E/M₁^a</u> |
|--------------------------|---------------------|--------------------------------------|
| Room Temp. | - | 4.5/13/79 |
| 300 | 24 | 4.1/13/79 |
| " | 48 | 3.6/9/66 |
| " | 72 | 3.6/9/66 |
| " | 84 | 2.8/6/22 |
| " | 150 | 2.5/6/22 |
| 350 | 10 | 3.0/4/66 |
| " | 18 | 2.4/3/40 |
| 400 | 1 | 3.8/15/80 |
| " | 1.5 | 1.0/6/60 |
| " | 6 | TWTT |
| 450 | 0.25 | 2.5/2.5/27 |
| " | 0.5 | Disintegrated |
| 500 | 0.25 | TWTT |
| " | 1 | Disappeared |

2) ULTRAVIOLET STABILITY OF POLY-2,2'-(m-PHENYLENE)-5,5'-BIBENZIMIDAZOLE FIBERS

| <u>Exposure Time^b (hours)</u> | <u>T/E/M₁</u> |
|--|--------------------------|
| 0 | 4.5/13/97 |
| 24 | 4.3/13/97 |
| 48 | 4.3/9/80 |
| 78 | 4.1/6/85 |
| 96 | 4.2/10/80 |
| 220 | 4.1/10/83 |

a) - See footnotes in Table I.

b) - One hour in Xenotester is the equivalent of three hours of Florida sunlight.

TABLE III

HYDROLYTIC STABILITIES OF POLY-2,2'-(m-PHENYLENE)-5,5'-
BIBENZIMIDAZOLE FIBERS

| <u>Medium</u> | <u>Time (hours)</u> | <u>T/E/M₁^a</u> |
|------------------------------------|---------------------|--------------------------------------|
| None | - | 4.5/13/97 |
| 10% NaOH | 1 | 3.9/22/74 |
| 95-100° | | |
| " | 3 | 3.8/26/61 |
| " | 6 | 4.2/29/70 |
| " | 24 | 3.9/38/55 |
| 20% NaOH | 1 | 4.4/23/75 |
| 95-100° | | |
| " | 3 | 4.0/23/70 |
| " | 6 | 3.8/25/65 |
| " | 24 | 3.8/25/68 |
| 40% NaOH | 1 | 4.1/49/56 |
| 95-100° | | |
| " | 3 | 3.0/56/50 |
| " | 6 | 2.8/50/39 |
| " | 24 | 3.0/54/33 |
| 10% H ₂ SO ₄ | 1 | 3.6/36/50 |
| 95-100° | | |
| " | 3 | 3.2/35/48 |
| " | 6 | 3.6/42/44 |
| " | 24 | 3.4/38/52 |
| 20% H ₂ SO ₄ | 1 | 3.4/42/44 |
| 95-100° | | |
| " | 3 | 3.5/37/45 |
| " | 6 | 3.3/49/39 |
| " | 24 | 3.6/37/52 |
| 40% H ₂ SO ₄ | 1 | 3.4/36/46 |
| 95-100° | | |
| " | 3 | 3.6/45/53 |
| " | 6 | 3.4/50/44 |
| " | 24 | 3.1/52/43 |

a) - See footnotes in Table I.

Films cast from DMAc are tough and self-supporting and, when subjected to a 400° oven for a half day, they are still tough but take on a purple-brown color and cannot be redissolved. This behavior strongly suggests crosslinking.

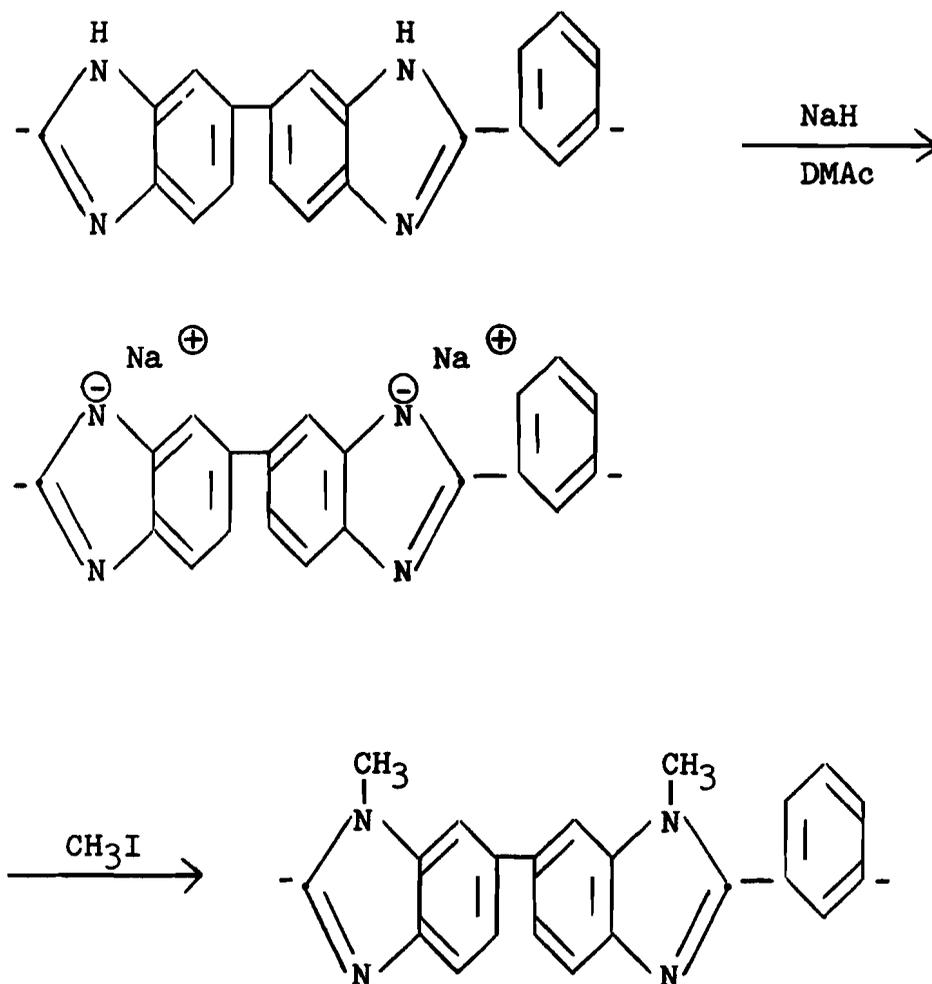
This same purple-brown coloration is observed in the fibers as they are drawn over the hot pin at 350-400°. The color disappears where the fiber is removed from the heat source suggesting a reversible thermal excitation. Samples of bulk polymer were submitted for Electron Spin Resonance studies to detect the presence of unpaired electrons and determine whether or not the process is reversible. The results obtained are qualitative but reveal an absorption band for unpaired electrons which is increased in intensity by light. The process appears not to be reversible, however.

The ability of this polymer to withstand exposure to high temperatures in the presence of air has been disappointing as indicated by the data in Table II, and this behavior has been theorized as due to the susceptibility of the N-H bond to undergo bond breaking at high temperatures and subsequent oxidation in the presence of air. Even in inert atmosphere (nitrogen) poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole subjected to temperatures up to 500°C. appears to crosslink since the resulting material, while not crystalline, is no longer soluble in the usual solvents, DMSO, DMF, DMAc, and formic acid.

Substituted Polybenzimidazoles

A long standing desire has been to obtain polybenzimidazoles substituted, preferably by an aromatic substituent in the 1-position of the heterocyclic ring. One approach to this type polymer is through the use of appropriately substituted tetraamines. Marvel and Vogel (2) have reported the synthesis of the polymer based on 1,3-diamino-4,6-dianilinobenzene and isophthalic acid and concluded that its ability to withstand thermal degradation is no better than the unsubstituted analog. The preparation of this polymer has been repeated in this laboratory, but only small quantities of low molecular weight polymer have been obtained.

An alternative approach to polybenzimidazoles substituted in the 1-position is by direct substitution at this position on preformed polymer. Such a reaction takes advantage of the acidic nature of the hydrogen on the heterocyclic ring and is a well-known general reaction of benzimidazoles. Thus, poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was converted to the N-methylated polymer by treatment of its sodium salt in DMAc with methyl iodide:



Infrared analysis of the methylated polymer indicated a decrease in N-H absorption intensity as well as a shift of this absorption band to a lower wave number. It is interesting to speculate that such a shift might be attributed to the decrease in hydrogen bonding which would be anticipated in the polybenzimidazole if most of the 1-positions in the polymer chain were methylated. This is analogous to the differences observed in the spectra of concentrated and dilute solutions of compounds capable of intermolecular hydrogen bonding. The appearance of aliphatic C-H absorption bands in the infrared spectra also indicates that the desired methylation has been effected. The methylated polybenzimidazole is soluble in formic acid and has been cast into tough films from that solvent. However, unlike the starting material, it is insoluble in DMSO, DMF, and DMAc. Such a difference might be expected between the amphoteric starting material and the basic product. X-ray analysis indicates that the methylated material is amorphous. The new polymer does not melt, but it does soften at approximately 400°C. A quantitative determination of the extent of alkylation is not yet possible as no reproducible chemical analysis of the polymer has been accomplished. However, the presence of the N-H absorption in the infrared spectra is ample indication that alkylation is incomplete.

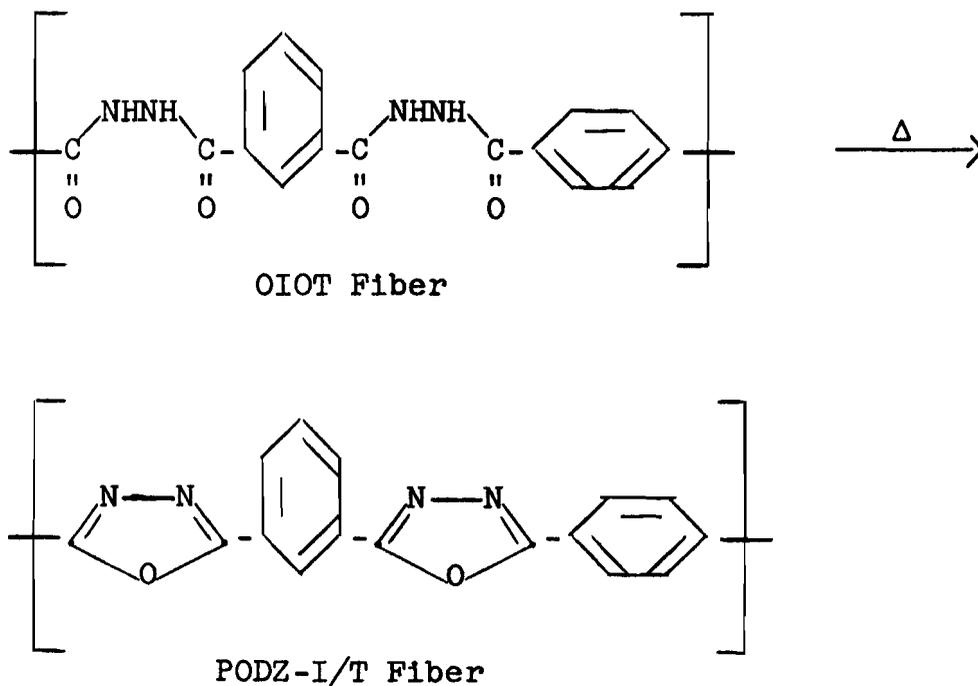
The sodium salt of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole has been treated in DMAc with iodobenzene with the hope of preparing the N-phenylated polymer. The infrared spectra of the product is identical to that of the starting material indicating that phenylation, if it occurred at all, is negligible. It may be necessary to resort to higher temperatures and sealed tubes to effect this reaction. However, even if N-arylated polybenzimidazoles may not be available by this method, it does appear to be a convenient means for the preparation of N-alkylated polymers, and possibly a method which will prove useful for the modification of polybenzimidazoles.

II. Poly-1,3,4-oxadiazoles - F. T. Wallenberger

Background

The search for high temperature-resistant fibers in the past years has resulted in two major developments. One was the preparation of poly[2,2'-(1,3-phenylene)-5,5'-benzimidazole] bulk polymer and films by Vogel and Marvel (1) and the subsequent fabrication of this polymer into tough fibers by Frazer and Kane.

The other development was that Frazer (2) discovered that aromatic poly[2,5-(1,3,4-oxadiazole)] fibers had superior high temperature-resistant properties as well as excellent fiber properties. The fabrication of these fibers was accomplished by a unique cyclodehydration of polyhydrazides in fiber form at elevated temperatures. This fiber conversion is presently the only route to poly(1,3,4-oxadiazole) fiber. There are two other synthetic routes that lead to bulk polymer (3,4), but lack of appropriate polymer solvents and infusibility of most poly(oxadiazoles) precludes fabrication of films and fibers.



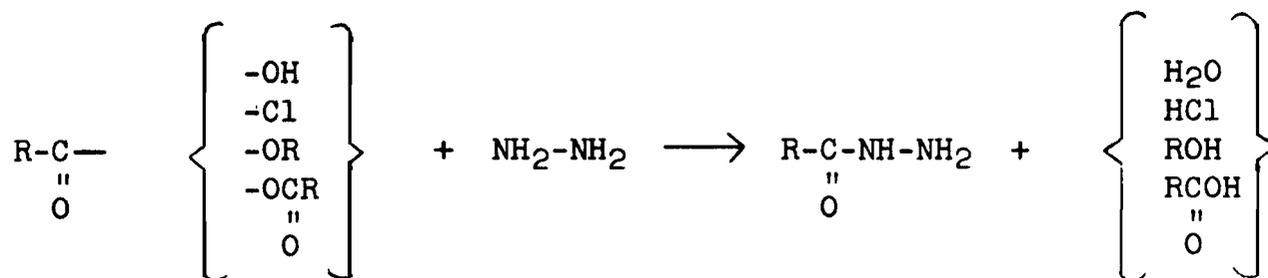
One polyoxadiazole fiber, namely, poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)] (50:50), PODZ-I/T, showed most promising thermal stabilities (2). It is obtained by cyclodehydration of the alternating polyhydrazide derived from terephthaloyl chloride and isophthalic dihydrazide.

This fiber conversion should be quantitative from the chemical standpoint in order to afford the desired high-temperature properties, and it must be carefully controlled from a mechanical standpoint in order to maintain the fiber properties through various intermediate polyhydrazide-polyoxadiazole stages. A combination of both requirements is even more difficult to meet on a practical scale since temperatures of at least 280°C. are required for a reasonable rate of the chemical reaction, and since sustained temperatures above 320° would degrade still unconverted polyhydrazide links. Finally, possible side reactions, as noticed by Stolle (5a) and Pellizzare (5c), for the thermal cyclodehydration of dibenzoylhydrazine may also prove to be detrimental in attaining polyoxadiazole fibers with optimum fiber properties and optimum thermal stabilities.

It was expected that reproducibility of this unique polymer reaction (in fiber form) would be difficult and would require research under accurately defined reaction conditions. This report summarizes our present knowledge of polyoxadiazoles, polyhydrazides, polyhydrazide chelates, and of model compounds.

Polyhydrazides

For a long time it has been recognized that the reaction between carboxylic acids, esters, anhydrides, or carbonyl chlorides with hydrazine affords carboxylic hydrazides.

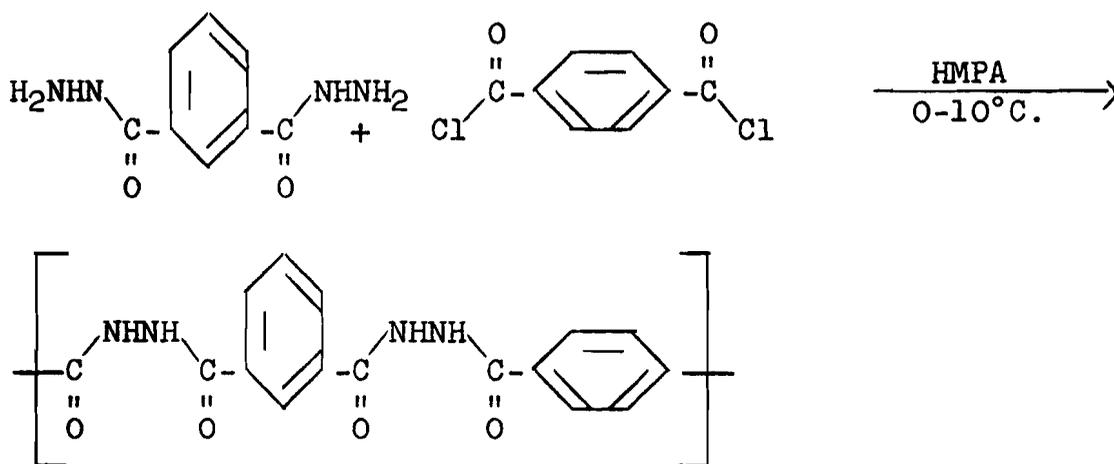


The reaction of esters with hydrazine or 85-100% hydrazine hydrate is regarded to be quantitative while the other acid derivatives frequently lead to undesirable mixtures of mono-, di-, tri-, and tetraacyl hydrazines. Diesters, when treated with hydrazine hydrate in alcohol, yield nearly quantitatively the desired dihydrazides which are polymer intermediates (8).

1. Preparation of Bulk Polymer

Low temperature polymerization of equimolar amounts of dihydrazide and carbonyl chloride in amide solvents, such as hexamethylphosphoramide (HMPA), N-methylpyrrolidone (NMP), containing 2-5% lithium chloride was found to be the only preparative method (2,6) that consistently yielded high molecular weight polyhydrazides. Preparative methods (7) found in the patent literature did not yield high molecular weight polyhydrazides which could be fabricated into films and fiber.

Thus, OIOT was prepared from equimolar amounts of isophthalic dihydrazide and terephthaloyl chloride in amide solvents, such as hexamethylphosphoramide (HMPA) or N-methylpyrrolidone (NMP). The reaction proceeds at room temperature (or below) and high molecular weight polymer is attained after 4-16 hours of reaction. The polymer, precipitated with water or methanol, has inherent viscosities (η_{inh}) in dimethyl sulfoxide (DMSO) ranging from 0.5-1.50. The preferred preparative solvent is hexamethylphosphoramide.



Since the resulting polyhydrazides often contain small amounts of ash after combustion, it is advisable to carry out the polymerization in polyethylene flasks and with "Teflon"* stirrers. Further washings with distilled and deionized water are in order to prevent facile chelation of hydrazide links with metal ions.

2. Fabrication of Fibers

Two spinning solvents have been used during this study, dimethyl sulfoxide (DMSO) and dimethyl acetamide (DMAc). The latter solvent allows spinning at lower temperatures, hence provides for milder operating conditions.

One batch of OIOT, $\eta_{inh} = 1.03$ (DMSO), was spun from DMSO (25% solids) and drawn 2X at 10 lbs. of steam, dried and redrawn 1.2X at 310°C. over a hot plate. As-spun yarn (T/E/M₁ = 1.8/117/41) was thus oriented (T/E/M₁ = 3.2/27/61) and finally crystallized (T/E/M₁ = 5.2/24/80). A one-year old sample ($\eta_{inh} = 1.6$) of an oriented yarn (T/E/M₁ = 3.5/38/69) would not allow redrawing and was not further investigated. A further batch, prepared in HMPA and spun from DMSO has been more thoroughly evaluated with respect to fiber properties, which are given in Table I.

Alternatively, DMAc may be used as spinning solvent. Results are also contained in Table I. Use of this solvent allows higher draw ratios, and lower spinning temperatures. When preparing DMAc solutions, excessive heating should be avoided since the polymer precipitates at about 120-130°C.

A number of spins were carried out with DMAc containing 2 or 5% LiCl as solvent. The advantage of this modified solvent is that solution commences more smoothly than in straight DMAc and that yarn with high moduli can be obtained. Results are listed in Table II.

Spinning of OIOT from DMSO customarily affords fiber with a dark yellow color, particularly after redrawing at 300°C. This may be attributable to the onset of conversion or to degradation. Even yarn obtained from DMAc was slightly yellow colored. To avoid this discoloration altogether, it was necessary to carry out the spinning operation with DMSO under nitrogen. Perfectly white yarn resulted after drawing at 100°C. and redrawing at 320°C.

*Trademark for Du Pont's TFE-fluorocarbon resin.

TABLE I
POLYHYDRAZIDE (OIOT) FIBER PROPERTIES

| | | |
|---|---------------|---------------|
| Spinning solvent/additives | DMSO/none | DMAc/none |
| % Solids | 25 | 25 |
| Spinning & column temp. °C. | 125/214 | 105/220 |
| Draw ratio/°C. | 2X; 10# steam | 2X; 10# steam |
| Redrawn/°C. | 1.2X; 310 | 2.0X/310 |
| Ten. (T), % Elong. (E), Mod. (M ₁) | 4.9/24/94 | 3.8/5.6/122 |
| Denier | 5.4 | 2.4 |
| Loop T/E/M ₁ | 1.9/6.3 | 0.4/0.5/85 |
| Denier | 4.7 | 2.3 |
| Knot T/E/M ₁ | 2.9/10/56 | 1.5/1.9/87 |
| Denier | 7.4 | 2.1 |
| Elevated T/E/M ₁ (90°C. air) | - | 6.0/11/110 |
| Denier | - | 2.1 |
| Work Recovery, WR, 3% [RT/RT wet/90°C. wet] | 34/33/36 | 39/23/24 |
| Work Recovery WR, 5% | 27/35/39 | 42/29/31 |
| Ten. Recovery TR, 3% [RT/RT wet/90°C. wet] | 65/64/78 | 68/45/47 |
| Tensile Recovery TR, 5% | 55/62/67 | 71/56/58 |
| Wash-Set Recovery Angle | 140 | 145 |
| X-ray crystal. (amt./perf.) | med./med. | low/low |
| X-ray orient. (degrees) | good | med. |
| Fiber Stick Temperature, FST, °C. | - | 305° |
| Melting Point °C. | - | >370° |

TABLE II

POLYHYDRAZIDE (OIOT) FIBER PROPERTIES

| Spinning solvent/additives | DMAc/5% LiCl | | DMAc/2% LiCl | |
|---|--------------|------------|------------------|-------------|
| % Solids | 20 | | 21 | |
| Spinning & column temp. °C. | 120/215 | | 120/215 | |
| Draw Ratio/°C. | as-spun | | 2.25X; 10# steam | |
| Redrawn/°C. | - | 1.6X; 320 | - | 1.6X; 320 |
| Ten. (T), % Elong. (E) | | | | |
| Mod. (M ₁) | 1.3/89/44 | 6.0/8/151 | 3.7/8.6/112 | 4.7/4.4/169 |
| Denier | 8.8 | 2.6 | 3.7 | 2.6 |
| Loop T/E/M ₁ | 1.1/78/35 | 0.3/0.5/59 | 0.7/0.7/64 | 0.3/0.6/50 |
| Denier | 9.8 | 2.5 | 3.5 | 2.6 |
| Knot T/E/M ₁ | 1.3/96/16 | 0.6/1.4/50 | 1.1/3.0/45 | 0.5/4.2/94 |
| Denier | 9.7 | 2.5 | 4.6 | 2.4 |
| Elevated T/E/M ₁ (90°C. air) | 1.8/90/38 | 4.9/13/78 | - | - |
| Denier | 8.7 | 3.8 | - | - |
| Work Recovery, WR, 3% | | | | |
| [RT/RT wet/90°C. wet] | 32/11/6 | 41/36/33 | 40/25/21 | 49/38/38 |
| Work Recovery, WR, 5% | 17/8/4 | 43/41/43 | 36/30/22 | 50/49/50 |
| Tensile Recovery, TR, 3% | | | | |
| [RT/RT wet/90°C. wet] | 66/29/17 | 72/67/50 | 73/51/39 | 78/68/64 |
| Tensile Recovery, TR, 5% | 44/20/12 | 72/72/72 | 69/62/44 | 78/77/76 |
| Wash-Set Recovery Angle | 85 | 185 | 105 | 195 |
| X-Ray Crystal. (amt./perf.) | trace | med./med. | low/low | med./med. |
| X-Ray Orientation | - | 40° (med.) | 56° | 40° (med.) |
| Density (fiber) | - | 1.4536 | - | 1.4529 |
| Fiber Stick Temperature, FST, °C. | - | - | - | - |

To even further broaden the scope of attainable OIOT properties prior to conversion, it was of interest to study the effects of heat setting on tenacity and x-ray crystallinity. The results are tabulated in Table III.

TABLE III
HEAT SETTING OF OIOT YARNS

| <u>Fiber (Spun from DMAc/5% LiCl)</u> | <u>T/E/M₁ Before</u> | <u>T/E/M₁ After</u> |
|---------------------------------------|---------------------------------|--------------------------------|
| 1) Drawn (oriented) | 3.2/27/61 | 3.7/19/85 |
| 2) Redrawn (oriented and crystalline) | 6.0/8/151 | 6.8/10/147 |

This treatment enhanced crystallinity and tenacity of the two fibers to high levels.

It may be seen that proper choice of spinning, drawing and heat setting conditions [Tables I to III] makes it possible to obtain OIOT with tenacities ranging from 3 to 7 gpd., with elongations ranging from 4-27% and with moduli ranging from 60-169.

This study, therefore, affords a great variety of yarns with various combinations of properties, each of which may be critical in attaining optimum properties of PODZ-I/T fiber after conversion.

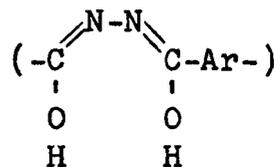
3. Stabilization of Polyhydrazide Enolates

Polyhydrazides, in basic solution, exhibit an intensely yellow color (presumably due to conjugation in the enol form) as has been discussed already (6). When films or fibers are exposed to tertiary amines, similar color changes occur. As the amine evaporates (on drying or prolonged exposure to air) the color disappears and the sample becomes colorless. "Dabco"*, a tert. amine, was added to polyhydrazide films and fibers, accomplishing a permanent and irreversible color change to yellow. Fibers in this form should be studied to see if the enol form is easier converted into PODZ than the normal structure.

*Trademark for Houdry Processing Corp.'s catalyst.



"Dabco", Diazabicyclooctane



Enol Form

Chelating Properties of Polyhydrazides

Polyhydrazides, in analogy to simple monomeric hydrazides (11), readily undergo chelation with a host of inorganic salts. When it was noticed that even carefully prepared polyhydrazides contained 0.2 to 2.0% ash after combustion, it was apparent that such salts might be detrimental and prevent complete cyclodehydration into polyoxadiazoles. A study designed to eliminate this trace chelation simultaneously led to experiments described here, which might possibly open up a new area of investigation, if utility for OIOT/chelate films or fibers can be found.

1. Preparation of Chelate Films

Initial chelating studies of OIOT polymer were carried out with film because of greater ease of handling. A OIOT/HgCl₂ chelate film which was prepared was completely transparent, colorless and could be dried in vacuum at 80° over the week-end without change of appearance. When heated at 80° in an air atmosphere, this film turned brown. The original HgCl₂/OIOT chelate film was placed in a Fade-Ometer and did not show the usual color break to yellow expected from ultraviolet ageing. Instead, the exposed side of the film turned dark gray and became very brittle after 150 hours of exposure.

Other metal salt chelate polymers of OIOT were prepared but films could not be cast, owing to their insolubility in various solvents.

Chelation of OIOT films occurred, however, readily on aluminum plates or on brass plates. The film cast on brass adhered well for 4 hours in boiling water. Discoloration of the OIOT

occurred simultaneously which is indicative of a picking up of metal ions. A film of OIOT cast on aluminum could not be removed by boiling the film with the aluminum plate in hot water. It was still firmly attached to the aluminum base after boiling the sample for 3-4 days in water. This interesting adhesion is possibly due to a polymer-to-metal self-bonding.

2. Fabrication of Chelate Fibers

Such chelate properties of films and fibers may lead to interesting applications in the field of high temperature materials. Chelated OIOT fibers might possibly afford a new class of high temperature resistant fibers. Such fibers which carry metal salts could be further treated by reducing the metal salts to Me^0 .

OIOT fibers were, therefore, chelated in a DMF bath containing about 10-15% of metal salt. In some cases, a small amount of tertiary amine, e.g., N,N'-dimethyl aniline, was added to make the salt bath more basic. This generally resulted in less extensive chelation.

When oriented (drawn) fiber ($T/E/M_1 = 3.2/27/61$) was used, the fiber properties, after chelation, as shown in Table IV appeared to correspond to those characteristic of unoriented (as-spun) OIOT fiber ($T/E/M_1 = 1.8/118/41$) with no indication of x-ray orientation.

Ions such as cobalt, chromium, silver, tin, and copper have been used in this exploratory investigation. A special case, however, seemed to result when $AgNO_3$ was used as metal salt. In DMF, chelation results in a straw colored OIOT/ $AgNO_3$ fiber. When this fiber is run through a subsequent N,N'-dimethyl aniline bath, the tert. amine, surprisingly, will reduce $AgNO_3$ on OIOT to give $Ag^0/OIOT$, with fibers having a silvery, grey, or black appearance depending upon conditions, such as temperature, exposure time and concentration of solutions.

The change in yarn properties and the reversion of oriented to amorphous yarn (Table IV) was paralleled by a similar property change when crystalline and oriented (drawn and redrawn) OIOT fiber was chelated (Table V, 27 and 28). The chelated yarn,

TABLE IV

POLYHYDRAZIDE/CHELATE FIBER PROPERTIES

| <u>Sample</u> | <u>OIOT Fiber</u> | | <u>Metal Salt</u> → | <u>Chelate Fiber</u> |
|---------------|--|-----------------------------|-----------------------------|---------------------------------------|
| | <u>DMF Bath (I)</u> | <u>Color of Dry Yarn</u> | <u>T/E/M₁***</u> | <u>Crystallinity of Yarn/Additive</u> |
| 3 | 13.9% CoCl ₂ | Dk. green | 0.5/16/22 | Amorphous/ Amorphous |
| 4 | 13.2% CoCl ₂ + 4.7% DMA* | Lemon | 1.1/96/38 | Amorphous/ Crystalline |
| 6 | 16.7% AgNO ₃ | Straw | 0.7/5/32 | Amorphous/ Cryst. (random) |
| 7-I | 9.7% AgNO ₃ | Black [Ag ^o] | 0.9/65/34 | Amorphous/ Crystalline |
| 7-II | 9.7% AgNO ₃ | Dk. grey [Ag ^o] | 1.3/99/36 | Amorphous/ Crystalline |
| 9 | 10.6% AgNO ₃ ** | Silvery [Ag ^o] | 1.3/101/36 | Amorphous/ Trace Cryst. |
| 10 | 9.7% CrCl ₃ | Olive | 1.2/82/37 | Amorphous/ Amorphous |
| 11 | 9.2% CrCl ₃ + 4.9% DMA* | Green | 1.2/90/38 | Amorphous/ Trace Cryst. |

* N,N'-Dimethylaniline

** Short contact time

*** Reference: T/E/M₁ = 1.8/118/41, undrawn, amorphous OIOT

in this instance, had lost its original crystallinity, and appeared to correspond to oriented (drawn) OIOT fiber (T/E/M₁ = 3.2/27/61) with respect to fiber properties.

TABLE V
HIGH TENACITY CHELATE FIBERS

| | <u>CoCl₂-Bath</u> | <u>OIOT Fiber</u> <u>T/E/M₁</u> | <u>Chelate Fiber</u> <u>T/E/M₁</u> | <u>Crystallinity</u> <u>of Additive</u> | <u>Color</u> <u>of Fiber</u> |
|----|------------------------------|---|--|--|---------------------------------|
| 27 | DMF | 5.2/24/80 | 2.3/15/55 | + | Green |
| 28 | DMF + DMA* | 5.2/24/80 | 3.4/27/59 | trace | Olive |

*DMA, N,N'-dimethyl aniline

These exploratory studies were not further continued since the resulting chelated fibers had the same polymer melt temperature as the original OIOT fibers (>375°C.). Chelation, in this case, did therefore not enhance the melting point of the initial polymer.

3. Reaction with Alkoxides

During the course of investigations on polyhydrazides, it was noticed that OIOT gave highly viscous and partly swellable solutions when treated with alkoxy derivatives such as sodium methoxide or aluminum isopropoxide. When a 1% solution of OIOT in dimethyl sulfoxide containing aluminum isopropoxide was warmed to 70°, an unusual viscous gel-like mass resulted. No change in appearance resulted on standing for over 2 days at room temperature. Evaporation on a steam bath resulted in a continuous film which was yellow in appearance and did not melt below 400°C. After drying in a drying oven overnight, it was analyzed and shown to contain 30% ash.

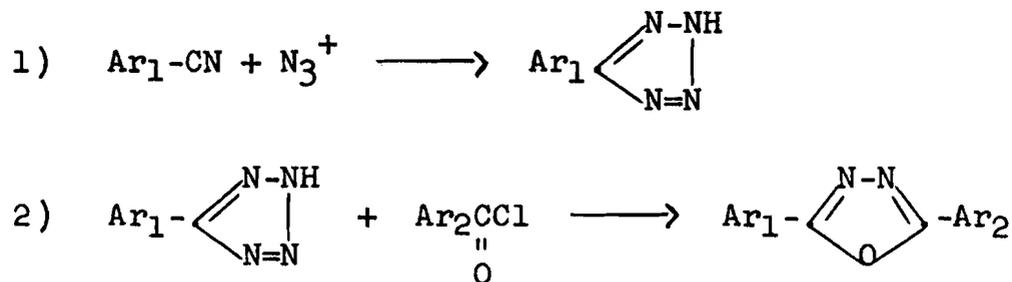
A similarly viscous solution resulted by treating a 1% solution of polyhydrazide in dimethyl sulfoxide with sodium methoxide. However, in this instance, a brown solid precipitated. It was washed with ethanol and dried. Microanalytical analysis showed it to contain 20.2% ash.

A structural analysis of both metal alkoxide derivatives of OIOT has not yet been successful.

Poly(1,3,4-oxadiazoles) and Fiber

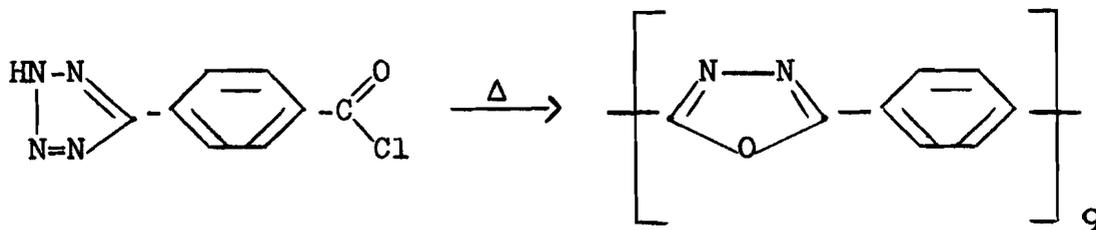
1. Synthetic Routes to Bulk Polymer

Huisgen and coworkers have reported extensively (12,13) on the reaction of tetrazoles with acid chlorides. It gives 1,3,4-oxadiazoles. He successfully



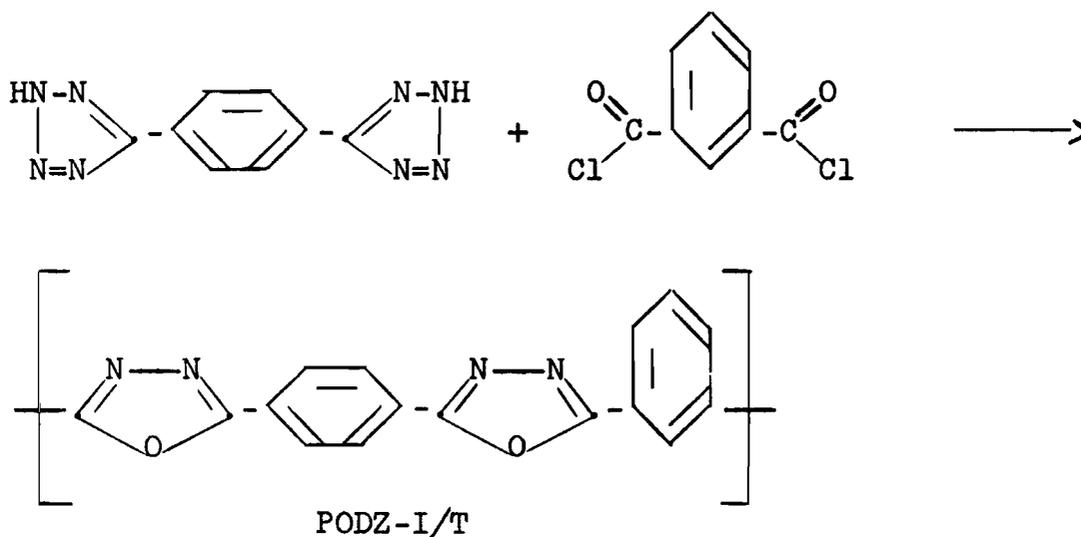
made oligocyclic oxadiazoles, including one consisting of a nine-membered ring system with alternating *p*-phenylene rings and oxadiazole rings. This reaction has been used to prepare a number of model compounds for PODZ-I/T as described in a later section.

Huisgen and coworkers attempted preparation of polyoxadiazoles (13) by the following variation of the initially explored reaction.



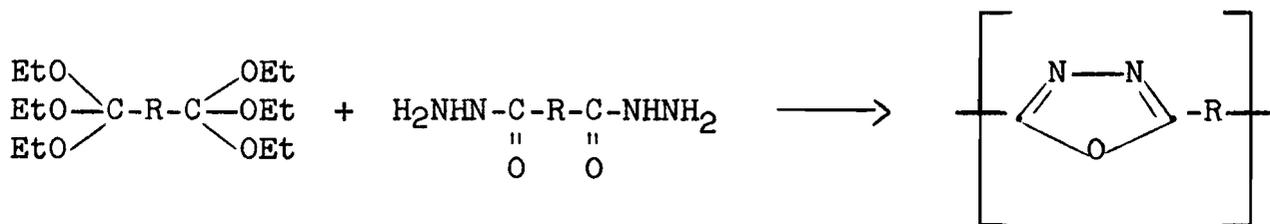
The resulting product resembled the 9-membered oligooxadia-
 diazole but could not be recrystallized. This polymerization was,
 therefore, not further pursued.

Abshire and Marvel (4) have reported the preparation of
 several aromatic polyoxadiazoles from ditetrazoles and diacid
 chlorides in inert solvents. This type of preparation was repeated



using amide solvents such as hexamethylphosphoramide in the hope
 that higher molecular weight polymer would result. A few experi-
 ments using this route yielded polyoxadiazole with viscosities
 lower than 0.3 (in sulfuric acid).

Another method for preparing polyoxadiazoles was briefly
 studied. It involves reaction of bis-ortho esters and dihydrazides
 in accordance with the monomeric model reaction reported by
 Ainsworth (14).

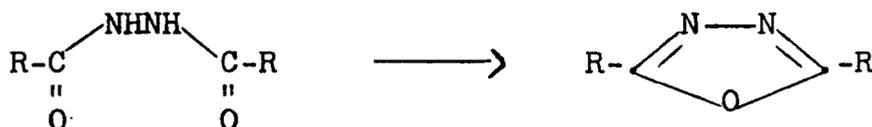


The preparation of bis-ortho esters can be carried out by treating diiminoesters with absolute alkanols according to monomeric model reactions (15). Three diiminoester hydrochlorides (16,17) have been prepared. They are: dimethyl iminosuccinate, diethyl iminosuccinate, and diethyl iminoisophthalate. The diethyl ortho-succinate has been prepared with great difficulty in reasonably pure form and reacted with isophthalic dihydrazide. No high polymer resulted.

2. Polyoxadiazole Bulk Polymer from OIOT

The inaccessibility of high molecular weight polyoxadiazoles by above routes, the lack of solvents for such polymers and the excellent synthesis of high molecular weight polyhydrazides discovered by Frazer (2) made OIOT and its fibers the potential intermediate for PODZ-I/T.

The cyclodehydration of monomeric model reactions is carried out at elevated temperatures (thermal conversion) or in solution with chlorosulfonic acid, sulfonyl chloride, toluene sulfonic acid, tosyl chloride, organic anhydrides, and sulfuric acid.



Hence, several types of conversions were studied and are described in the following paragraphs. Thermal conversion of polyhydrazide fibers is described in a later chapter.

Conversion of polyhydrazide bulk polymer at elevated temperatures was studied by heating a finely ground (40 mesh) sample of OIOT for 48 hrs. at 283° (0.4 mm.). The resulting PODZ-I/T bulk polymer analyzed correctly for polyoxadiazole, as judged by carbon, hydrogen, and oxygen analyses.

Six samples of polyhydrazide fiber were heated in a steel bomb with steam at 254°C. (inside temperature) and 585 lbs. pressure. Steam at this temperature did not effect cyclization and the fiber degraded badly.

Thermal conversions of polyhydrazides in solution were also attempted in hexamethylphosphoramide at 200°C. by heating a 10% solution for 24 hrs. under nitrogen. During the course of the reaction, solid polymer precipitated which analyzed for polyoxadiazole with a 90% degree of conversion as judged by carbon, hydrogen, and oxygen analyses.

Mild dehydrating agents in solution, such as N,N-dicyclohexylcarbodiimide, trichloroacetonitrile, and tetrachlorodifluoroacetone were without effect. No change in oxygen analysis was obtained when samples were withdrawn over a period of four days. Strong dehydrating agents such as acids or bases degraded the polyhydrazide partially or totally while conversion occurred.

Klingsberg (19) had reported that symmetrical aromatic dihydrazides could be converted into 2,5-disubstituted 1,3,4-oxadiazoles by the reaction of phosphoazo-derivatives of cyclohexylamine [$C_6H_{11}N=PNHC_6H_{11}$]. Thus, a 2.5% solution of OIOT in a mixture of dimethyl sulfoxide and o-dichlorobenzene was treated with the phosphoazo-derivative of cyclohexylamine and of aniline. After heating on a steam bath a yellow color appeared in each case; both solutions were precipitated with acetone, washed and dried. The analytical results showed that high molecular weight polyhydrazide was recovered unchanged in each case. Hence, this method is not suitable for conversion of polyhydrazides into polyoxadiazoles.

The polymer from the above solution and bulk conversions was not soluble in conventional polymer solvents including trifluoroacetic acid, hence could not be fabricated into films and fibers. For this reason, it was necessary to convert polyhydrazide fibers by thermal conversion into polyoxadiazole fibers.

3. Conversion of Fiber in Vacuum

This study was designed to furnish information about the dehydration-cyclization mechanism in conjunction with fiber properties. The goal was to find optimum conversion conditions. Such conversions were carried out with polyhydrazide (OIOT) fibers at 222°, 242°, 265° and 283°C., whereby the fiber samples were wound around small perforated metal bobbins. These bobbins were placed in a tube which was evacuated and then heated in solvent vapors corresponding to above boiling points. A sample of bulk polymer (40 mesh) was likewise converted at 283° (vac.).

For fiber conversions, OIOT yarn (T/E/M₁ = 5/24/80) was used. Samples of individual runs, comprising 3-6 bobbins, were periodically withdrawn in order to follow the conversion with time.

The withdrawn samples were analyzed (T/E/M₁, %O, IR) and showed the following results which are typical for this type of conversion.

No conversion occurred at 222° within 72 hrs. as evidenced by virtually unchanged oxygen analyses. However, the yarn properties changed from T/E = 5.2/20 to 2.6/9.

At 242° there was a slow conversion, estimated by oxygen analysis to be 50% in about 48 hrs. The yarn properties gradually changed from T/E = 5.2/20 to 1.9/5.

At 265° the yarn conversion proceeded with noticeable rate but within 30 hrs. the yarn properties had changed from T/E = 5.2/20 to 0.7/0.6. After 72 hrs. at 283° the same result (T/E = 1.0/1.0) was observed with nearly complete conversion to PODZ.

Conversion studies in vacuum were cumbersome and gave inhomogeneous fiber samples after conversion.

4. Conversion of Fiber in Solvent Vapors

It was believed that conversion in solvent vapors at temperatures ranging from 265-290°C. would provide better conversion conditions because of better heat transfer. Thus, a number of

conversions were carried out in refluxing diphenylmethane, 265°C., and diphenylethane, 283°C. Because of the known chelating tendency of polyhydrazides, the conversion of skeins of OIOT was carried out on "Teflon" bars, thus avoiding glass rods or metal bobbins. A larger sample of OIOT, after conversion at 265°, was used for thermal stability studies which provided a second heating cycle. The initial polyoxadiazole properties are given in Table VI.

TABLE VI
POLY-1,3,4-OXADIAZOLE (PODZ-I/T) FIBER PROPERTIES

| | |
|--|-------------|
| Ten. (T), % Elong. (E), Mod. (M ₁) | 2.6/3.1/124 |
| Denier | 3.0 |
| Loop (Tenacity/Elongation) | 1.8/2.8 |
| Denier | 3.9 |
| Knot (Tenacity/Elongation/Modulus) | 2.3/2.8/79 |
| Denier | 3.0 |
| X-ray Crystallinity (amount/perfection) | low/low |
| X-ray Orientation (degrees) | 31° (outer) |
| | 38° |
| Oxygen Analysis (Theor. 11.10%) | 12.1% |

Throughout the investigation it was noticed that micro-analytical data are not as reliable as would be desirable. Incomplete combustion or actual presence of ash of unknown origin would require a detailed analytical study.

When microanalytical results begin to indicate completion of conversion (with consistently high oxygen values) data such as those shown in Table VII are characteristic for initial polyoxadiazole fiber properties. Further heating of such initial polyoxadiazole fibers at 280° or, more efficiently, at 300-400°C. slightly changes initial properties, T/E/M₁ = 2.6/3.1/124 to final properties, T/E/M₁ = 1.0/1.0/109 which then no longer change on continued heating, but still show high oxygen values and occasionally ash of undetermined origin.

5. Conversion of Fibers in Nitrogen

In order to obtain large samples and to circumvent the cumbersome procedure of exposing fibers to solvent vapors (whereby solvents quite often show signs of degradation), it was decided to use muffle furnaces (with N₂ leads) for conversion of OIOT fibers at 280°C.

Hence, a great variety of polyhydrazides was converted. Small or large samples were placed in furnaces and allowed to react for periods usually in excess of 2 days, until microanalytical data showed constant values as sign of complete conversion.

Only a few representative samples, as shown in Table VII, indicate that conversion proceeds to the initial polyoxadiazole fiber.

TABLE VII
INITIAL POLYOXADIAZOLE PROPERTIES

| | <u>T/E/M₁/Den.</u> | <u>0%</u> | <u>Note</u> |
|------|-------------------------------|-----------|--|
| 29 | 2.6/3.1/124 | 12.10 | Converted in boiling diphenylmethane 273°C. |
| 49-1 | 2.8/3.6/104/3.9 | 13.38 | Converted in nitrogen at 280°C. (furnace). |
| 49-3 | 2.4/6.6/102/3.5 | 12.40 | Converted in N ₂ at 280°C. |
| 49-4 | 3.0/3.2/149/2.8 | 11.89 | Cyclized in furnace (N ₂ , 280°C.). Sample contained ash. |
| 70-2 | 3.2/7.4/140/3.5 | 12.20 | Courtesy W. Sweeny and C. Smullen. Sample contained ash. |

Further heating at 300-400°C., in analogy with above-mentioned cases, produces final polyoxadiazole properties (T/E/M₁ ~ 1.0/1.0/90) as will be discussed in conjunction with thermostability studies in a later section.

Thus, conversions in muffle furnaces at 280°C. represent the most suitable means of converting polyhydrazide fibers into polyoxadiazole fibers. While some improvements can be visualized, such as better conversion control with standardized analytical methods, there appears to be much reason to believe that these properties are representative of polyoxadiazole fibers derived from all-aromatic polyhydrazide fibers. Since PODZ-I/T effectively represents a polyphenyl analogue, its fibers are expected to possess high chain stiffness, as expressed by low elongations and high moduli.

Thermal Stabilities of Polymers

1. Fiber Properties at Elevated Temperatures

Polyoxadiazole fibers, PODZ-I/T were investigated carefully by a study concerned with the thermal stability with respect to fiber properties.

A number of PODZ-I/T fiber samples, on perforated metal bobbins, were placed into muffle furnaces, the temperature of which was accurately controlled by Pyrovans. By this procedure, samples - in air or in nitrogen atmosphere - were kept at constant temperatures between 300° and 450°C. for prolonged periods of time. At given time intervals, samples were withdrawn and fibers were tested (T/E/M₁/den./%O).

The results of this study are contained in Table VIII. Fiber samples of PODZ-I/T, with initial fiber properties after boil-off such as T/E/M₁/den. = 2.6/3.1/124/3.0 were heated and attained final PODZ-I/T fiber properties [T/E/M₁/den. ~ 1.1/1.1/90] after a certain time at temperatures between 300° and 400°C. (in air or nitrogen).

The PODZ-I/T fibers disintegrated at temperatures between 400° and 450°C.

2. Final Fiber Properties after HT-Exposure

Inspection of Table VIII shows that the initial fiber PODZ-I/T properties change when samples are exposed to temperatures above 300°C. Generally retention of about 50% of initial properties is observed. In order to assess this change in terms of structural changes it was of interest to obtain oxygen analyses of those PODZ-I/T samples that had sustained longest exposure times at 300°C, 375°C. and at 400°C. (Table IX).

TABLE IX
FINAL PODZ-I/T FIBER PROPERTIES

| Sample | Fiber Treatment | | | T/E/M ₁ /Den. | % Oxygen |
|--------|-----------------|-------------|----------------|--------------------------|----------|
| | Temp., °C. | Time (hrs.) | Medium | | |
| 39-4 | 300 | 168 | air | 1.2/1.2/112/2.7 | 11.80 |
| 54-4 | 375 | 48 | N ₂ | 1.3/1.1/92/3.0 | 11.40 |
| 48-4 | 400 | 48 | air | 1.6/1.8/136/3.6 | 11.64 |

It is conceivable that the change in fiber properties is partly due to a final completion of the cyclodehydration reaction between 300 and 400°C. This follows from the change of the average oxygen value from 12.15 (Table VII) to 11.61 (Table IX) as compared to a theoretical value of 11.10. Such high final values for oxygen which have also been observed in earlier studies remain, however, unexplained.

Thus, it appears that the initial PODZ-I/T fiber (Table VIII) gradually changes into a thermally more stable but stiffer structure. The final polyoxadiazole structure has lower elongations and higher moduli.

Summary

1. Poly(1,3,4-oxadiazole)Fiber Properties

Poly(1,3,4-oxadiazole) fiber, PODZ-I/T, with high thermal stabilities has been prepared by cyclodehydration of polyhydrazide fiber, OIOT.

TABLE VIII

THERMAL STABILITY OF PODZ-I/T FIBER (300-400°C.)

Initial Fiber Properties T/E/M₁/den. = 2.6/3.1/124/3.0

| <u>Hours</u> | <u>300°C., Air (b.o.)</u> | | <u>300°C., Nitrogen (b.o.)</u> | |
|--------------|-------------------------------|-----------------------------|--------------------------------|--------------------------------|
| | <u>T/E/M₁/Den.</u> | <u>%T/%E/%M₁</u> | <u>T/E/M₁/Den.</u> | <u>%T/%E/%M₁</u> |
| 2 | 2.5/4.8/102/3.2 | 96.5/>100/50.0 | 2 2.7/4.2/104/3.3 | >100/>100/84.0 |
| 4 | -- | -- | 4 2.8/3.6/91/2.8 | >100/>100/74.5 |
| 6 | 2.6/3.2/102/3.0 | 100.0/>100/81.2 | 6 2.3/2.2/104/2.7 | 92.5/71.5/84.0 |
| 24 | 1.3/1.4/114/2.9 | 50.0/45.2/90.0 | 24 2.3/2.4/107/2.9 | 92.5/77.5/86.5 |
| 52 | 1.1/1.1/93/3.2 | 42.4/35.2/75.0 | 150 1.7/1.6/87/2.9 | 65.4/51.6/70.0 |
| 72 | | | <u>325°C., Nitrogen (b.o.)</u> | |
| 96 | 1.2/1.2/87/2.7 | 46.2/38.1/70.0 | 2 2.6/2.7/145/2.5 | 100.0/87.1/>100 |
| 120 | 1.7/1.6/87/3.0 | 65.4/51.6/70.0 | 4 2.8/3.9/139/2.9 | >100/>100/>100 |
| 144 | 2.0/1.8/105/3.1 | 76.9/58.1/84.7 | 6 2.4/2.0/136/2.9 | 92.3/64.5/>100 |
| 168* | 1.2/1.2/112/2.7 | 46.2/38.7/90.3 | 24 2.0/1.8/149/2.8 | 76.9/58.1/>100 |
| | | | 48 | Not tested -- |
| | <u>350°C., Air (b.o.)</u> | | <u>350°C., Nitrogen (b.o.)</u> | |
| | | | 1 | 2.8/3.9/102/2.8 >100/>100/82.5 |
| | | | 2 | 2.4/2.8/101/3.2 92.5/90.5/81.5 |
| | | | 6 | 2.7/3.4/118/2.8 >100/>100/69.0 |
| | | | 12 | 1.9/1.9/105/2.9 73.2/61.2/84.5 |

TABLE VIII (CONT'D.)

| <u>Hours</u> | <u>350°C., Air (b.o.)</u> | | <u>350°C., Nitrogen (b.o.)</u> | |
|--------------|-----------------------------------|-----------------------------|-----------------------------------|--------------------------------|
| | <u>T/E/M₁/Den.</u> | <u>%T/%E/%M₁</u> | <u>T/E/M₁/Den.</u> | <u>%T/%E/%M₁</u> |
| 24 | 2.1/2.2/103/2.7 | 80.8/71.0/83.1 | 24 | 2.3/2.2/132/2.9 88.5/71.0/>100 |
| 48 | 2.1/2.2/113/2.9 | 80.8/67.7/91.1 | 48 | 2.5/2.6/128/2.8 96.2/83.9/>100 |
| 72 | 1.7/1.6/110/3.0 | 65.4/51.6/88.7 | 72 | 1.7/1.4/164/2.9 65.4/45.2/>100 |
| 96* | 1.1/1.1/102/3.3 | 42.3/32.3/82.3 | 96* | 1.2/1.2/83/2.7 46.2/38.7/66.9 |
| | <u>375°C., Air (b.o.)</u> | | <u>375°C., Nitrogen (b.o.)</u> | |
| 2 | 1.8/1.8/81/2.9 | 69.2/58.1/65.3 | 2 | 1.5/1.3/118/2.9 57.7/42.9/95.2 |
| 4 | 1.9/2.2/72/2.8 | 73.1/71.0/58.1 | | |
| 6 | 1.7/1.7/66/2.7 | 65.4/54.89/53.2 | 6 | 1.2/1.2/97/3.3 46.2/38.7/78.2 |
| | | | 24 | 1.6/1.4/112/2.7 61.5/45.2/90.3 |
| 48* | 1.6/1.3/100/2.7 | 61.5/41.9/80.6 | 48* | 1.3/1.1/92/3.0 50.0/35.5/74.2 |
| | <u>400°C., Air (b.o.)</u> | | <u>400°C., Nitrogen (b.o.)</u> | |
| 1 | 2.0/2.3/77/2.6 | 76.9/74.2/62.1 | | |
| 2 | 2.4/2.7/64/3.1 | 92.3/87.1/51.6 | | |
| 4 | 2.1/1.9/81/2.5 | 80.8/61.3/65.3 | 4 | 1.7/1.8/100/3.0 65.8/58.1/80.6 |
| 24 | 2.5/2.6/67/2.6 | 96.2/83.9/54.0 | 6 | 1.6/1.5/89/2.9 59.6/48.4/71.8 |
| 40* | 1.8/1.8/84/2.8 | 69.2/58.1/67.7 | 24* | 1.3/1.2/102/2.8 50.4/38.7/82.3 |
| | <u>450°C., Air</u> | | <u>450°C., Nitrogen</u> | |
| | Samples partly burnt and degraded | | Samples partly burnt and degraded | |

*Longer exposure times produced fiber which was too brittle to test.

OIOT fiber for this study was prepared with various levels of properties and with various degrees of crystallinity. In general, tenacities (T) ranged from 3 to 7 gpd., elongations ($\%E$) from 10-24% and moduli (M_1) ranged from 80-169.

Optimum conversion of OIOT fiber proceeds at 280°C. in a muffle furnace under positive nitrogen pressure and is completed in 48-72 hrs., as evidenced by analyses.

PODZ-I/T fiber obtained in this manner had the following typical fiber properties: T/E/ M_1 /den. = 2.6/3.1/124/3.1 and was thermally stable when exposed to prolonged periods of time to temperatures of 400°C.

During heat treatment between 300 and 400°C. the initial polyoxadiazole fiber apparently undergoes a structural change and final and reproducible polyoxadiazole fiber properties are: T/E/ M_1 /den. \sim 1.3/1.1/92/3.0.

Chemically, the polyoxadiazole structure was found to degrade severely between 450-500°C.

2. Conclusions

The preparation of poly(1,3,4-oxadiazole) fiber represents a major breakthrough in modern polymer technology. While reactions on polymers are usually not very efficient, poly-(1,3,4-oxadiazoles) readily result by thermal cyclodehydration of polyhydrazides. The reaction goes to completion even in fiber form, and the resulting poly(1,3,4-oxadiazole) fibers have measurable fiber properties even after prolonged exposure to 400°C. in air or nitrogen.

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