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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### High-Modulus Wholly Aromatic Fibers. I. Wholly Ordered Polyamide-Hydrazides and Poly-1,3,4-oxadiazole—Amides

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**To cite this Article** Preston, J. , Black, W. B. and Hofferbert JR., W. L.(1973) 'High-Modulus Wholly Aromatic Fibers. I. Wholly Ordered Polyamide-Hydrazides and Poly-1,3,4-oxadiazole—Amides', *Journal of Macromolecular Science, Part A*, 7: 1, 45 — 65

**To link to this Article:** DOI: 10.1080/00222337308061131

**URL:** <http://dx.doi.org/10.1080/00222337308061131>

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## High-Modulus Wholly Aromatic Fibers. I. Wholly Ordered Polyamide-Hydrazides and Poly-1,3,4-oxadiazole—Amides

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### ABSTRACT

Several completely ordered polyamide-hydrazide copolymers were prepared via low temperature polycondensation of aromatic diacid chlorides with symmetrical aromatic diamines containing preformed dihydrazide linkages. Highly crystalline, hot-drawn fibers of the polyamide-hydrazide containing only para-oriented phenylene units showed unusually high strength and exceptionally high initial modulus: 10.8 and 508 g/den, respectively, at 2.9% elongation-to-break. The as-spun fibers also exhibited rather high tensile strength and unusually high initial modulus: 8.2 and 291 g/den, respectively, at 9.4% elongation-to-break. The hot-drawn fiber retained considerable strength at elevated temperatures, exhibiting a tenacity of 1.4 g/den and an initial modulus of 169 g/den at 350°C. Heat-aging of the as-spun fiber at 185°C in air

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showed that 66% of the original tenacity, 41% of the elongation, and 86% of the modulus were retained even after 336 hr. Substitution of as little as 25 mole % meta-oriented phenylene rings for para-oriented ones resulted in loss of the ultra-high strength and modulus, giving tensile properties comparable to those of fibers from wholly aromatic polyamides of the meta-oriented type. Fibers from the polyamide-hydrazides containing 50 mole % meta-oriented rings showed similar properties. Although ordered oxadiazole-amide copolymers were obtained from diamines containing two preformed oxadiazole linkages separated by *m*-phenylene rings, fibers could not be spun from them. Fiber of an ordered oxadiazole-amide copolymer was obtained, however, by heat treatment of the wholly *p*-phenylene ordered polyamide-hydrazide copolymer precursor fiber. Such a fiber exhibited a tenacity of 15.3 g/den, 3.6% elongation-to-break, and 564 g/den initial modulus.

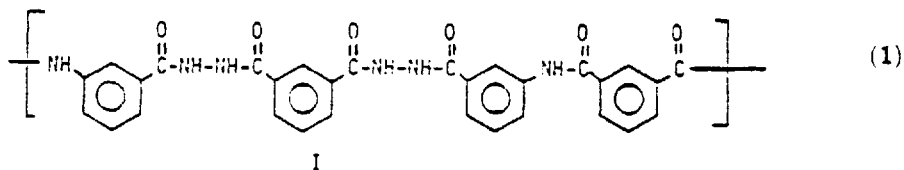
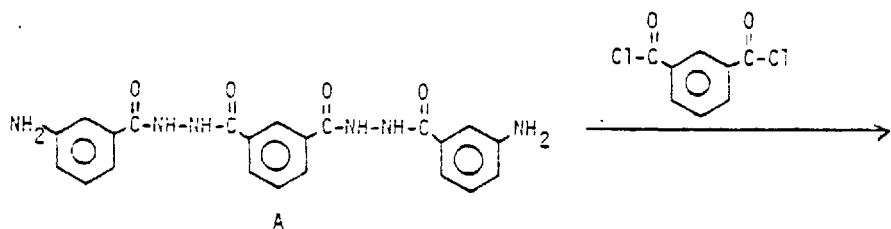
## INTRODUCTION

Previously we have reported the synthesis of wholly ordered poly-1,3,4-oxadiazole-amides [1] and the properties of fibers [2] from such polymers were described. Monsanto Co. patents [3, 4] have described the use of an ordered polyamide-hydrazide as precursor to an ordered poly-1,3,4-oxadiazole-amide but heretofore the fiber properties of such polyamide-hydrazide precursors have not been described.

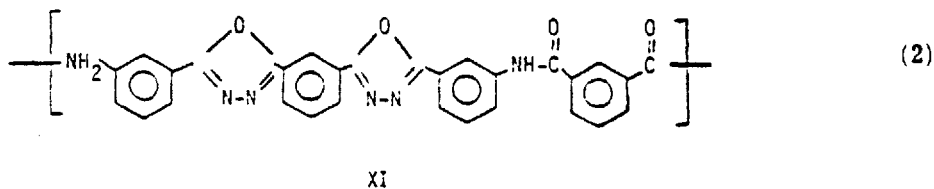
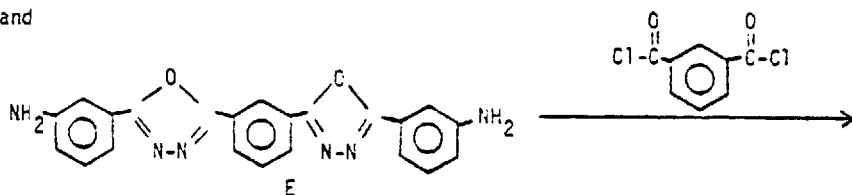
In the past, several workers have published on matters related to the present work. Thus Frazer [5] has reported the preparation of fibers from some wholly aromatic polyhydrazides and the subsequent conversions of such fibers to poly-1,3,4-oxadiazole fiber [6]. Culbertson and Murphy reported [7, 8] the synthesis of some polyamide-hydrazides which could be converted into polybenzoxazole-1,3,4-oxadiazoles or poly-1,3,4-oxadiazole-amides, depending on the selection of monomers. Polymerizations of the latter type, however, employ unsymmetrical monomers which allow for the possibility of "head-to-head" and "head-to-tail" units in the polymer repeat units; i.e., such polymers conceivably can be of the "limited order" type [9].

The polymers discussed in this paper are of the wholly ordered

type; i.e., only symmetrical hydrazide diamines (Table 1) or 1,3,4-oxadiazole diamines (Table 2) are used for the preparation of polymers (Tables 3 and 4). Typical reactions are given by Eqs. (1) and (2).







and



In another paper of this series, the properties of "partially ordered" polyamide-hydrazides from unsymmetrical monomers are discussed and the properties of selected fibers are reported [14]. The interested reader will find it profitable to compare the properties of the polymers of this report with those of the "partially ordered" type.

TABLE 1. Aromatic Hydrazone Diamines<sup>a</sup>

No.	Structure	mp (°C) <sup>b</sup>
A		153-155 (280-281 <sup>c</sup> )
B		300-302 (344-346)
C		305-306 (327-329 <sup>d</sup> )
D		350-352 (358-360)

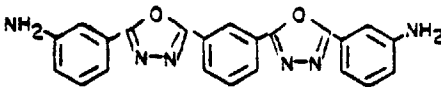



<sup>a</sup>The melting points of the precursor dinitro compounds are given in parentheses.

<sup>b</sup>Uncorrected capillary melting points determined in a Mel-Temp apparatus.

<sup>c</sup>Previously reported [ 11 ] as 288-290°C.

<sup>d</sup>Previously reported [ 11 ] as 316°C (decomp).

TABLE 2. Aromatic 1,3,4-Oxadiazole Diamines<sup>a</sup>

No.	Structure	mp (°C) <sup>b</sup>
E		285-287 <sup>c</sup> (334-336 <sup>d</sup> )
F		360-363 (320-322)
G		372-374 (380-382)
H		>470 (418-420)

<sup>a</sup>The melting points of the precursor dinitro compounds are given in parentheses.

<sup>b</sup>Uncorrected capillary melting points determined in a Mel-Temp apparatus.

<sup>c</sup>Previously reported [ 11 ] as 328-331°C; the fact that both diamine and dinitro precursors are reported to have the same mp suggests a typographical error or that the dinitro compound was not in fact reduced.

<sup>d</sup>Previously reported [ 11 ] as 328-331°C.

TABLE 3. Polyamide-Hydrazides

No.	Polymer from		Polymerization media <sup>b</sup>	$\eta_{inh}^c$	Remarks
	Diamine	Diacid chloride <sup>a</sup>			
I	A	IC	DMAc	0.38 <sup>d</sup>	Good film
II	A	TC	DMAc/5% LiCl	0.63 <sup>d</sup>	Good film which was readily converted at 350°C to poly-1,3,4-oxadiazole-amide film
III	B	IC	DMAc/5% LiCl	0.48 <sup>e</sup>	Good film
IV	B	TC	NMP	1.08 <sup>e</sup>	Good film
V	C	IC	NMP	0.53 <sup>f</sup>	Good film
VI	C	TC	NMP	0.95 <sup>f</sup>	Good film and fiber, both of which could be converted to poly-1,3,4-oxadiazole-amide
VII	D	IC	2(DMAc/5% LiCl):1(NMP)	1.59	Good film and fiber
VIII	D	TC	DMAc/5% LiCl	5.10 <sup>g</sup>	Good film and excellent fiber
IX	D	BBC	NMP/5% LiCl	-	Good film
X	D	NDC	NMP/5% LiCl	-	Good film

<sup>a</sup>IC = isophthaloyl chloride; TC = terephthaloyl chloride; BBC = 4,4'-bibenzoyl chloride; NDC = 2,6-naphthalenedicarbonyl chloride.

<sup>b</sup>DMAc = dimethylacetamide; NMP = N-methyl pyrrolidone.

<sup>c</sup>Determined at 30°C on solutions of 0.5 g. of polymer dissolved in 100 ml of solvent.

<sup>d</sup>Determined in DMAc.

<sup>e</sup>Determined in 1:1 NMP/DMAc.

<sup>f</sup>Determined in NMP.

<sup>g</sup>Determined in DMSO (dimethylsulfoxide).

TABLE 4. Polyoxadiazole-Amides

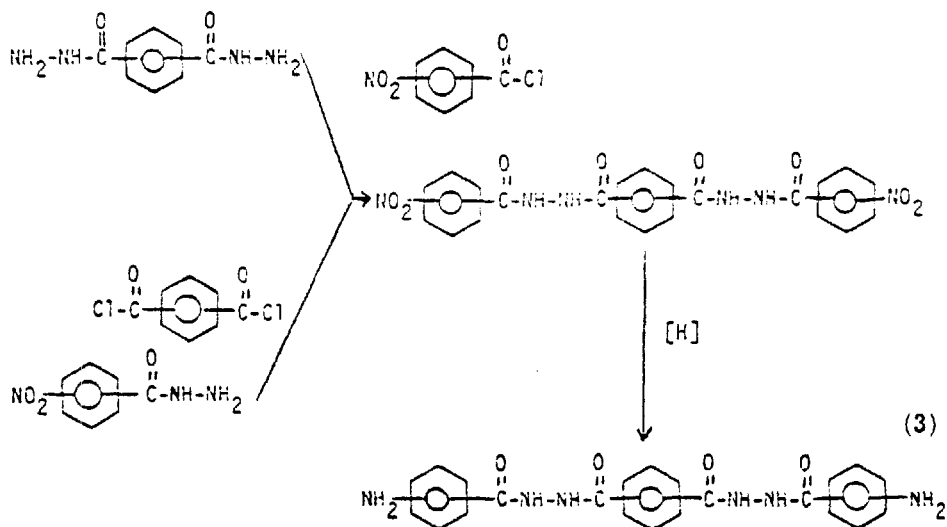
No.	Polymer	Polymerization media	Inherent viscosity <sup>a</sup>
XI		DMAC/5% LiCl	-
XII		DMAC/5% LiCl HPT(50:50)	0.91
XIII		DMAC/5% LiCl	-
XIV		DMAC/5% LiCl. HPT(30:70)	0.11

<sup>a</sup> Determined at 30°C on a solution of 0.5 g/100 ml DMAC.

## DISCUSSION AND RESULTS

Preparation of Diamines

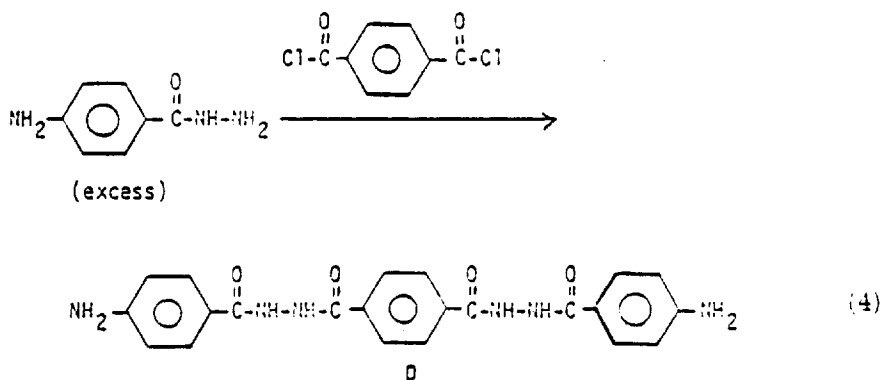
The hydrazide and 1,3,4-oxadiazole diamines (Tables 1 and 2, respectively) were prepared via reduction from dinitro precursors following previously reported procedures. The hydrazide precursors were prepared by the reaction of nitrobenzoyl chlorides with isophthaloyl or terephthaloyl dihydrazides; alternatively, isophthaloyl or terephthaloyl chlorides were reacted with nitrobenzhydrazides.



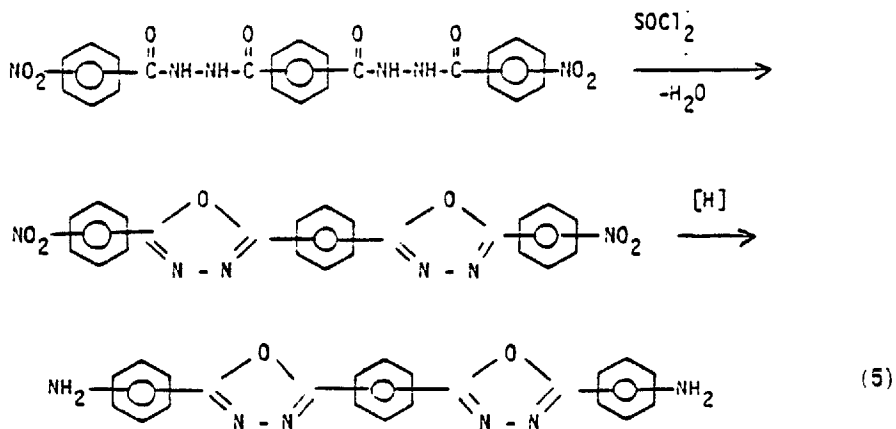
The wholly-phenylene hydrazide diamine D also was prepared directly via a synthesis which did not require the reduction of a dinitro precursor. This novel synthesis is based on the selective reactivity of a diacid chloride with an aminobenzhydrazide; i.e., under proper experimental conditions, 1 mole of a diacid chloride can be made to react with 2 moles of an aminobenzhydrazide to yield a symmetrical diamine containing hydrazide linkages [10].

The 1,3,4-oxadiazole dinitro precursors were obtained from corresponding dinitrohydrazides via cyclodehydration, employing thionyl chloride or fuming sulfuric acid (alternately, polyphosphoric





acid [ 11 ]), in a manner similar to that published earlier for 2,5-bis(m- or p-nitrophenyl)-1,3,4-oxadiazoles [ 12 ].



### Polymerization

Low temperature solution polycondensation was employed because it has been previously shown that the interfacial polymerization of large, relatively insoluble diamines with diacid chlorides generally leads to polymers of low inherent viscosity [ 13 ]. However, when monomers of high purity were condensed with diacid chlorides in amide-type solvents (Eqs. 1 and 2) to yield soluble polymers, it was

possible to obtain polymers of high inherent viscosity (Tables 3 and 4).

Those polymers containing predominantly meta-oriented rings were soluble in solvents such as dimethylacetamide (DMAc), but the polymers containing a high proportion of para-oriented rings required the addition of lithium chloride to the solvent. Mixed solvents of DMAc and N-methylpyrrolidone (NMP) or DMAc and hexamethylphosphorictriamide (HPT) were particularly effective, especially when the DMAc or NMP contained dissolved lithium chloride (neat HPT apparently does not dissolve an appreciable amount of LiCl).

In general the polymerizations were carried out at  $-10$  to  $0^{\circ}\text{C}$  and at a concentration of polymer of about 5-10%. The solubility of the polymers decreased with increasing substitution of para-oriented rings; polyoxadiazole-amides were less soluble than similarly structured polyamide-hydrazides.

### Preparation of Films and Fibers

Films were readily prepared from all of the Polymers I-XIV; three of the polymers, VI-VIII, were selected for the preparation of fibers. The polymers were fabricated into film or fiber from the polymer solution resulting directly from the polymerization; the solutions generally were neutralized prior to fabrication.

Most of the polymers could readily be redissolved in DMAc, NMP, or HPT or in these solvents containing dissolved lithium chloride. The polyamide-hydrazides could be so dissolved and additionally were quite soluble in dimethylsulfoxide without dissolved salts. Concentrated sulfuric acid was a suitable solvent for the polyoxadiazole-amides but caused degradation of the polyamide-hydrazides.

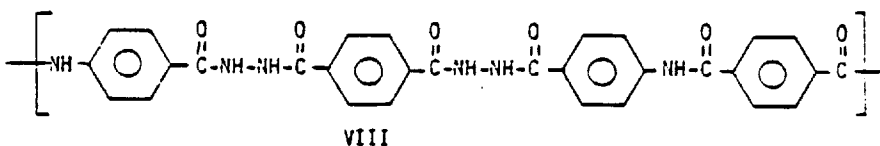
### Film Properties

In general the polyamide-hydrazide films were converted with great difficulty and with poor translation of properties to polyoxadiazole-amide films. However, a few films, e.g., those of II and VI, were converted by programmed heating in nitrogen according to the following schedule:  $140^{\circ}\text{C}$ , 16 hr;  $290^{\circ}\text{C}$ , 15 min;  $300^{\circ}\text{C}$ , 30 min;  $315^{\circ}\text{C}$ , 15 min;  $350^{\circ}\text{C}$ , 30 min. Infrared spectra of the film indicated that the hydrazide units of the polymers had been converted to 1,3,4-oxadiazole units.

### Fiber Properties

The properties of the three fibers obtained from the polyamide-hydrazides are given in Table 5. The tensile strengths of Fibers VI and VII are relatively low and may reflect the low molecular weight, as indicated by low inherent viscosities of the parent polymers (Table 3). In particular the tenacity and modulus of Fiber VII seem to be low, but the inherent viscosity of VII is exceptionally low for a polymer which contains a high percentage of para-oriented rings. (Compare [14] tensile properties of fibers from high molecular weight "partially ordered" polyamide-hydrazides having the same structural units as VI and VII.)

The fiber of VIII has excellent tenacity and very high initial modulus, probably because of the high degree of orientation and



crystallinity developed during the spinning and drawing of this high molecular weight wholly para-oriented polymer. (Note: Except for certain reports in the patent literature, VIII is apparently the second wholly aromatic and wholly para-oriented fiber reported; the first such fiber appears to have been the polyterephthalamide of 4,4'-diaminobenzanilide [15]. The fiber of VIII has an extraordinarily high initial modulus owing no doubt to the very great chain stiffness of a wholly para-oriented polymer which is capable of extensive hydrogen bonding.

The density of Fiber VIII (Table 5) suggests a highly crystalline material, as does the x-ray diffraction diagram (Fig. 1). It is interesting to compare the density of the hot-drawn fiber, 1.47 g/cc, with the theoretical density, 1.51 g/cc, obtained by study of the unit cell using x-ray diffraction [16, 17]. The high birefringence (Table 5) for the fiber of VIII (both with and without hot-drawing) indicates that a very high degree of molecular orientation has been achieved.

The retention of tensile properties (Table 6) of Fiber VIII is quite good to above 350°C, at which temperature the cyclodehydration reaction undoubtedly causes the rapid loss of strength due to disruption of the fiber's fine structure.

TABLE 5. Fiber Properties of Wholly Ordered Polyamide-Hydrazides

Properties	VII			VIII <sup>b</sup>	
	VI, as-spun <sup>a</sup>	As-spun	Hot-drawn (hand)	Without hot-draw <sup>c</sup>	Hot-drawn <sup>d</sup>
Tenacity, g/den	1.3 (1.6)	1.7	2.6	8.2 <sup>e</sup>	10.8 <sup>f</sup>
Elongation, %	31 (22.9)	60.2	22.1	9.4	2.9
Initial modulus, g/den	47 (47)	56	99	291	508
Denier	9.5 (9.8)	8.3	6.0	3.6	2.7
Density, g/cc	1.35 (-)	(-)	1.44	1.44	1.47

<sup>a</sup> Collapsed on hot rolls; values in parentheses are for air dried fiber.

<sup>b</sup> As-spun (low orientation)  $T/E/M_i$  (den) = 5.2/33.4/81 (4.6).

<sup>c</sup> Best single filament properties:  $T/E/M_i = 8.5/12.0/323$ .

<sup>d</sup> Best single filament properties:  $T/E/M_i = 10.9/2.7/590$ .

<sup>e</sup> Birefringence, 0.421.

<sup>f</sup> Birefringence, 0.455.

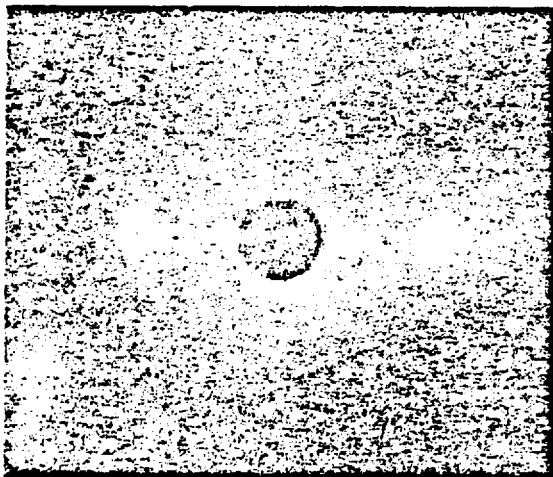


FIG. 1. X-ray diffraction pattern of hot-drawn fiber VIII.

TABLE 6. Tensile Properties of Fiber VIII at Elevated Temperatures

T, °C	$T, E/M_i^{a,b}$	
	Without hot-draw	Hot-drawn
100	5.9/16.7/222	8.3/2.8/381
200	3.9/26.2/142	4.7/2.3/263
300	1.9/3.3/154	3.1/1.6/223
350	1.4/1.5/125	1.4/1.1/169
360	1.1/1.3/96	-/-/123

<sup>a</sup> $T/E/M_i$  = Tenacity, g/den; elongation, %; initial modulus, g, den.

<sup>b</sup>For tensile properties at RT, see Table 5.

The retention of properties after heat-aging at 185°C in air for Fiber VIII is relatively poor (Table 7) for a fiber intended for use as a thermally stable fiber, but these properties are quite good relative to a conventional textile fiber; e.g., a high-modulus poly-nosic fiber used as a control was too brittle to test after heating.

TABLE 7. Heat-aging of Fiber VIII<sup>a</sup> at 185°C in air<sup>b</sup>

Time, hr	$T/E/M_1^c$
	(work) den
0	$\frac{8.2 \ 9.4 \ 291}{(-) \ 3.65}$
24	$\frac{7.3 \ 6.6 \ 262}{(0.326)3.67}$
50	$\frac{7.0 \ 6.7 \ 250}{(0.326)3.85}$
73	$\frac{7.2 \ 5.8 \ 283}{(0.295)3.58}$
192	$\frac{6.8 \ 5.2 \ 273}{(0.248)3.63}$
336	$\frac{5.4 \ 3.9 \ 251}{(0.144)3.82}$

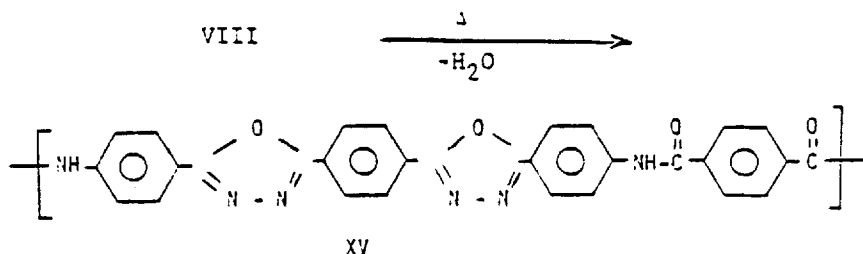
<sup>a</sup>Fiber VIII without hot-draw.

<sup>b</sup>Exposed to 185°C in air for the periods of time indicated and broken at room temperature.

<sup>c</sup> $T/E/M_1$  = Tenacity, g/den; elongation, %; initial modulus, g/den.

### Conversion of Polyamide-Hydrazides to Ordered Oxadiazole-Amide Copolymers

In general the polyamide-hydrazide fibers were converted with great difficulty and with poor translation of tensile properties to polyoxadiazole-amide fibers. However, fiber of the wholly para-oriented polyamide-hydrazide, VIII, was converted to fiber of the corresponding ordered oxadiazole-amide copolymer, XV, with the best retention of tensile properties (Table 8) of the various fibers which were heat-treated. Probably this was so because VIII



softened the least of the various polymers examined, hence losing less of the fine structure of the original fiber. The tensile properties (Table 3) of the derived poly-1,3,4-oxadiazole-amide fiber XV, obtained by heating at 250-285°C for 2 hr and at 300°C for 1 hr 45 min, were virtually identical with those of the precursor fiber VIII before heat-treatment. It might be possible, however, to heat-treat a fiber which softens considerably when undergoing cyclodehydration and to restore tensile strength by hot-drawing, which should result in reorientation of the fiber.

### Thermal Properties

It is a most difficult task to determine the melting points for the bulk polyamide-hydrazides because their melting points are often obscured by the cyclodehydration reaction which yields polyoxadiazole-amides. In particular this is true for the polyamide-hydrazides containing a high proportion of meta-oriented rings. The latter type of polymer, it may be observed, is of little interest for the preparation of thermally stable fibers because of low softening points and is of little interest otherwise because of relatively low tensile strength and modulus. Therefore, only Polymers I-V and XI-XIV were studied extensively.

Films and fibers of the completely para-phenylene polyamide-hydrazide, VIII, in short-term tests, show fairly good thermal stability to about 350°C where the cyclodehydration reaction apparently begins to take place to an appreciable degree. The reaction apparently is most rapid at about 390 to 430°C as shown by differential thermal analysis (DTA) in nitrogen (Fig. 2a) and by loss of weight (water) in the weight retention curve (TGA) above 350°C (Fig. 3). Fiber prepared via heat treatment of VIII (to yield XV) showed no change in the DTA curve (Fig. 2b) up to the decomposition point, 525°C.

TABLE 8. Fiber Properties of Wholly Ordered Oxadiazole-Amide Copolymer XV

	Denier (den/fil)	Tenacity (g/den)	Elongation (%)	Initial modulus (g/den)	Work-to-break (g-cm/den-cm)
Average	2.61	12.3	3.0	561	0.275
Single filament, highest tenacity	2.58	15.3	3.6	564	0.419



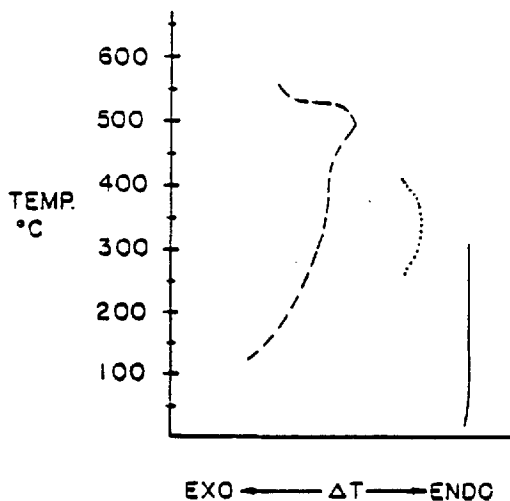
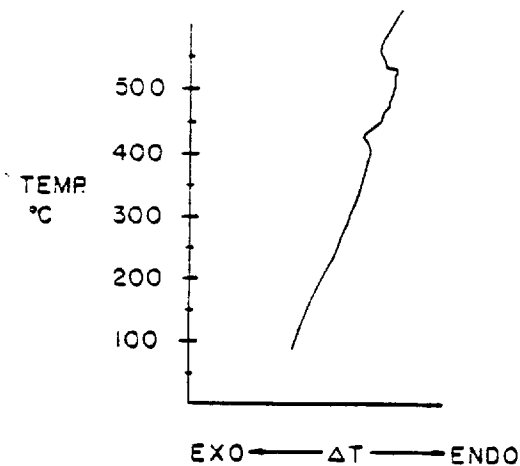


FIG. 2a. Programmed DTA (rate = 20°C/min) in nitrogen of hot-drawn fiber from VIII: continuous trace.

FIG. 2b. Programmed DTA (rate = 20°C/min) in nitrogen of hot-drawn fiber from VIII: (—) heated to 310°C and cooled to 260°C; (· ·) reheated to 415°C and cooled to 125°C; (- -) reheated to 560°C.

Film of the polyoxadiazole-amide XV prepared via cyclodehydration from the corresponding polyhydrazide-amide VIII showed good flexibility and good color even after 72 hr exposure at 350°C in air.

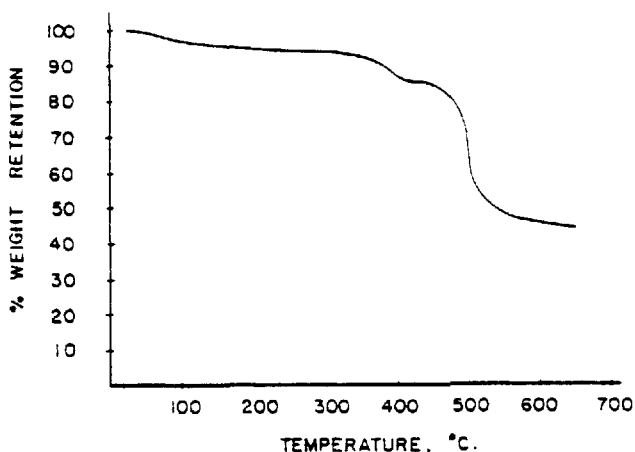


FIG. 3. Programmed TGA (rate = 15°C/min) in nitrogen of fiber from VIII.

### Preparation and Properties of Fiber of an "Essentially Ordered" Polyamide-Hydrazide VIII'

Diamine D (Eq. 4) was prepared in situ and polymerized in situ to give a polymer, VIII', which was "essentially ordered" as indicated by a comparison of the x-ray and electron diffraction patterns [16], respectively, of a fiber and a thin film of this polymer with that of a fiber and a thin film of the wholly ordered polymer VIII [16].

Fiber prepared from the "essentially ordered" polymer VIII' showed rather high tensile strengths and moduli (Table 9) but not so high as for the wholly ordered fiber from VIII (Table 8). However, this is probably a consequence of not optimizing fiber properties in the case of VIII'.

## EXPERIMENTAL

### Preparation of Diamine D

Into a 3-liter resin kettle was charged 25.37 g (0.168 mole) of p-aminobenzhydrazide and 540 ml of DMAc. The resulting solution was cooled to -10°C under a nitrogen blanket and 3.41 g (0.0168 mole)

TABLE 9. Fiber Properties of "Essentially Ordered" VIII'

	As-spun (degree of stretch during spinning)			Hot-drawn (degree of hot-stretch)		
	Low	Medium	High	Low	Medium	High
Tenacity, g/den	4.5	5.5	5.8	8.2	9.9	10.8
Elongation	43.0	28.5	10.0	9.4	3.5	3.5
Initial modulus, g/den	83.0	136.0	180.0	291.0	390.0	446.0
Denter/filament	0.5	4.8	4.4	-	3.2	3.1
Density, g/cc	1.42	1.425	1.43	-	1.44	1.45

of terephthaloyl chloride (TCl) in 600 ml of tetrahydrofuran (THF) was added dropwise over a period of 40 min; another 40 ml portion of THF was used to rinse the contents of the dropping funnel into the reactor. Stirring was continued at  $-10^{\circ}\text{C}$  for 1 hr, then the stirrer was stopped and the contents of the flask allowed to warm to room temperature (RT).

After 16 hr, crystallization of the product was induced by scratching the kettle with a glass rod and the solution was stirred for 3 hr prior to filtration. The yield of white product, after it was washed with ethanol and dried at  $170^{\circ}\text{C}$  in air, was 4.8 g, mp  $360\text{--}363^{\circ}\text{C}$ .

Alternatively, TCl in DMAc may be added to p-aminobenzhydrazide in DMAc and the product precipitated with THF. Also, THF may be present in DMAc at the start. All such processes yield the same product.

### Preparation of Diamine C

The procedure for diamine D was repeated using isophthaloyl chloride. Analysis of the product by NMR showed that at least 97% of the hydrazide groups were attached to an isophthaloyl moiety.

### Preparation of Diamine B

The procedure for diamine D was repeated using m-aminobenzhydrazide. The product produced no depression in melting point when mixed with a sample of authentic diamine B reprepared via reduction of the dinitro precursor.

### Preparation of Polymer VIII

A solution of 4.32 g (0.01 mole) of D in 70 ml of DMAc containing 5% dissolved lithium chloride was cooled to  $-10^{\circ}\text{C}$  and 2.03 g (0.01 mole) of solid terephthaloyl chloride was added with stirring. After 10 min the clear, viscous solution was allowed to warm to  $0^{\circ}\text{C}$  and an additional 10 ml of solvent was added. After another 10 min at  $0^{\circ}\text{C}$  the solution was allowed to warm to RT and 20 ml more of solvent was added.

The solution of polymer was neutralized by the addition of 0.67 g of lithium carbonate prior to spinning. The spinning "dope" was

stirred for 1 hr followed by heating to 50°C for 30 min with continued stirring, then followed by heating at 80°C for 20 min, again with continued stirring. The clear, light yellow and very viscous solution of polymer contained approximately 5% polymer solids. The inherent viscosity of the dried bulk polymer VIII (Table III) was 5.1.

### Preparation of "Essentially Ordered" VIII'

A solution of 5.38 g (0.0356 mole) of p-aminobenzhydrazide in 125 ml of DMAc containing 5% dissolved lithium chloride was cooled to -10°C and a solution of 7.23 g (0.036 mole) of terephthaloyl chloride in 160 ml of tetrahydrofuran (THF) was added dropwise over a period of 45 min. About 2/3 of the THF solution was added during 35 min, at the end of which time the solution was clear; as the remaining 1/3 of the solution was added, the solution of polymer became cloudy. The solution was stirred for 10 min after addition of all of the THF solution, then allowed to warm to RT under vacuum (~60 mm) over a period of about 90 min, during which time most of the THF was removed.

Prior to spinning, the very viscous solution was diluted by the addition of 80 ml of solvent and neutralized by lithium carbonate with heating. The inherent viscosity of the dried bulk polymer was 4.76 (determined at 30°C for 0.5 g/100 ml of dimethyl sulfoxide).

### Fiber Testing

Tensile properties were measured on an Instron Tester using single filament breaks (average of 10 breaks) made at 21°C. Gauge length was 1 in. and the rate of extension was 100%/min. Breaks at elevated temperatures were conditioned at temperature for 1 min, then broken at temperature. In the heat-aging tests, fibers were exposed for the indicated periods of time and broken at 21°C.

### ACKNOWLEDGMENTS

The authors wish to express their appreciation to Mr. H. S. Morgan for the preparation of certain fibers. The assistance of Dr. R. W. Morrison in connection with the synthesis of one of the monomers is gratefully acknowledged.

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