SYNTHESIS AND PROPERTIES OF HETEROCYCLIC POLYMERS
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. This hypothesis will be tested by preparation of N-substituted polymers although such substitution appears to introduce increased solubility problems and may render dry-spinning impossible.

Polyhydrazide fibers have been prepared and were converted into polyoxadiazole fibers by thermal cyclodehydration. Good yarn properties and potentially high temperature resistance were observed. Specifically, alt. poly(1,3-/1,4-phenylene hydrazide) (50:50) fiber [T/E/Mi = 5/24/94], alt. poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)] (50:50) fiber [T/E/Mi = 3/3/124] were prepared. The investigation also afforded interesting chelating properties of polyhydrazide fibers and a study of thermal cyclodehydration of model compounds consisting of oligohydrazides and oligooxadiazoles which were prepared for the purpose of studying the reaction mechanism.

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.

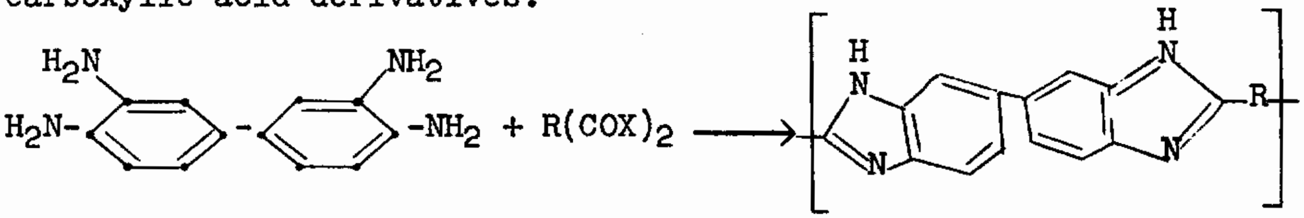
Two such highly aromatic polymeric systems which appear to meet the above specifications - the polybenzimidazoles and the poly(1,3,4-oxadiazoles) - have been the subject of the following research effort.

I. Polybenzimidazoles

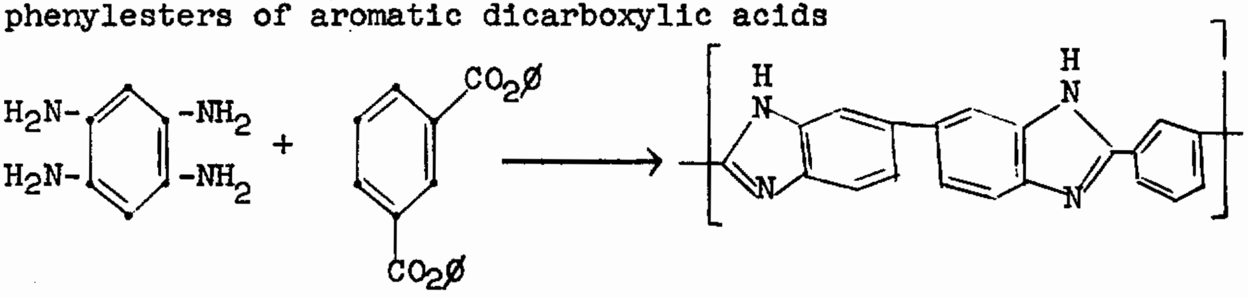
Introduction

Recently, Marvel and Vogel[1] reported the synthesis of a series of polybenzimidazoles having the general property of high thermal stability and therefore of interest for candidacy in satisfying the present demand for super thermal stability in synthetic yarns.

Benzimidazole derivatives are synthesized from o-phenylene diamines and carboxylic acids or derivatives[2]. Extension of this reaction to polymer synthesis was accomplished by Brinker and Robinson[3] by the reaction of bis-o-phenylene diamines and bis-carboxylic acid derivatives:



A modification of this method to produce polybenzimidazoles containing recurring aromatic units was developed by Marvel and Vogel[1] through the melt polymerization of aromatic tetraamines and diphenylesters of aromatic dicarboxylic acids



The work herein reported is concerned with the preparation of poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole, spinning of this polymer from the solvents dimethylsulfoxide and dimethylacetamide, and the physical properties of yarns so obtained. Further, attempts to prepare the polybenzimidazole based on 3,3',4,4'-tetraaminodiphenylsulfone and isophthalic acid will be reported.

Discussion

Benzimidazoles are generally high melting crystalline solids possessing both acidic and basic characteristics. They are quite resistant to acids, bases, and oxidizing agents[4]. The tautomeric nature of benzimidazole is a well known phenomena rendering both nitrogens in the heterocyclic system equivalent. Hydrogen bonding in benzimidazole 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[4].

The polymers prepared by Marvel and Vogel exhibited unusually high thermal stabilities and it was decided to prepare one of them in sufficient quantity for spinning and fiber evaluation. Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole was chosen as the first to be evaluated because of the commercial availability of 3,3'-diaminobenzidine tetrahydrochloride, the salt precursor to the required tetraamine.

Techniques employed for purification of tetraamine and polymerization were those devised by Marvel and Vogel. The reactants are polymerized at 260-290° under nitrogen followed by removal of most of the water and phenol by-products by reducing the pressure to 0.1 mm. The resulting low polymer is ground and powder polymerized at temperatures ranging from 290-400° and 0.1 mm. The reaction appears to involve simultaneous or nearly simultaneous evolution of water and phenol rather than preliminary condensation and evolution of phenol to produce a polyaminoamide which then undergoes cyclic dehydration to yield polybenzimidazole. This supposition is given credence by the fact that polyaminoamide prepared by low temperature condensation of isopathalyl chloride and diaminobenzidine does not cyclize on heat treatment to yield polybenzimidazole[5].

Product yields of the polymerization are generally 95%. The bulk polymer is reprecipitated from dimethylsulfoxide or dimethylacetamide with water. In the reprecipitation process about 10% of the solids are insoluble, probably crosslinked materials.

The polymer has been spun from dimethylsulfoxide and dimethylacetamide solvents. Typical fiber properties are summarized in Table I. Yarn obtained by spinning from DMAc is golden yellow in color while the material spun from DMSO is brown. The physical properties of the two yarns are, in general, comparable although the one spun from DMSO exhibits superior loop and knot properties. It is unlikely that this result is a solvent effect. The polymer spun from DMAc was lower molecular weight material than that spun from DMSO. This fact would account for the inferior loop and knot properties of the former material.

The fibers exhibit strong resistance to concentrated acid and basic solutions. Samples subjected to 40% aqueous sodium hydroxide or 40% aqueous sulfuric acid for 24 hours retained 66% of their original tenacity. Data for hydrolytic stability is summarized in Table II.

Thermal stabilities for poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole fibers were conducted in air. The results of these tests are summarized in Table III and indicate impressive stability at elevated temperatures. Under nitrogen atmosphere the polymer is reported[1] to retain 99% of its original weight after one hour at 500° while in air a sample of fiber disappeared in the oven (Table IV) after one hour at 500°.

The fibers were steam drawn and subsequently re-drawn over a hot pin at temperatures up to 400°. All fibers so treated were highly oriented but amorphous as demonstrated by x-ray diffraction patterns. Additional heat setting experiments failed to induce any crystallinity in the fiber. Mixed solvent experiments employing various concentrations of dimethylformamide-water were also ineffective. A small degree of crystallinity was induced in samples treated with a mixture of formic acid; water (50:50 by volume).

Fiber samples exposed to ultra-violet radiation darken quickly but their physical properties are virtually unaltered after periods up to 220 hours in the Xenotester.

With the hope of reducing the rigidity of the polybenzimidazole chain and possibly enhancing solubility properties, several attempts have been made to prepare the polymer based on 3,3',4,4'-tetraaminodiphenylsulfone and isophthalic acid. Thus far the reactions have yielded only low molecular weight polymer in poor yield. The tetraamine is prepared by conversion of 3,3'-dinitro-4,4'-dichlorodiphenylsulfone to the 4,4'-diamino analog and subsequent reduction of the nitro functions to yield the tetraamine. Purification has proven to be a problem and impurities are probably the cause of the unsatisfactory polymerization experiments.

TABLE I

A) Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole spun from DMAc fiber properties

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

	T	E	Mi	TR 3	TR 5	TR 10	WR 3	WR 5	WR 10
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						

B) Poly-2,2'-(m-phenylene)-5,5'-bibenzimidazole spun from DMSO fiber properties

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

	T	E	Mi	TR 3	TR 5	TR 10	WR 3	WR 5	WR 10
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 (gr./denier)

c) Mi= Initial Modulus (gr./denier)

d) TR= Tensile Recovery

e) WR= Work Recovery

TABLE II

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

Medium	Time (Hours)	T/E/Mi[a]
None	-	4.5/13/97
10% NaOH 95-100°	1	3.9/22/74
"	3	3.8/26/61
"	6	4.2/29/70
"	24	3.9/38/55
20% NaOH 95-100°	1	4.4/23/75
"	3	4.0/23/70
"	6	3.8/25/65
"	24	3.8/25/68
40% NaOH 95-100°	1	4.1/49/56
"	3	3.0/56/50
"	6	2.8/50/39
"	24	3.0/54/33
10% H_2SO_4 95-100°	1	3.6/36/50
"	3	3.2/35/48
"	6	3.6/42/44
"	24	3.4/38/52
20% H_2SO_4 95-100°	1	3.4/42/44
"	3	3.5/37/45
"	6	3.3/49/39
"	24	3.6/37/52
40% H_2SO_4 95-100°	1	3.4/36/46
"	3	3.6/45/53
"	6	3.4/50/44
"	24	3.1/52/43

a) See footnote in Table I

TABLE III

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

T (in air) °C	Time (Hours)	T/E/Mi[a]
Room Temp.	-	4.5/13/79
300	24	4.1/13/79
"	48	3.6/9/66
"	72	3.6/9/66
"	144	2.8/6/22
"	240	2.5/6/22
350	18	3.0/4/66
"	24	2.4/3/40
400	1	3.8/15/80
"	2.5	2.3/10/60
"	6	1.0/6/60
"	18	TWTT
450	1	2.5/2.5/27
"	3	Disintegrated
500	0.25	TWTT
"	1	Disappeared

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

Exposure Time[b] (Hours)	T/E/Mi
0	4.5/13/97
24	4.3/13/97
48	4.3/9/80
78	4.1/7/85
96	4.2/10/80
220	4.1/10/83

a) See footnotes in Table I.

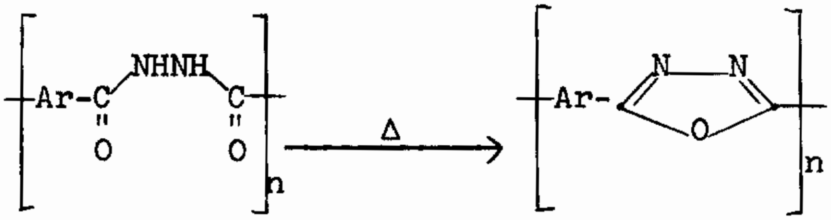
b) One hour in Xenotester is the equivalent of the Florida sunlight.

II. Poly(1,3,4-Oxadiazoles)

1. Introduction

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[6] discovered and reported aromatic poly[2,5-(1,3,4-oxadiazole)] fibers which had superior high-temperature resistance and excellent fiber properties. Their preparation was accomplished by cyclodehydration of aromatic polyhydrazide fibers at elevated temperature. This fiber conversion is presently the only route to polyoxadiazole fibers since appropriate preparative and spinning solvents are unavailable[6,7].



The most promising polyoxadiazole fiber, alt. poly[1,3-/1,4-phenylene-2,5-(1,3,4-oxadiazole)]*, was that obtained from alt. poly(1,3/1,4-phenylene hydrazide)** (50:50). The fiber conversion must be quantitative from the chemical standpoint in order to afford the desired high-temperature properties. The fiber conversion 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 the polyhydrazide or any remaining hydrazide link.

As a matter of fact, Stolle[8] and Pellizzare[9] reported that the thermal cyclodehydration of dibenzoylhydrazine, the simplest model, at a temperature of 250-280°C., gave 2,5-diphenyl-1,3,4-oxadiazole, but also traces of diphenyltriazole as signal of such possible degradation and side reactions.

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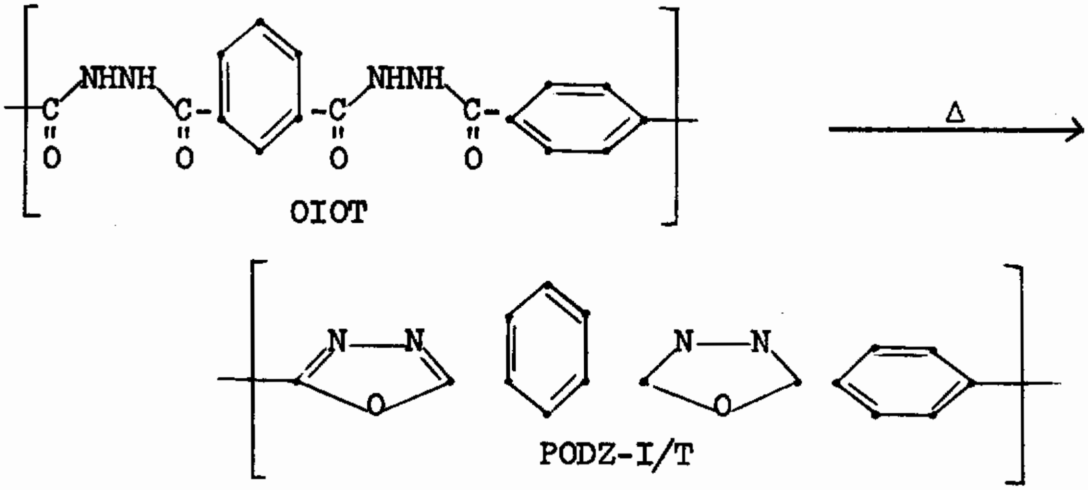
* Abbreviated and coded as PODZ-I/T.
** Abbreviated and coded as OIOT.

When PODZ-I/T fibers with thermal stabilities and fiber properties superior to those of polybenzimidazoles had been obtained by Frazer[6] it was not unexpected to find that reproducibility (in the context of the foregoing) would be difficult. At least it would require research under most accurately defined reaction conditions using most sensitive analytical tools.



OIOT

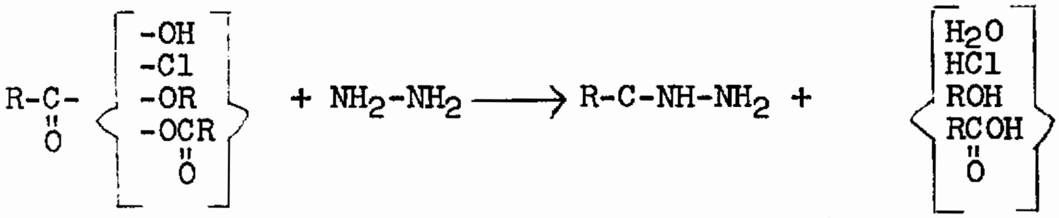
PODZ-I/T

Such an investigation was initiated and the initial effort is reported here. It involved a study of preparing the polyhydrazide OIOT as bulk polymer under various conditions, it involved a study of spinning solvents for OIOT, of drawing ratios and conditions for the yarn and a number of conversion studies of OIOT into PODZ-I/T. Chelation of OIOT fibers, as observed, was noted and assessed and model oligohydrazides and oligooxadiazoles were prepared to aid the study of conversion conditions. Alternate preparations of polyoxadiazoles, such as that by Abshire and Marvel[10] was repeated in amide solvents. New approaches were attempted by reacting bis orthoesters and with dihydrazides and by cyclizing polyhydrazides in solution with the phosphoazo-derivative of cyclohexylamine, and other cyclizing agents.

In short, this report summarizes our present knowledge of polyoxadiazoles, polyhydrazides, polyhydrazide chelates, and of model compounds.

2. Polyhydrazides

For a long time it has been recognized that the reaction between carboxylic acids, esters[11], anhydrides[12], or carbonyl chlorides[13] with hydrazine affords carboxylic hydrazides.



$$\underset{\overset{\|}{O}}{R-C}-\left\{\begin{matrix}-OH\\-Cl\\-OR\\-O\underset{\overset{\|}{O}}{C}R\end{matrix}\right\} + NH_2-NH_2 \longrightarrow R-C-NH-NH_2 + \left\{\begin{matrix}H_2O\\HCl\\ROH\\R\underset{\overset{\|}{O}}{C}OH\end{matrix}\right\}$$

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 tetra-acyl hydrazines[12,14,15,16]. Diesters, when treated with hydrazine hydrate in alcohol yield nearly quantitatively the desired dihydrazides which are polymer intermediates.

Low temperature polymerization of equimolar amounts of dihydrazide and carbonyl chloride in amide solvents such as hexamethylphosphoramide (HMPA), N-methylpyrrolidone (NMP), and N-methylpyrrolidone containing 2-5% lithium chloride was found to be the only preparative method that consistently yielded high molecular weight polyhydrazides.

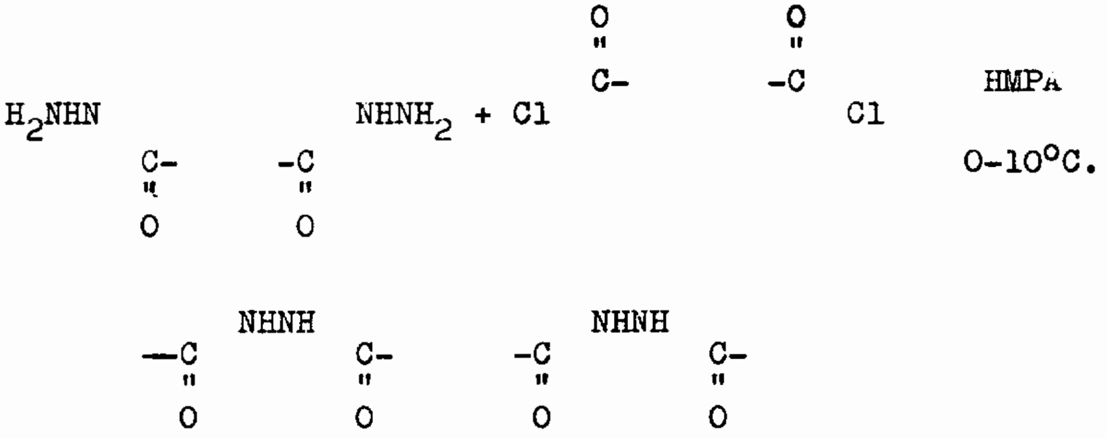
This preparation was discovered by Frazer[6] and was successfully employed[6,7] to cover the whole range of all-aromatic heteroaromatic, aromatic-oxalic, aromatic-aliphatic and all-aliphatic polyhydrazides. For high-temperature resistant polymers it was of course of greatest interest to prepare all-aromatic polyhydrazides and to study their properties and utility. Such polyhydrazides, when obtained in above manner, possessed high melting points (>300°C.) and were of high molecular weight. They were soluble in hot dimethyl sulfoxide, but insoluble in conventional polymer solvents.

3. Polyhydrazide Fibers

At the outset of this program, the polyhydrazide derived from terephthaloyl chloride and isophthalic hydrazide, poly(isophthalic-terephthalic hydrazide), OIOT, was selected for the conversion of its fibers into polyoxadiazole fibers.

a. Preparative Procedures

This polyhydrazide, OIOT, is best prepared in hexamethylphosphoramide (HMPA) from equal amounts of intermediates and in the absence of inorganic salts. The polymerization proceeds for 4-15 hours at room temperature.



The polymer is then washed several times with distilled water and several times with dry methanol and is dried at 80°C. in a vacuum oven. This routine polymerization has been carried out several times during the period covered by this report. Since it was noticed that resulting polyhydrazides contain still small amounts of ash after combustion, it was decided that the polymerization should be carried out in polyethylene flasks with a stirrer manufactured from a nylon rod and a "Teflon"* blade.

Further washings are now carried out with distilled water and deionized water.

b. Spinning Solvents

The polyhydrazide, OIOT, prepared and dried in above manner may be spun from dimethylsulfoxide (DMSO), but is best spun from dimethylacetamide (DMAc). The latter solvent is extremely useful because it allowed to lower the spinning temperature. Various spins have been carried out with DMAc as solvent containing small amounts (2-5%) of lithium chloride. When DMAc without lithium chloride was used as spinning solvent, it was necessary to spin between 100-105°C. because crystallization of the polymer was observed at higher temperatures. Dimethylformamide (DMF) causes rapid crystallization below 100°. The use of DMAc as spinning solvent as compared to DMSO or DMF has other advantages: DMAc is easier removed from the fiber by washing with water than is DMSO; unlike DMSO it does not attack the fiber on heat drawing. This is very important because any degradation of the polyhydrazide from heat drawing prior to conversion influences the fiber properties of the resulting polyoxadiazoles. DMAc as spinning solvent allows to draw the yarn to different levels of properties. Oriented and crystalline yarns are now available with a tenacity ranging from 3 to 6 gpd, elongations ranging from 4 to 24% and moduli ranging from 94 to 169. Table I contains a comparison of fiber properties obtainable when OIOT is spun from DMSO and DMAc. In addition, this spinning solvent affords yarn with various intermediate levels of orientation and crystallinity. Thus, wide ranges of properties are now attainable to

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*Trademark for Du Pont's TFE-fluorocarbon resin study the conversion of polyoxadiazole fibers. For the present report, it has to be noted that conversion studies have been carried out with yarn (OIOT) which still contains appreciable amounts (0.2-0.7%) of ash. Polyhydrazide fibers from ash-free yarn have not been studied up to the present time.

d. Ultraviolet Stability

Films of OIOT were not only used to determine the retention of the polymer but also to study the ultraviolet stability of the material. Polyhydrazide films cast from DMAc or from HMPA showed no color break up to 1000 hours in the Fade-Ometer.

e. Chelate Films

Initial chelating studies of OIOT polymer were also carried out with film because of greater ease of handling. These studies of chelation are now being carried out with fibers (see below). As far as our studies with chelating films are concerned, we have prepared a OIOT/$HgCl_2$ chelate film which was completely transparent, colorless, and could be dried in vacuum at 80° over the weekend without change of appearance. When the same film was heated at 80° in an air atmosphere this film turned brown. Other metal salt chelate polymers of OIOT were prepared but films could not be cast, owing to their insolubility in various solvents. The mercuric chloride/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.

The most interesting results in our chelation studies with OIOT films were obtained when these films were cast on aluminum plates or on brass plates. These still preliminary results may be indicative of OIOT chelating of metal. The film cast on brass adhered well for four hours in boiling water. Discoloration of the OIOT occurred simultaneously which is indicative of a picking up of metal ions. More interesting was the film of OIOT cast on aluminum. It 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. This interesting adhesion is possibly due to a polymer-to-metal self-bonding.

f. Chelate Fibers

The rather qualitative results observed for chelate films were followed up with more detailed experiments of chelating on polyhydrazide fibers. This study involves OIOT fibers of various degrees of orientation and crystallization.

TABLE I

POLYHYDRAZIDE (OIOT) FIBER PROPERTIES

Spinning solvent	Dimethylsulfoxide		Dimethylacetamide	
% 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. (#), Mod. (Mi)	3.3/20/76	4.9/24/94	1.9/21/56	3.8/5.6/122
Denier	6.2	5.4	4.4	2.4
Loop T/E/Mi	1.6/5.5	1.9/6.3	1.1/4.6/52	0.4/0.5/85
Denier	5.5	4.7	4.5	2.3
Knot T/E/Mi	2.3/9/52	2.9/10/56	1.4/7.7/40	1.5/1.9/87
Denier	7.1	7.4	4.5	2.1
Elevated T/E.Mi (90°C. air)			2.2/27/46	6.0/11/110
Denier			5.3	2.1
Work Recovery, WR, 3% [RT/RT wet/ 90°C. wet]	35/26/25	34/33/36	33/17/18	39/23/24
Work Recovery, WR, 5%	29/25/26	27/35/39	31/18/16	42/29/31
Ten. Recovery, TR, 3% [RT/RT wet/ 90°C. wet]	66/52/48	65/64/78	63/35/35	68/45/47
Tensile Recovery, TR, 5%	57/52/52	55/62/67	62/38/34	71/56/58
Wash-Set Recovery Angle	120	140	130	145
X-ray crystal. (amt./perf.)	amorph.	med./med.	low/med.	low/low
X-ray orient. (degrees)	64°	good	low	med.
Fiber Stick Temperature FST °C.				305°
Melting Point °C.				370°

The study of chelating fibers was carried out because it was felt that we could produce high temperature resistant fibers other than polyoxadiazoles from OIOT by chelating the fibers with metal salts and if possible, by reducing the metal salts to Me°.

We have, therefore, started up a program of chelating OIOT fibers in a DMF/salt bath. The salt bath contained about 10-15% of metal salt. The bath temperature was maintained as 100 ± 5°C. In some cases, there was added a small amount of tertiary amine in order to make the salt bath more basic. Visually, there was observed differences in chelation, and generally more chelation occurred at the less basic conditions. Table II summarizes the results obtained with amorphous OIOT fiber. The most interesting case observed so far is the chelation of OIOT fiber with silver nitrate. While silver nitrate gives a straw colored chelate fiber, this fiber can be run through a subsequent bath of a tertiary amine such as dimethylaniline. Interestingly enough this tertiary amine bath has reduced $AgNO_3$ on OIOT to Ag°. The resulting polyhydrazide chelate fibers had a silvery gray to black appearance.

4. Model Compounds

The investigation described in this study necessitated the preparation of model compounds for polyhydrazides, polyoxadiazoles and the cyclodehydration reaction. Huisgen[17,18] has reported aromatic oligooxadiazoles but they are exclusively para-linked and not immediately useful here.

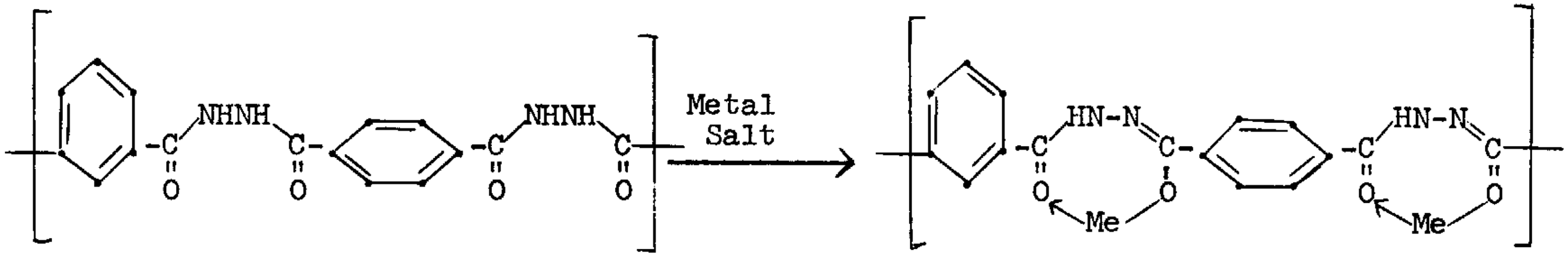
a. Oligohydrazides

A number of model compounds have been prepared which have the alternating sequence of isophthalic and terephthalic hydrazide links. These oligohydrazides are listed in Table III.

Examples 1 and 2 were prepared from dimethyl terephthalate and dimethylisophthalate by treating the respective methanol solution with hydrazine hydrate. Example 3 was prepared by reacting an aqueous solution of hydrazine sulfate simultaneously with sodium hydroxide and benzoyl chloride[19] or by reacting a pyridine solution of benzoyl chloride with hydrazine hydrate. Examples 4 and 5 were obtained by reacting DMAc or pyridine solutions of isophthalic or terephthalic dihydrazide carefully with benzoyl chloride. Example 6, OIOT, is shown in Table III, to depict the relevance of the model compounds for this study.

TABLE II

POLYHYDRAZIDE/CHELATE FIBER PROPERTIES



Sample	DMF Bath (I)	Bath II	Color of Dry Yarn	T/E/Mi***	Crystallinity of Yarn/Additive
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% $AgNO_3$	DMA*	Black [Ag°]	0.9/65/34	Amorphous/ Crystalline
7-II	9.7% $AgNO_3$	DMA*	Dk. grey [Ag°]	1.3/99/36	Amorphous/ Crystalline
9	10.6% $AgNO_3$**	DMA*	Silvery [Ag°]	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.

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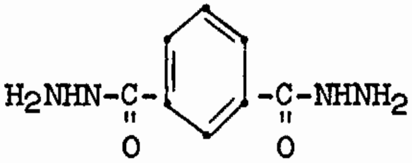
* N,N'-Dimethylaniline
** Short contact time
*** Control 1.8/118/41, undrawn, amorphous

TABLE III

OLIGOHYDRAZIDES

1.

2.



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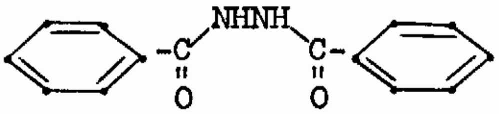

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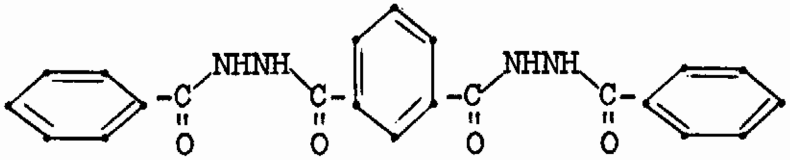
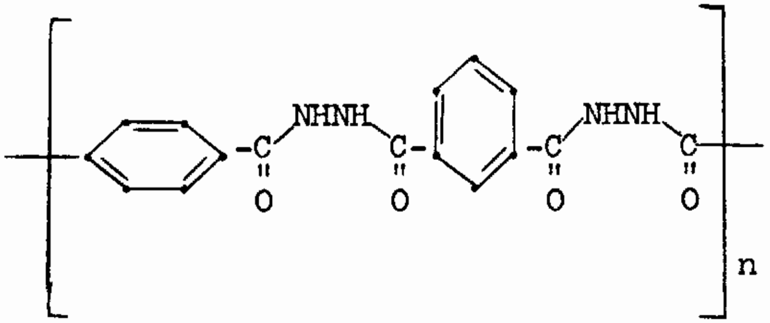


5.

6.



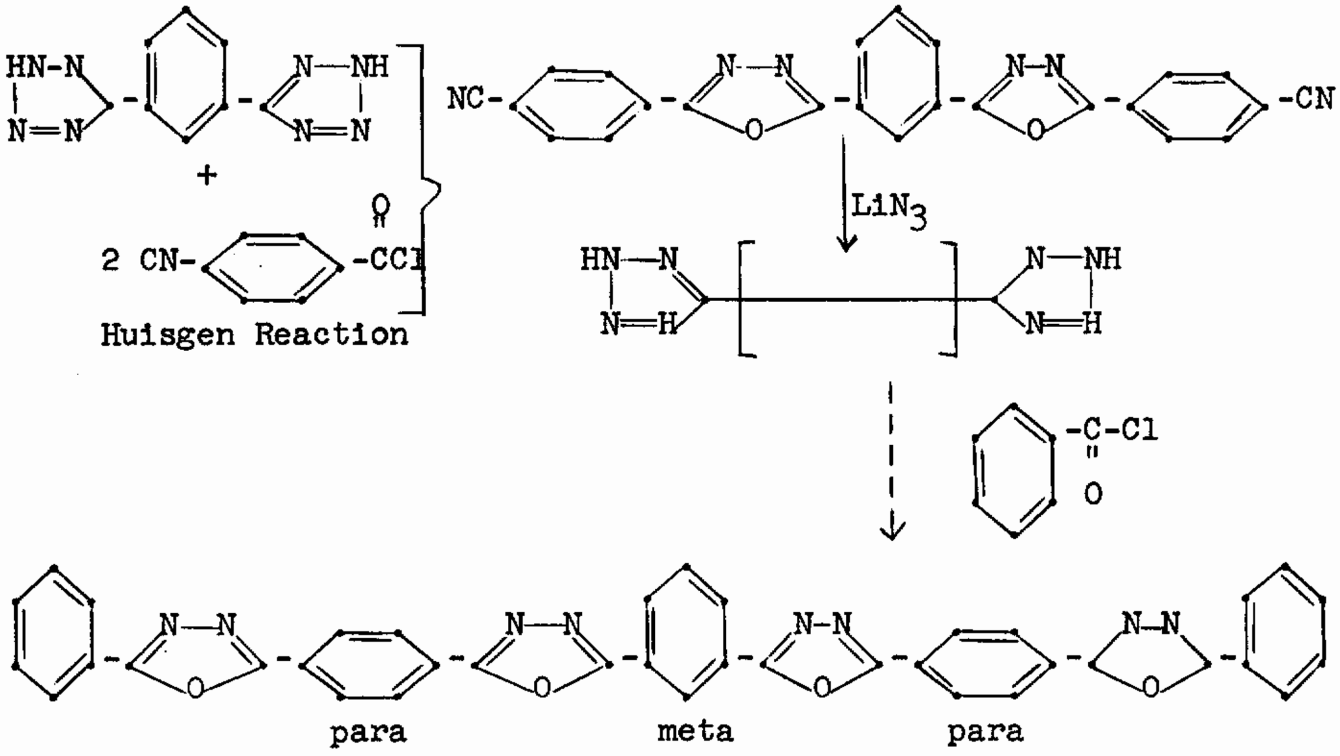
OIOT

These hydrazides were prepared as model compounds for the conversion into the corresponding oligo-1,3,4-oxadiazoles by thermal cyclation and dehydration. This conversion is analogous to the conversion of polyhydrazides into polyoxadiazoles. It is presently carried out on a thermogravimetric balance in order to study the exact course and possible kinetics of the conversion.

b. Oligo-1,3,4-oxadiazoles

A number of model compounds containing the polyoxadiazole unit have also been prepared and in some cases are still in the preparative stage (Table IV). These are model oxadiazoles which have two oxadiazole rings per three benzene rings, one of them meta- or paraphenylene rings. They have either been prepared by cyclodehydration of oligohydrazides in pyridine[20] or DMAc or by the Huisgen reaction [17,18], whereby high yields of 1,3,4-oxadiazoles result from treatment of acid chlorides with tetrazoles.

The preparation of the 9-membered oligo-1,3,4-oxadiazole (see below) is analogous to that described by Huisgen for a 9-membered oxadiazole consisting of exclusively p-phenylene rings and oxadiazole rings. The oligooxadiazole described here, however, is much more pertinent as model compound for PODZ-I/T because of its alternating structure, consisting of m-phenylene, p-phenylene and 2,5-disubstituted 1,3,4-oxadiazole rings.



The dinitrile was prepared from p-cyanobenzoyl chloride[21], and was subsequently treated with lithium azide. This is essentially the principle of the Huisgen Reaction[17,18] which allows building up of oligooxadiazoles resembling polyphenyls.

5. Poly(1,3,4-oxadiazoles)

a. Preparative Methods

Abshire and Marvel[10] have reported the preparation of polyoxadiazoles from ditetrazoles with diacid chlorides in inert solvents. This type of preparation was repeated with amide solvents such as hexamethylphosphoramide (HMPA). It was hoped that higher molecular weight polyoxadiazole would result. A few experiments using this variation of Marvel's route yielded polyoxadiazole with low viscosities (ηinh <0.3). No solvents other than sulfuric acid were found.

Another method for preparing polyoxadiazoles was briefly studied. It involves the reaction of bis orthoesters and dihydrazides as an application of the nonfunctional model reaction reported by Ainsworth[22]. Thus the diethyl succinate was prepared with great difficulty[23] in reasonably pure form but no high molecular weight polymer was obtained in this condensation. Three other intermediates[24,25] for the preparation of bis orthoesters were also prepared: dimethyliminosuccinate, diethyliminosuccinate and diethyliminoisophthalate. No further attempts are contemplated to prepare polyoxadiazoles by these or other routes. Hence no further effort will be made to prepare the bis orthoesters from these iminosuccinates by treatment with absolute alkanols.

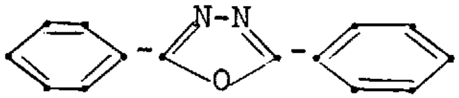
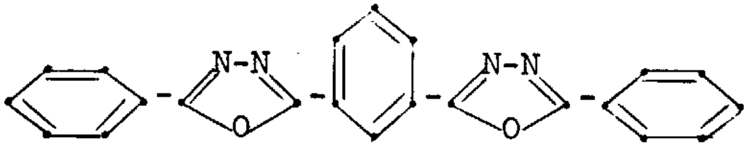
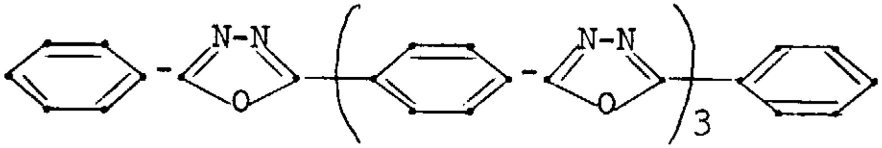
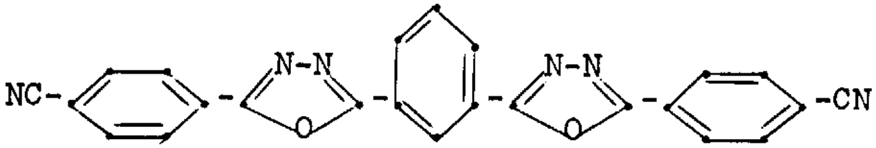
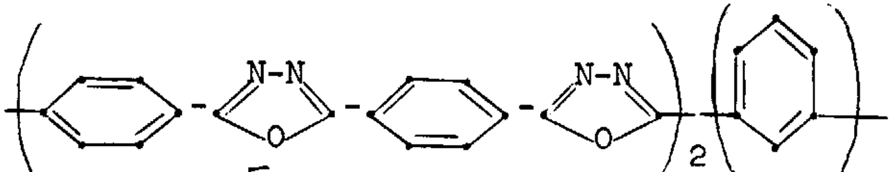
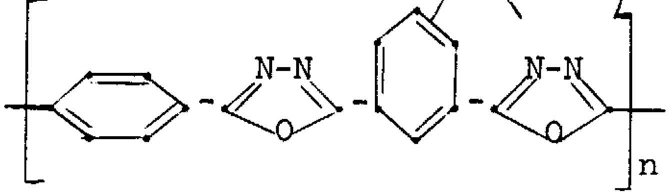
b. Cyclodehydration of Polyhydrazides

The inaccessibility of polyoxadiazoles by such routes as described above, the lack of solvents for such polymers and the excellent synthesis of high-molecular weight polyhydrazides discovered by Frazer[6], made this polymer and its fibers the potential intermediate for polyoxadiazole fibers. For example, the alternating isophthalic/terephthalic polyhydrazide, poly-(1,3-/1,4-phenylene hydrazide) (50:50), as bulk polymer, was shown to be more or less convertible into polyoxadiazole under a variety of conditions patterned after monomeric model reactions.

The cyclodehydration of monomeric model reactions[26] is carried out at elevated temperatures (thermal conversion) or in solution with chlorosulfonic acid, sulfuryl chloride, toluene sulfonic acid, tosyl chloride, organic anhydrides, and sulfuric acid.

TABLE IV

OLIGO-1,3,4-OXADIAZOLES

	Ref.	Max.	log	Solvent
 	17	280.0 280.0	4.44 4.45	EtOH DMF
 	1 17,18 -	323 312.5 312.0	- 4.69 4.69	H_2SO_4 DMF DMF
 	- 1	287.5 297.0	4.74 -	DMF H_2SO_4
 	18	327.5	-	DMF
 	-	295.0	4.80	DMF
 	-	-	-	-
Polymer: PODZ-I/T  	-	332.0	-	H_2SO_4

Hence, several types of conversions were studied and are described in the following paragraphs. They are thermal cyclization of polyhydrazide bulk and fiber samples in the absence of a solvent, and cyclodehydration in solution by thermal or chemical means.

Thermal conversion of polyhydrazide fibers is described in a later chapter. Conversion of polyhydrazide (OIOT) bulk samples at elevated was studied by various means. A finely ground (40 mesh) sample of polyhydrazide was heated for 48 hrs. at 283° (0.4 mm). The resulting sample analyzed clearly 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. It was hoped that steam at this temperature might effect cyclization. However, 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.

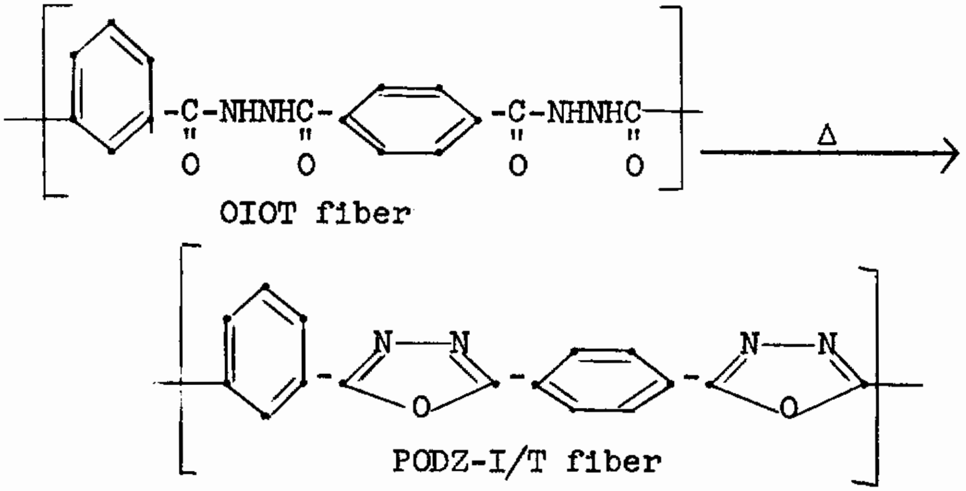
Mild dehydrating agents in solution, such as N,N'-dicyclohexylcarbodiimide, trichloroacetonitrile, and tetrachlorodifluoroacetone were without effect. No change in oxygen analysis was obtained when samples were withdrawn over a period of four days. Strong dehydrating agents such as acids or bases degraded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

Klingsberg[27] had reported that symmetrical aromatic dihydrazides could be converted into 2,5-disubstituted oxadiazoles by the reaction of phosphoazo-derivatives of cyclohexylamine [$C_6H_{11}N{=}PNHC_6H_{11}$]. In an attempt to convert polymeric hydrazides into polymeric oxadiazoles, a 2.5% solution of OIOT in a mixture of dimethylsulfoxide 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. The microanalytical results on the dry specimens 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 solution and bulk conversions was not soluble in trifluoroacetic acid which occasionally dissolves this polyoxadiazole. Owing to insolubility of polymeric oxadiazoles in a large number of solvents, it appeared that thermal conversion of solid polyhydrazides into solid polyoxadiazoles was the most promising route for this polymer post-reaction. Hence, polyhydrazide fibers were converted into polyoxadiazole fibers.

6. Polyoxadiazole Fibers

A study of thermal conversion of OIOT into the corresponding oxadiazole (PODZ-I/T) was carried out and is still in progress. This study was designed to furnish information about the dehydration-cyclization mechanism with the objective to find the optimum conversion conditions. Such conversions were attempted on polyhydrazide fibers in vacuum at 222, 242, 265, and 283°C. Thermal conversions were also attempted on finely ground (40 mesh) polyhydrazide powder at 283° in vacuum. In addition, a number of attempts of thermal and chemical conversions of polyhydrazide solutions were studied.



OIOT fiber

PODZ-I/T fiber

a. Conversion in Vacuum

The thermal conversion studies on polyhydrazide yarn (T/E/Mi = 5/24/80) in vacuum were carried out by heating 3 to 6 samples of yarn wound around a perforated metal bobbin. Periodically samples were withdrawn to follow the conversion with time. Withdrawn samples were analyzed and showed the following results: No conversion occurred at 222°C. within 72 hrs., as evidenced by virtually unchanged oxygen analysis. At 242°, there was a slow conversion (about 50% in 50 hrs.) with gross deterioration of yarn properties. At 265°, the conversion proceeded fairly rapidly. However, the final yarn properties were poor. At 283°, complete conversion was noticed in less than 12 hrs. When this sample was further heated at 283°, it was noted that a continuous drop in yarn properties occurred which leveled off after about 100 hrs. (T/E/Mi = 0.6/0.8/87).

This suggests that the history of the starting polyhydrazide, despite its excellent yarn properties, is definitely important for the subsequent conversion characteristics. Traces of solids such as ash or degradation products of the spinning solvents may clearly influence the final polyoxadiazole properties.

b. Conversion in Solvent Vapors

A bobbin of oriented and crystalline polyhydrazide yarn (T/E/Mi = 5/24/80) was boiled in diphenylmethane vapors (b.p. 265°) for 100 hrs. Eighty to ninety percent conversion, as judged by oxygen analysis, occurred but the properties of the resulting polyoxadiazoles had decreased to T/E/Mi=2.2/3/92. A similar conversion in boiling diphenylethane (b.p. 284°) was found to be complete after about two days (T/E/Mi = 0.7/0.7/85). Yarn converted in boiling diphenylmethane degraded badly after one-hour exposure to 400°C.

The properties of polyoxadiazole fibers listed in Table V are the result of a more detailed study to develop techniques for the conversion rather than large amounts of yarn sample. These fibers were obtained in an oven in nitrogen atmosphere using good circulation at 280°C. Because of the chelating tendency of polyhydrazide, it was advisable to use "Teflon" bars to support the skeins of polyhydrazides during conversion studies rather than glass or metal bars.

TABLE V

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

Ten. (T), % Elong. (E), Mod. (Mi)	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°
Wash-Set Recovery Angle	290°

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