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High-Modulus Wholly Aromatic Fibers. II. Partially Ordered Polyamide-Hydrazides

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ABSTRACT

Partially ordered polyamide-hydrazides were produced by the polycondensation of diacid chlorides with aminobenzhydrazides, the order that results being a consequence of the considerably more rapid reaction of a diacid chloride with the hydrazide group in competition with the aromatic amine group of the aminobenzhydrazide. Fibers were produced from a series of such polymers containing from 50 mole % meta-oriented phenylene rings to 100 mole % para-oriented ones. Fiber from the wholly para-oriented type of polymer exhibited very high strength and modulus: 12.5 and 468 g/den, respectively, at 4.3% elongation-to-break. Although the crystallinity and density observed for hot-drawn fibers of partially ordered completely para-oriented polyamide-hydrazides were comparable to the crystallinity and density of fibers of the isomeric wholly ordered polymer, the partially ordered polymers were more readily spun to the ultra-high strength and high modulus type fibers, probably because their greater solubility made them easier to spin.

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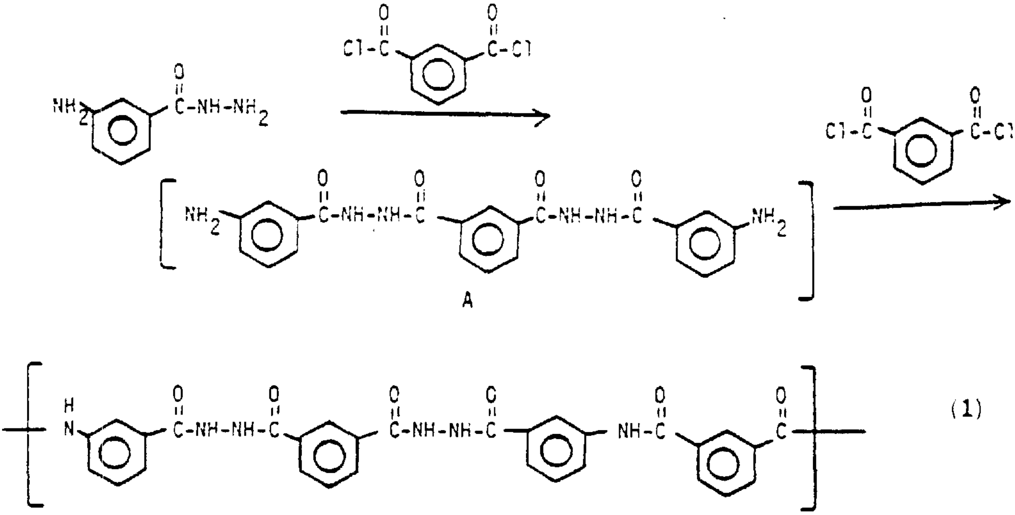
Retention of tensile strength and modulus at elevated temperatures for fiber from the wholly para-oriented partially ordered polymer was quite good; tenacity at 300°C was 3.6 g/den. the elongation was 2.3%, and the initial modulus was 208 g/den. The retention of properties upon heat-aging at 300°C in air of a fiber of polymer containing wholly para-oriented rings and a fiber of the polymer containing 50 mole % meta-oriented phenylene rings showed that the partially ordered polyamide-hydrazides may be considered to be marginally high temperature resistant fibers. Chemical resistance is considerably better than that for fibers from polyhydrazides and approaches that of the fibers from aromatic polyamides. Light stability for fibers from the polyamide-hydrazides, however, is relatively poor.

INTRODUCTION

In the first paper of this series, the properties of fibers and films from wholly ordered polyamide-hydrazides were described [1]. This paper will discuss the synthesis of "partially" ordered polyamide-hydrazides and fibers from these polymers.

Other reports by us have described the self-regulating polycondensation reaction of diacid chlorides with aminophenols [2] and with aminobenzhydrazides [3, 4]. The self-regulation in the latter reaction, which is employed to prepare the polymers used to make the fibers of this report, is accounted for on the basis of the difference in reactivity between aromatic amino groups and hydrazide groups toward an acid chloride. Thus self-regulation results to the extent that m-aminobenzhydrazide reacts (Eq. 1) with isophthaloyl chloride (ICl) to produce in situ a dihydrazide-diamine, A, which further reacts with ICl to produce a polyamide-hydrazide (I). The in situ dihydrazide diamine A may be reacted (Scheme 1) with terephthaloyl chloride (TCl) to produce II. If, however, the initial reaction of the m-aminobenzhydrazide is with TCl, a new in situ diamine, B, is produced which may be reacted (Scheme 1) with ICl to produce III, or with more TCl, to produce IV.

For p-aminobenzhydrazide, a similar sequence of reactions with ICl and TCl can take place (Scheme 2) to produce polyamide-hydrazides V-VIII.



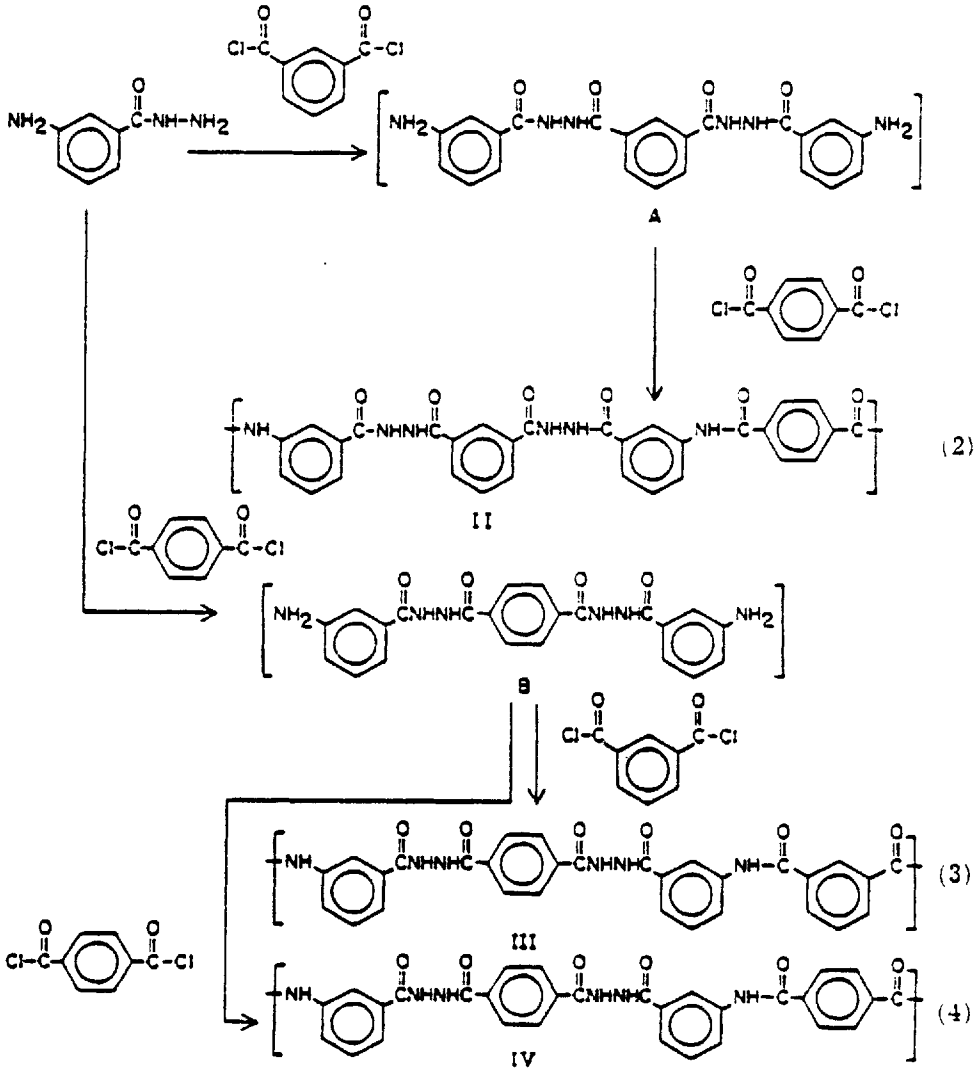
A

I

(1)

Although these reactions are illustrated as yielding wholly ordered polymers, it is to be borne in mind that structural irregularities are to be expected because, in the environment of excess acid chloride, depletion of the hydrazide group allows for reaction of the diacid chloride with the amine group. Studies of this reaction [4] show that such irregularities are relatively few when mixing is rapid, but but because they do occur, the authors refer to polyamide-hydrazides produced by way of in situ hydrazide diamines as being partially ordered.

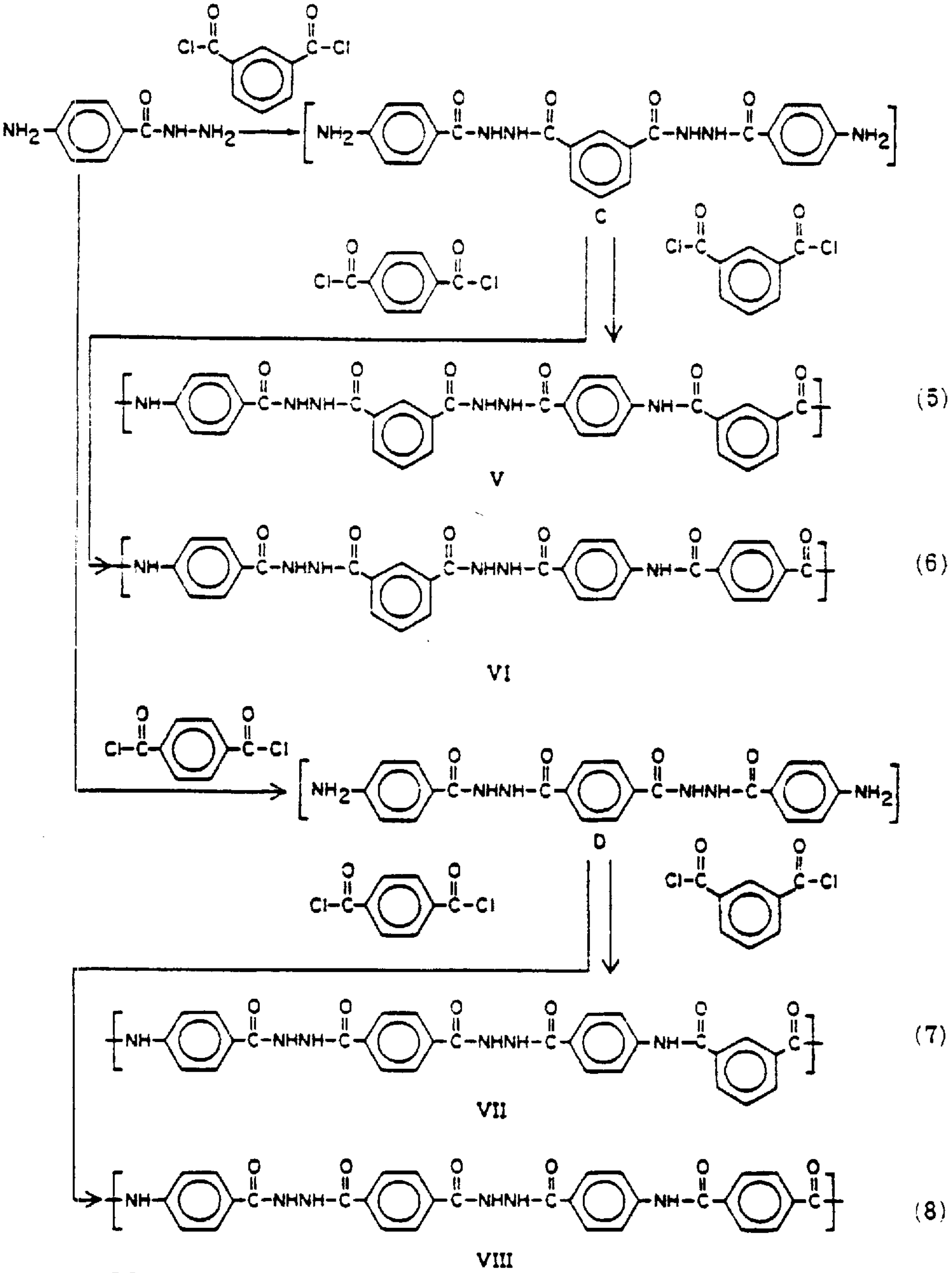
(Note: Wholly ordered aromatic polyamide-esters (Eq. 9), which bear similarities in structure and mode of preparation to the partially ordered polyamide-hydrazides, owe their wholly ordered structure to the fact that only an in situ diphenol amide is produced from the reaction of an aminophenol with a diacid chloride in the presence of a weak base [2]. Only the amine group can react due to the fact that the phenolic group is unactivated to the phenoxide species in the presence of a weak base; addition of a strong base to the diphenol amide intermediate permits further reaction with a diacid chloride. Thus absolute control of structure is effected for aromatic polyamide-esters whereas the structural regularity of the polyamide-hydrazides depends upon a number of factors,



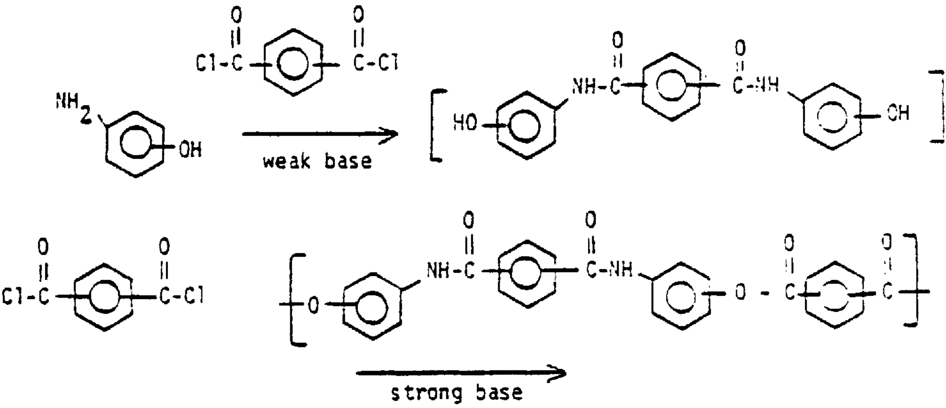
SCHEME 1

chief of which are kinetic and diffusion control, or in practical terms, stirring.)

Earlier, Culbertson reported reactions of m- and p-aminobenzhydrazides with isophthaloyl and terephthaloyl chlorides [5]; such reactions would lead to polymers having the Structures I, IV, V, and VIII but would not account for the preparation of Polymers II, III,



SCHEME 2



(9)

VI, and VII. The structural convention used by Culbertson to represent his polymers, modeled after that of Preston and Smith for copolyamides of limited order [6], anticipates the possibility of complete order and varying degrees of order for polyamide-hydrazides, I, IV, V, and VIII, but conditions for the control of the chemical ordering process were not disclosed nor were the Structures II, III, VI, and VII.

While the partially ordered nature of the polyamide-hydrazides, and particularly the wholly para-oriented polyamide-hydrazide, of this report is stressed, it must be pointed out that the properties of such polymers very closely resemble those of wholly ordered polymers rather than those of random copolymers or even copolymers of limited order [6].

DISCUSSION AND RESULTS

Polymerization

All of the polymers were prepared via low temperature polycondensation in amide type solvents, e.g., dimethylacetamide (DMAc), with added lithium chloride in many cases. The inherent viscosities (Table 1) of the several polyamide-hydrazides indicate that high molecular weight polymers were obtained. For Polymer VIII it was possible to obtain much higher inherent viscosity values than that reported in Table 1 once the purity of the monomers was increased and the polymerization conditions were optimized; then

TABLE 1. Partially Ordered Polyamide-Hydrazides

Polymer No.	Polymerization medium	η_{inh}[a]
I	DMAc	-
II	DMAc	-
III	DMAc	-
IV	DMAc/5% LiCl	2.35[b]
V	DMAc/5% LiCl	1.07[c]
VI	DMAc/5% LiCl	1.78[c]
VII	DMAc/5% LiCl	2.32[c]
VIII	DMAc/5% LiCl	3.48[b,d]
IX	DMAc/5% LiCl	2.17[c]

[a] Determined at 30°C on solutions of 0.5 g of polymer dissolved in 100 ml of solvent.

[b] Determined in DMAc containing 5% dissolved lithium chloride.

[c] Determined in dimethylsulfoxide (DMSO).

[d] η_{inh} = 5.50 by dilution of an aliquot of solution with DMAc/5% LiCl.

inherent viscosities of 5-8 were commonplace and inherent viscosities up to 13 were observed. However, in order to be able to make meaningful comparisons of the various fibers taken from Polymers IV-VIII, materials of comparable molecular weight were used. It is important to note here that while inherent viscosity values are generally higher for the polyamide-hydrazides of high para content, the molecular weights ($\overline{M}_w$ = 40-50,000) of the various polymers are generally comparable.

In those instances where more than one acid chloride was used in a given polymerization, the order of addition of the acid chlorides is critical in the determination of the final structure of the polymer, as already discussed in the Introduction and illustrated in Schemes 1 and 2. Subtle but nevertheless real differences in physical properties are to be found between polymers formed by reversing the order of addition of the diacid chlorides. Simultaneous addition of the two diacid chlorides, of course, leads to a random copolymer as regards distribution of meta- and para-units along the polymer chain. One such copolymer, IX (Table 1), which was prepared from p-aminobenzhydrazide and equal parts of ICl and TCl, was spun to fiber (Table 2).

TABLE 2. Tensile Properties of Polyamide-Hydrazide Fibers

No.	Ratio of p-/m-	$\frac{T/E/M_i}{(\text{work})\ \text{den}}$[a]	
		As-spun	Hot-drawn
IV	2/2	$\frac{1.3/95.8/28}{(-)14.4}$	$\frac{5.4/18.6/85}{(0.676)4.23}$
V	2/2	$\frac{1.5/82.9/47}{(1.051)8.17}$	$\frac{6.0/9.6/114}{(0.353)2.82}$
VI	3/1	$\frac{2.7/58.8/70}{(1.270)7.30}$	$\frac{6.7/3.3/289}{(0.149)2.80}$
VII[b]	3/1	$\frac{2.8/67.6/66}{(1.450)5.60}$	$\frac{10.5/4.8/323}{(0.284)1.85}$
VIII	4/0	$\frac{6.6/28.0/149}{(-)3.9}$	$\frac{12.5/4.3/468}{(\sim 0.35)2.79}$
IX	3/1	$\frac{3.0/56.1/76}{(1.310)21.0}$	$\frac{8.7/4.4/321}{(0.294)8.80}$

[a] $T/E/M_i$ = tenacity, g/den; elongation, %; initial modulus, g/den.

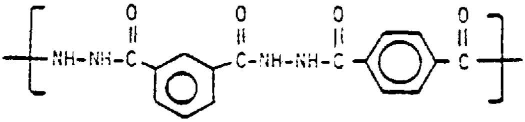
[b] $\frac{T/E/M_i}{(\text{work})\ \text{den}} = \frac{4.7/14.4/171}{(0.549)3.96}$ for fiber not hot-drawn to the maximum.

For VIII, the kinetics of the competitive reaction between amine and hydrazide groups with terephthaloyl chloride in the early stages of polycondensation have been determined [7] from analysis of the species present and identified by NMR [4]. Based on this study, only one amide linkage would be formed for every seven pairs of hydrazide linkages even under the most adverse conditions which prevailed in the low temperature polycondensations, until all of the free hydrazide groups are exhausted. Thus under some conditions the in situ dihydrazide-diamine, D (Scheme 2), is produced almost exclusively and a high degree of order for the wholly para-oriented polyamide-hydrazide VIII is produced in turn. That a high degree of chemical order can be achieved by the self-regulating mode of polymerization is strongly indicated independently by the fact that as many as seven meridional reflections of a large repeat length (29.7 Å or multiple thereof) has been observed in X-ray diffraction patterns [8]. The 29 Å repeat unit corresponds to that calculated for the wholly ordered polyterephthalamide from the complex diamine D (Scheme 2).

Fiber Properties as Related to Polymer Structure

Fibers were prepared from five of the polymers taken from the eight structural isomers possible by combinations of the meta- and para-oriented monomers. Polyamide-hydrazides containing high proportions of meta-oriented rings exhibit little potential for high tenacity/high modulus fibers nor possess high enough softening points to serve as precursors for high temperature fibers. Therefore, Polymers I-III were not studied in fiber form.

Three polymers, IV and V plus the polyhydrazide X, which have equal numbers of meta- and para-oriented rings, were spun to fibers having roughly comparable tensile properties for both the as-spun

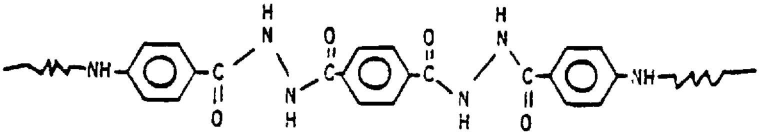


X

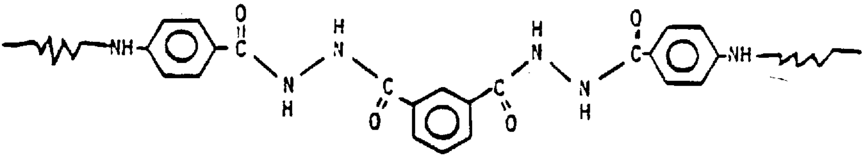
and hot-drawn fibers (for the tensile properties of IV and V, see Table 2; for the tensile properties of X, see Table 7).

Two polymers, VI and VII, having three para- and one meta-oriented rings per polymer repeat unit, were spun to fibers which exhibited comparable tensile properties prior to hot-drawing. However, after hot-drawing, fibers of VII were found to have considerably higher tensile strength and modulus (and at a higher elongation-to-break as well) than fibers of VI.

That the tensile strength and modulus are higher for fibers of VII than for fibers of VI, despite the fact that both contain equal amounts of meta- and para-oriented rings, possibly can be traced to the more rodlike structure of the dihydrazide-diamine moiety of VII, E, compared to that of VI, F; the latter would be expected to produce more of a "crank-shaft" motion when rotated upon its axis.



E



F

The fiber of Polymer IX has tensile properties intermediate between those of VI and VIII, probably because IX is obtained by the simultaneous addition of ICl and TCl (1:1) which results in a random distribution of m- and p-phenylene rings along the polymer chain of IX.

The wholly para-oriented polyamide-hydrazide VIII gave fiber of by far the highest tensile properties (Table 2) of the fibers reported here. (Note: Much higher tensile properties for fiber of VIII have been obtained when higher molecular weight polymers have been used and the spinning conditions have been more nearly optimized for a given number-average molecular weight. The properties of such fiber, VIII, known experimentally as a member of the X-500 class of fibers, are the subject of a separate report [9].)

Fiber Properties in Relation to Spinning and Solvent

The role of polymer solvent and spinning method was demonstrated by spinning polymer VIII (isolated from solution in DMAc and dried) from a solution of dimethylsulfoxide using the dry-spinning method and the same wet-spinning method used for the preparation of Fiber VIII (Table 2). The as-spun fiber (Table 3) obtained by wet-spinning was comparable to Fiber VIII (Table 2) spun from DMAc containing dissolved LiCl; however, hot-drawing of the fiber failed to develop the high tensile strength and modulus which characterize hot-drawn VIII. The as-spun fiber obtained by dry-spinning had low strength and failed to develop high strength

TABLE 3. Fiber VIII Spun from Dimethylsulfoxide

	$T/E/M_i$[a]	(work) den[b]
Via wet-spinning		
As-spun	5.6/55.1/122	(2.310)12.4
Hot-drawn	7.2/4.6/239	(0.206)14.5
Via dry-spinning		
As-spun	1.2/54.4/40	(-)17.9
Hot-drawn	4.6/3.3/257	(-)9.3

[a] T = tenacity, g/den; E = elongation-to-break, %; initial modulus, g/den.

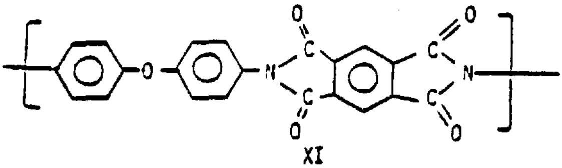
[b] Work, g-cm/den-cm; denier, den/filament.

and modulus upon hot-drawing. However, no attempt was made to optimize the dry-spinning method for Fiber VIII, and it should not be concluded that a high tenacity, high modulus fiber cannot be made via this method of spinning.

Tensile Properties as Related to Hot-Drawing

It is a rather difficult matter to predict on the basis of as-spun fiber properties (Table 2) those structures which will yield fibers having very high strength fibers. (Compare as-spun fibers VI and VII with hot-drawn fibers VI and VII.) Even for as-spun fiber VIII, which has rather high strength and modulus relative to most hot-drawn fibers from wholly aromatic polyamides, it is a remarkable fact that hot-drawing by merely 1.1-2.0X at 300°C results in a twofold increase in tenacity and a more than threefold increase in initial modulus.

If it is difficult to predict tensile properties of hot-drawn fibers based on the tensile properties of as-spun fibers, it is much more hazardous to predict the high tenacity/high-modulus fiber properties on the basis of film data. This is amply illustrated for film and fiber of VIII by contrasting (Table 4) its sonic moduli with those of a film and fiber of an aromatic polyimide, XI.



XI

TABLE 4. Variation of Sonic Modulus with Drawing

	Sonic modulus (g/den)	
	VIII	XI
Unoriented film	50	37.5
Extruded fiber (no stretch)	62	-
As-spun fiber (oriented by stretching)	251	-
Hot-drawn fiber (stretched to the maximum)	550	72.2

Dynamic Mechanical Modulus (E') and Sonic Modulus

The moduli of the hot-drawn fibers from VIII were determined by means of the Vibron instrument at 0% relative humidity (RH) and were found to be comparable to those found by means of the Instron Tester at 65% RH and 21°C, i.e., 455 and 468 g/den, respectively. The modulus (E') as measured by means of the Vibron instrument remained constant to the temperature limits of the instrument, 220°C, whereas the modulus obtained from the Instron Tester dropped to a value of 331 g/den at 200°C and to a value of 187 g/den at 250°C.

The sonic moduli determined at 0% RH for fibers of IV and VIII, however, were considerably higher than the moduli obtained by means of either the Vibron instrument or the Instron Tester. Thus, at 30°C, the sonic modulus for IV was 136 g/den and for VIII, 680 g/den. However, the sonic moduli were found to decrease with increasing temperature; e.g., the moduli of IV and VIII at 100°C were, respectively, 120 and 600 g/den, and at 150°C the sonic modulus for IV was 104 g/den.

Color, Density, and Birefringence

All of the fibers were white in the initial gel state. As the fibers collapsed on the drier rolls, some of these developed a slight yellow tint, although even the hot-drawn version of VIII could be obtained as a nearly white fiber if great care was exercised to maintain a low pH for the water used to wash the fiber and to exclude metal ions from the wash water. Exposure to base or heavy metal salts produced a yellow color even after the hot-drawing of fiber of VIII, undoubtedly because of the production of the enol form of the hydrazide linkage or the formation of a metal ion chelate.

The density of the fibers was found to be dependent upon the structure, the degree of regularity of the structural units, and the degree of orientation and crystallinity. In general, the density ranged from that corresponding to aromatic polyamides to a high of about 1.46 g/cc. This range is remarkably broad when it is considered that the range for most fibers from aromatic polyamides is only 1.35-1.36 g/cc [10]. The density of as-spun fiber of IV was 1.34 g/cc while that of hot-drawn fiber of IV was 1.37 g/cc; the density of as-spun fiber of VIII was 1.43 g/cc while that of hot-drawn fiber of VIII was 1.46 g/cc. The latter density is ~97% of the theoretical density of 1.51 g/cc [11].

The fact that aromatic polyamide-hydrazides possess higher densities than wholly aromatic polyamides is made more understandable when it is considered that polyhydrazides have relatively high densities, e.g., as-spun fiber of X has a density of 1.38 g/cc and the hot-drawn fiber of X has a density of 1.40 g/cc. A fiber from an aromatic polyamide having equal proportions of meta- and para-oriented rings was reported to have a density of 1.36 g/cc [12].

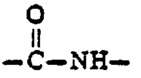
Another factor which must be taken into consideration in attempting to understand the very high densities observed for the all para-oriented polyamide-hydrazides is that of close packing of the aromatic rings which probably tend to lie in the plane parallel to the fiber axis. The same is probably true for hot-drawn fibers from the all para-oriented polyamides, for they have quite high densities, 1.37 to 1.47 g/cc [13].

The birefringence of fibers from VIII was quite high for both the as-spun fiber, 0.220, and the hot-drawn fiber, 0.356.

Orientation and Crystallinity

The x-ray diffraction patterns for hot-drawn fibers of IV and VIII (Fig. 1) show high orientation and crystallinity. The crystallinity index for hot-drawn fiber of VIII determined from x-ray analysis is in excess of 90%, which is in good agreement with the ~97% crystallinity estimated from density determinations. The crystallinity index for as-spun fiber of VIII was of the order of only 30%.

Moisture Regain

The moisture regain for fiber of VIII was found to be related to orientation. Thus cast film of VIII was found to have a moisture regain at 21°C and 65% RH of 5.8%; this value is comparable to that for hot-drawn fibers from aromatic polyamides [12]. However, the as-spun fiber of VIII has an appreciably lower moisture regain, 4.9%, while the hot-drawn fiber has a rather low moisture regain, 2.9%, for an aromatic polymer containing  $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$ groups, i.e., amide and hydrazide linkages. (A fiber of XI, which is wholly

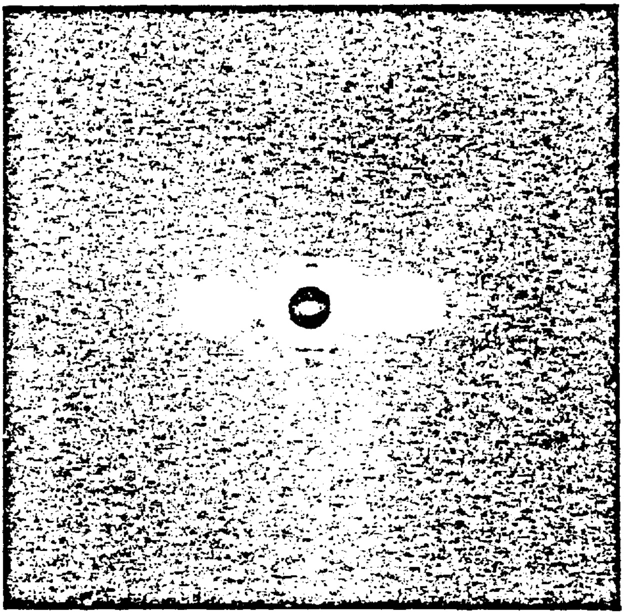


FIG. 1. X-ray diffraction pattern of hot-drawn fiber from VIII.

aromatic but does not contain amide linkages, has a moisture regain of 1.7%, which is a considerably greater value than that of PET fiber.)

Thermal Properties

As pointed out by Culbertson [5], it should be possible to prepare thermally stable ordered oxadiazole-amide copolymers by cyclodehydration of precursor polyamide-hydrazides. The programmed differential thermal analysis (DTA) of fibers from Polymers IV-VIII and the fiber from the polyhydrazide, X, shows (Table 5) the temperatures at which cyclodehydration occurs. The temperatures at which the polyoxidazole-amides and the polyoxadiazole melt are likewise given in Table 5.

It is interesting to note that the temperature of cyclodehydration for the polymers of Table 5 is about 360-370°C except for the all para-oriented polyamide-hydrazide, which resists cyclodehydration to 395°C.

The melting points of the polymers containing oxadiazole groups,

TABLE 5. Thermal Properties of Fibers from Polymers Containing Hydrazide and Oxadiazole Groups

Polymer	Temperature of cyclodehydration (°C)[a]	Melting point of polymer containing oxadiazole group (°C)[a]
IV	370	450
V	365	370
VI	365	390
VII	370	455
VIII	395	495 (525 dec[b])
X	360	450

[a] Endothermic transition observed by differential thermal analysis (DTA) in nitrogen (rate = 20°C/min).

[b] Decomposition temperature observed by exotherm in the DTA curve; this temperature is confirmed by the thermogravimetric analysis (TGA) in nitrogen (rate = 15°C/min).

with the exception of the all para-oriented polymer, occur at about 450°C when the precursor contains a terephthaloyl moiety attached to a hydrazide linkage. The two polymers containing an isophthaloyl moiety attached to a hydrazide linkage have melting points at about 370-390°C. (See the earlier discussion regarding greater rodlike structure for polymers containing terephthaldihydrazide-diamine moieties.) The all para-oriented ordered oxadiazole-amide copolymer has the highest melting point, as might be expected, and appears to be stable up to the temperature, 525°C, at which the oxadiazole ring is ruptured.

Although the programmed DTA curves show that cyclodehydration occurs even during the very rapid rate of heating used for the analysis, a more practical procedure is to heat the fiber to a temperature slightly above the temperature at which cyclodehydration occurs. Thus heating of the hot-drawn fiber from VIII to 410°C and retracing the curve shows (Fig. 2) that cyclodehydration is completed. Heating

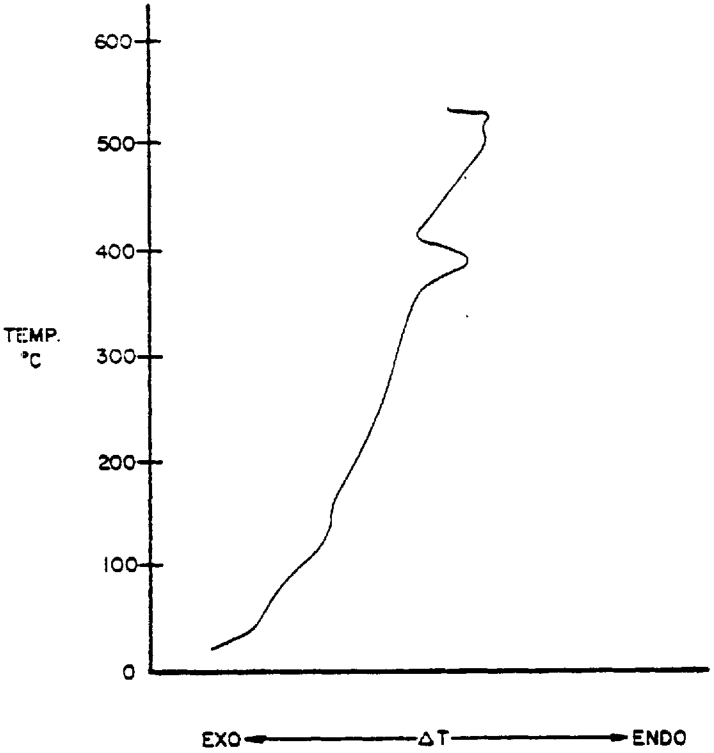


FIG. 2a. Programmed DTA (rate = 20°C/min) in nitrogen of hot-drawn fiber from VIII: continuous trace.

to 300°C, which is sufficient for the cyclodehydration of the fiber of X if the heat treatment is continued for several hours [14] (or is catalyzed [15]), does not effect cyclodehydration for fiber of VIII.

The programmed weight retention curve (TGA) for fiber of VIII shows (Fig. 3) initial weight loss from absorbed water with loss of weight from cyclodehydration occurring from 350-400°C. Weight loss is rapid at 525°C, the temperature at which the oxadiazole group is thermally ruptured.

Despite the fact that cyclodehydration can be shown to occur rather completely for the polyamide-hydrazides, fibers of good tensile properties were not obtained by thermal treatments of Fibers IV and VIII. Possibly the disruption of the fine structure

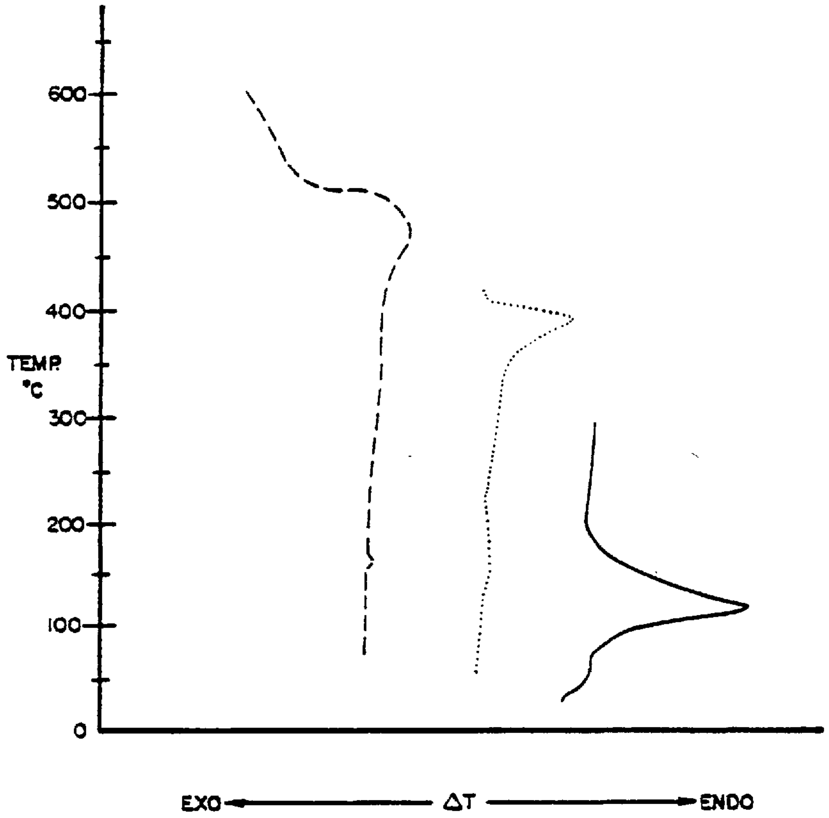


FIG. 2b. Programmed DTA (rate = 20°C/min) in nitrogen hot-drawn fiber from VIII: (——) heated to 300°C and cooled to room temperature; (· ·) reheated to 410°C and cooled to room temperature; (- -) reheated to 600°C.

of the precursor fibers is too great to yield fibers of the ordered oxadiazole-amide copolymer type having good tensile properties. Perhaps use of catalyzed cyclodehydration, such as that reported [15] for fiber of X, might allow for the preparation of the desired fibers.

The Effect of Heat on Fiber Tensile Properties

The retention of tensile properties (Table 6) for Fibers IV and VIII to 250°C is remarkable (Figs. 4 and 5). Above 300°C (Fig. 4)

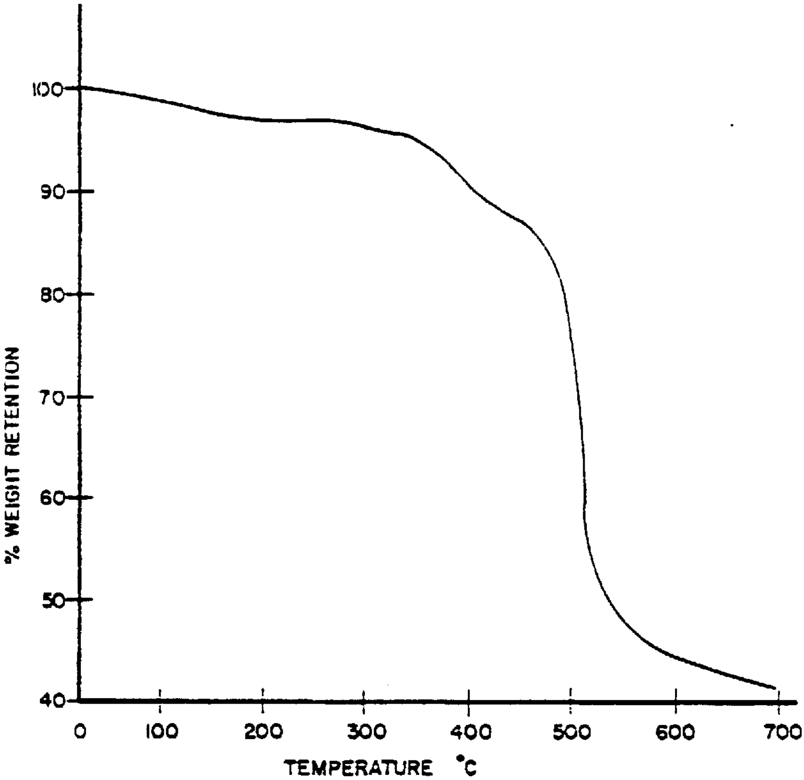


FIG. 3. Programmed TGA (rate = 15°C/min) in nitrogen of fiber from VIII. (The curves for the as-spun and hot-drawn fiber were superimposable.)

there is a sharp drop in tensile strength, possibly because of the onset of conversion (cyclodehydration) of the hydrazide groups to oxadiazole groups. Such chemical reactions within the fiber necessarily result in disruption of the fine structure of the fiber, hence poorer tensile properties. The higher para-phenylene ring content in VIII relative to IV does not confer on it higher retention of tensile properties at the elevated temperatures. But the as-spun fiber of VIII can be compared favorably with the hot-drawn fiber of IV.

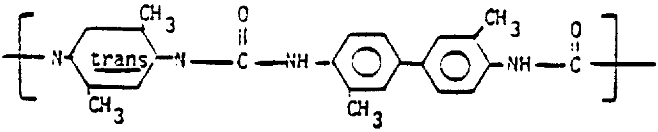
The retention of tensile properties for fibers of IV and VIII after prolonged heat-aging in air at 125, 185, 225, and 300°C were determined. At 125°C, both the as-spun and hot-drawn fibers of VIII remained unchanged in tensile properties through 40 days. At

TABLE 6. Retention of Tensile Properties at Elevated Temperatures

	T/E/M_i		
	VIII		
T (°C)	As-spun	Hot-drawn	IV, hot-drawn
21	6.6/28.0/49	12.5/4.3/468	5.4/18.6/85
50	6.1/30.3/122	10.9/3.6/478	4.5/16.6/63
100	5.1/33.1/106	9.1/3.0/530	4.6/17.3/63
150	4.5/36.8/84	8.5/3.2/444	4.2/21.1/54
200	4.3/35.6/75	6.0/3.5/331	3.3/19.8/50
250	2.7/56.6/52	3.9/10.2/187	2.5/22.9/41
300	1.6/14.6/62	3.6/2.3/208	1.2/14.8/14
350	-	0.5/0.6/136	0.2/3/-

125°C, nylon 66 and polyethylene terephthalate (PET) tire cords relaxed considerably so that their elongations increased 50% and the initial modulus of the PET tire cord decreased 25%. At 185°C, hot-drawn fibers of IV and VIII were unchanged for the 48 hr of test and the as-spun fiber of VIII remained unchanged through 24 hr; the nylon 66 and PET tire cords lost 20% of their tenacity and their elongations doubled, i.e., they relaxed considerably.

A high modulus polyurea, XII, previously reported [16] in the patent literature, was prepared as a control: tenacity, 7.0 g/den;



XII

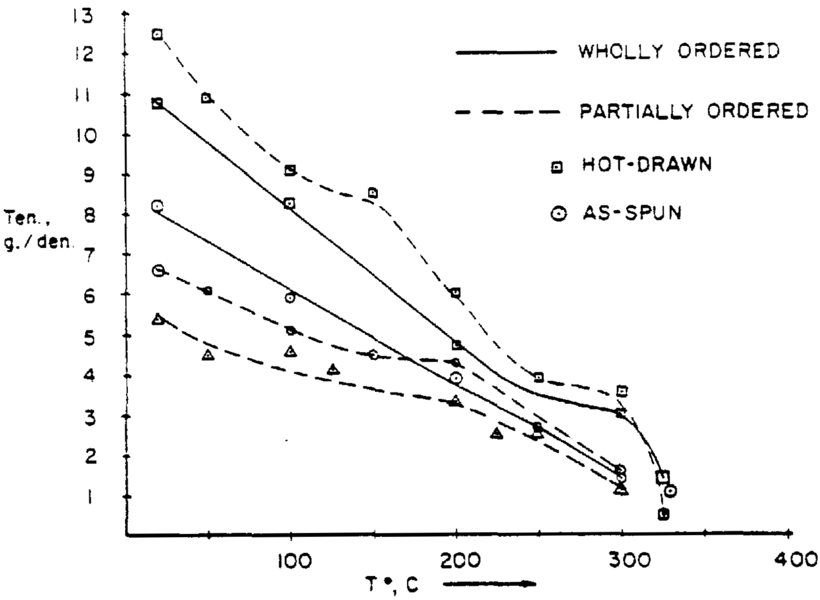
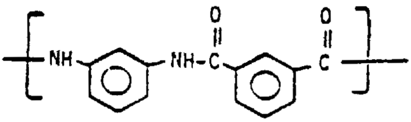


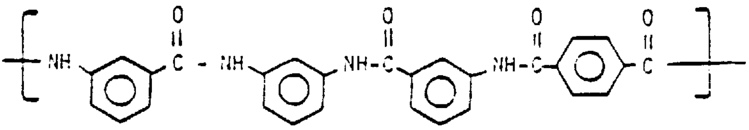
FIG. 4. Tenacity of some polyamide-hydrazide fibers at elevated temperatures in air. (△) Hot-drawn fiber of IV; (- -) fiber of partially ordered VIII; (——) fiber of wholly ordered VIII.

elongation, 2.4%; initial modulus, 356; denier, 9.4 den/filament. The polyurea fiber was too degraded to be tested after 4 hr exposure at 185°C in air.

Heat-aging at 225°C in air produced a 50% drop in tenacity for both as-spun and hot-drawn VIII after 10 days; the drop in elongation for the hot-drawn fiber was likewise 50% but the as-spun fiber after the heat-soak retained only 15% of its original elongation. However, the tensile properties of the as-spun fiber did not change from the 10th day through the duration of the test, 42 days. Aromatic polyamide fibers, such as XIII and XIV, were unchanged by the heat-aging at 225°C through the 42 days of the test.



XIII



XIV

The heat-aging of the fibers of IV and VIII at 300°C in air produced some remarkable results (Table 7). The as-spun fiber of IV dropped in tenacity and elongation through 8 hr but the properties were unchanged thereafter to 120 hr. A probable explanation for these results may be that this fiber was converted to an ordered oxadiazole-amide copolymer, a type of fiber which has been reported [17] to possess considerable thermooxidative stability—appreciably greater than that of fibers from aromatic polyamides such as XIII and XIV. Presumably the hydrazide linkage of IV, because of the lower polymer softening point of IV compared to that of VIII, can more readily undergo cyclodehydration to the oxadiazole group. Fibers of X underwent rapid loss of tensile

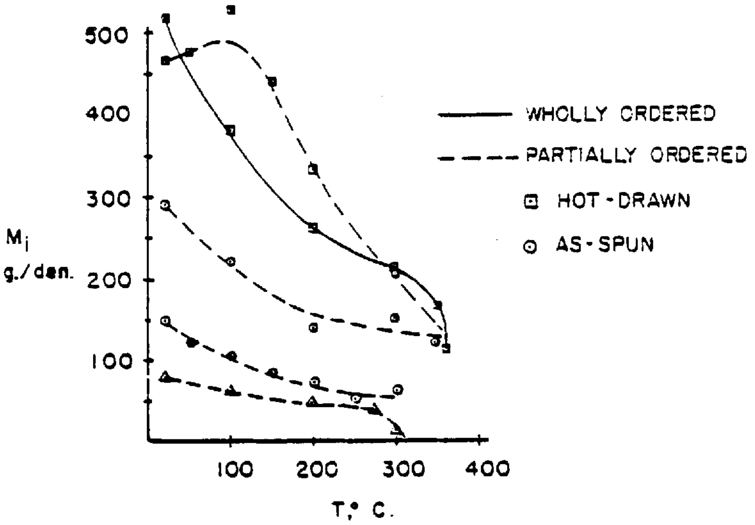


FIG. 5. Initial moduli of some polyamide-hydrazide fibers at elevated temperatures in air. (△) Hot-drawn fiber of IV; (- -) fiber of partially ordered VIII; (——) fiber of wholly ordered VIII.

TABLE 7. Heat-aging in Air at 300°C for Fibers From Polymers Containing Hydrazide Linkages

Time (hr)	$\frac{T/E/M_i}{den}$					
	VIII		IV		X[a]	
	As-spun	Hot-drawn	As-spun	Hot-drawn	As-spun	Hot-drawn
0	6.62/28.3/- (4.18)	12.5/4.3/468 (2.79)	3.04/20.4/56 (7.97)	5.4/18.6/85 (4.23)	2.49/19.0/53 (15.16)	4.19/11.1/77 (10.82)
4	6.39/2.6/- (3.63)	- -		2.0/14.1/58 (4.71)	1.55/1.5 (13.67)	1.27/1.60 (9.26)
8	3.32/1.4/- (3.78)	- -	1.05/11.04 (11.4)	1.8/10.8/58 (4.71)	0.88/1.6 (13.5)	1.21/1.8 (9.74)
24	3.51/1.7/- (3.6)	- -	1.16/12.1 (10.13)	1.7/7.4/61 (4.67)	0.84/1.64 (13.6)	1.30/1.57 (9.7)
48				1.6/7.6/57 (4.87)		
96	1.34/0.82/0 (3.93)	3.3/1.5/253[b]	1.32/14.5 (10.8)			
120	1.47/1.4/- (4.61)	2.3/1.6/212[c]	1.32/11.9 (9.1)	1.7/7.1/61 (4.67)		
168				1.5/5.8/57 (4.63)		

[a] Inherent viscosity at 30°C for 0.5 g/100 ml DMSO, 3.08.

[b] 72 hr highest single break: 4.1/2.0/258.

[c] 136 hr highest single break: 4.6/2.5/226.

properties in the test. In Figs. 6 and 7 the effects of heat-aging on tenacity and elongation at 185 and 300°C on several polyamide-hydrazide fibers are compared.

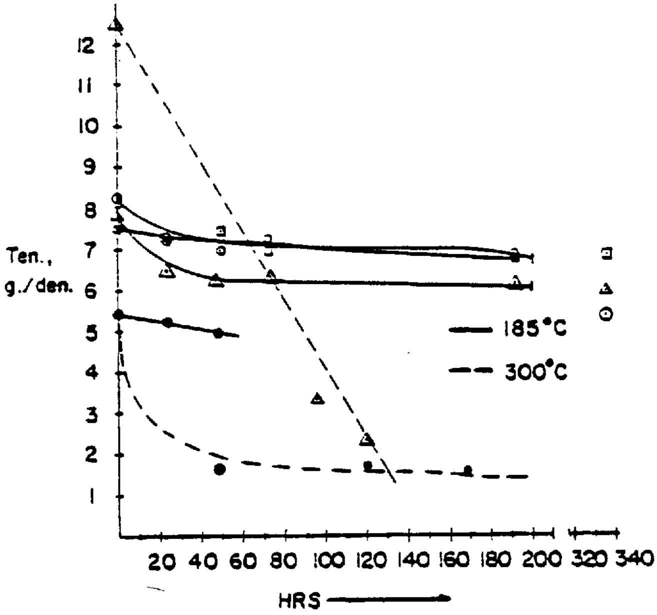


FIG. 6. Retention of tenacity for some polyamide-hydrazide fibers after heat-aging in air. (●) Hot-drawn fiber of IV; (⊙) as-spun fiber of wholly ordered VIII; (▲) as-spun fiber of partially ordered VIII used for 185°C test and hot-drawn fiber used for 300°C test; (□) as-spun fiber of random copolymer produced from the simultaneous addition of 20 mole % ICl and 80 mole % TCl to a solution of p-aminobenzhydrazide in DMAc.

The dry heat-shrinkage (Table 8) of hot-drawn VIII is very small, even less than that for fiber of XIII and about the same as that for fiber of XIV to about 350°C. Although above 350°C some degradation (i.e., some discoloration) was noted, it is remarkable that no large amount of shrinkage occurred when it is considered that cyclodehydration of the hydrazide linkage can occur on long exposure above about 300°C.

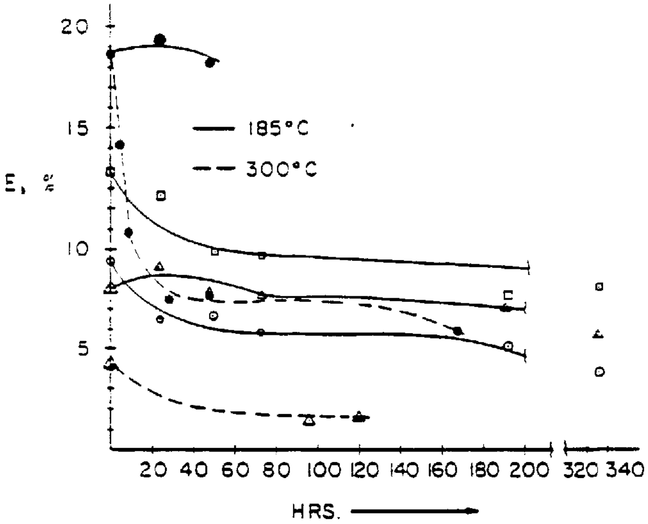


FIG. 7. Retention of per cent elongation for some polyamide-hydrazine fibers after heat-aging in air. (●) Hot-drawn fiber of IV; (□) as-spun fiber of wholly ordered VIII; (⊖) as-spun fiber of partially ordered VIII used for 185°C test and hot-drawn fiber used for 300°C test; (△) as-spun fiber of random copolymer produced from the simultaneous addition of 20 mole % ICl and 80 mole % TCl to a solution of p-aminobenzhydrazide in DMAc.

TABLE 8. Dry Heat-Shrinkage of Hot-Drawn Fiber VIII

T (°C)	% Shrinkage
150	0.0
200	1.3
250	1.5
300	1.9
350	2.3
400	5.5[a]

[a] Some degradation occurs at temperatures above 350°C.

Chemical Resistance

The chemical resistance (Table 9) for fibers of polyamide-hydrazides is considerably better than that for fibers of polyhydrazides and approaches that of the fibers from aromatic polyamides [18]. It should be noted that the poor resistance of fibers of IV and VIII toward DMAc when compared to fiber of X can be accounted for by the fact that DMAc with added salts is a solvent for IV and a partial solvent for VIII, whereas DMAc is not a solvent for polyhydrazide X.

Additional data on the resistance of Fiber VIII toward heated water are to be found in Table 10. The tensile properties measured in water at 21 and 90°C are rather good when it is considered that most fibers lose considerable strength and modulus in both these tests. Further, when the 8.2 g/den tenacity at 90°C in water is compared to the 9.1 g/den tenacity at 100°C in air (Table 6), the effect of the water is remarkably small. No shrinkage after boil-off is observed for Fiber VIII. Even more striking are the results (Table 10) obtained after exposure to steam at an elevated temperature. Both nylon 66 and PET tire cords used as controls in the test became too cemented together to be broken for their tensile properties.

Unlike glass fiber which is adversely affected by water even at room temperature, fiber of VIII, particularly the hot-drawn fiber, shows excellent retention of strength and modulus in water at 50°C to 210 days (Table 11).

The fiber from the polyurea (XII), when subjected to the test conditions of Table 9, was unchanged in tensile properties under basic conditions at 21 and 95°C but failed under acid conditions at 95°C. Exposure to DMAc caused the fibers to fuse together.

Light Stability

The UV light stability (Fade-Ometer) of the fibers from polymers containing hydrazide linkages is quite poor (Table 12), even poorer than that of fibers from aromatic polyamides, such as XIII and XIV, which have been compared to fibers of nylon 66 containing no light stabilizers [18].

TABLE 9. Chemical Resistance of Fibers Containing the Hydrazide Linkage

Chemical	Concn (%)	T (°C)	Time (hr)	T/E/M_i VIII (hot-drawn)	 IV (as-spun)	 X (hot-drawn)
None	-	21	-	12.5/4.3/468	5.4/18.6/85	4.2/11.1/77
Acids						
Sulfuric	10	21	168	10.8/3.6/451	3.5/15.6/76	2.8/7.50/80
Sulfuric	10	95	5	2.8/0.9/432	1.8/5.4/65	Failed
Bases						
Sodium hydroxide	10	21	168	Failed[a]	Failed[a]	Failed[a]
Sodium hydroxide	10	60	5	2.1/3.0/187	Failed[b]	Failed[b]
Ammonium hydroxide	38	21	168	7.9/3.8/380	3.9/35.9/53	2.2/26.4/52
Miscellaneous						
Water	100	100	24	12.3/3.5/405	4.5/22.5/63	3.9/13.5/68
Dimethylacetamide	100	21	168	1.3/2.9/66	Failed[b]	4.3/12.5/83

[a] Dissolved when washed with water at conclusion of test.

[b] Too brittle to test.

TABLE 10. Hydrolytic Stability of Polyamide Hydrazide Fiber VIII

Tensile properties at elevated temperatures in water

T in water (°C)	$T/E/M_i$[a,b] As-spun	$T/E/M_i$[a,b] Hot-drawn
21	6.3/17.2/222	11.2/2.7/512
90	4.0/37.9/123	8.2/2.9/404

Tensile properties after 15 min exposure to 215 psi steam at 170°C

	$T/E/M_i$[a,c]
Control fiber	9.7/2.6/569
Test fiber	7.0/1.3/660

[a] T = tenacity, g/den; E = elongation, %; M_i = initial modulus, g/den.
[b] Single filament breaks.
[c] Yarn breaks.

EXPERIMENTAL

Monomers and Solvent

Isophthaloyl and terephthaloyl chlorides were used as received from Hooker Chemical Corp., or alternatively, from the Union Carbide Corp. p-Aminobenzhydrazide was used as obtained from Gallard-Schlesinger Chemical Manufacturing Corp.; DMAc from the DuPont Co. was dried over molecular sieves prior to use. The m-aminobenzhydrazide was prepared by conventional synthesis.

Polymerizations

A typical polymerization, that for Polymer VIII, was performed as follows. To a dry 3 liter resin kettle fitted with an anchor-type

TABLE 11. Tensile Properties of Fiber VIII after Soaking in Water at 50°C[a]

	T/E/M_i[b,c] (work) den	
Time (days)	As-spun	Hot-drawn
0	5.9/18.2/179 (0.875)4.3	10.0/3.0/445 (-)2.95
30	5.3/11.0/179 (-)4.0	-
60	4.9/12.2/165 (0.460)4.2	9.3/3.0/424 (0.189)2.9
120	4.3/8.7/167 (0.296)4.1	-
180	-	9.2/2.8/437 (0.175)3.6
210	-	8.6/2.5/496 (0.152)2.8

[a] The fiber yarn was sealed in capped polymerization tubes containing water. The handling of the fibers, i.e., entangling, could partially be responsible for the slightly lower breaks obtained compared to the control.

[b] T = tenacity, g/den; E = elongation to break, %; M_i = initial modulus, g/den; work = work to break, g-cm/den-cm; den = denier per filament.

[c] Single filament breaks.

stirrer was added 83.05 g (0.55 mole) of p-aminobenzhydrazide and 1.5 liters of DMAc containing 5% dissolved lithium chloride (the solution was stored over molecular sieves prior to use in order to assure dryness of the solvent). The resulting solution was cooled to -10°C and 111.65 g (0.55 mole) of terephthaloyl chloride was added with vigorous stirring. After 5 min the reaction mass

TABLE 12. UV Stability of Fibers Containing Hydrazide Linkages

S.F. hr[a]	VIII hot-drawn	IV as-spun	X hot-drawn (m-/p-phenylene hydrazide)
0	11.35/3.6/571 (2.81)	5.60/17.1/88 (3.97)	4.89/10.9/89 (9.78)
20	6.44/3.8/343 (2.8)	2.17/7.3/67 (4.23)	2.82/6.35/89 (9.78)
40	-	1.83/6.0/68 (4.16)	1.96/4.32/72 (10.2)
60	1.15/1.35/189 (2.76)	1.35/3.06/70 (4.16)	1.59/3.0/83 (10.1)
80	-[b]	1.09/2.60/56 (3.88)	1.48/3.1/81 (9.85)

[a] Standard Fade-Ometer hours.

[b] Too brittle to test; note that the original elongation was much lower for this fiber than for the other fibers used in this test.

was allowed to warm to 0°C and, after 5 min at 0°C, the polymer solution was allowed to warm to room temperature (RT). At the end of 30 min a highly viscous solution was obtained.

Prior to spinning, the acid solution was neutralized by the addition of 40.64 g (0.55 mole) of lithium carbonate slurried in 300 ml of DMAc-5% LiCl solvent. The mass was stirred for 30 min at RT, then warmed to 35°C. After 30 min at 35°C, the polymer solution was heated to 55°C and after 30 min it was heated to 65°C at which temperature it was stirred for 45 min prior to the addition of another 50 ml portion of DMAc-5% LiCl. Finally, the spinning dope was heated to 80°C and held at that temperature for 1 hr at atmospheric pressure and 45 min at approximately 60 mm pressure to remove dissolved gases. The solids content of the dope was 7.7%.

A portion of the dope was precipitated into water and the isolated polymer was dried. The inherent viscosity of the polymer, determined on 0.5 g polymer in 100 ml of dimethylsulfoxide (DMSO) at 30°C, was 3.90.

Similar results were obtained for VIII in DMAc (without added salts), NMP, and HPT.

Determination of Tensile Properties

Tensile properties were obtained on single filaments with an Instron Tester at 70°F and 65% RH. Gauge length was 1 in. and the rate of extension was 100%/min. In the elevated temperature tests, fibers were held at the indicated temperatures in air for 1 min, then broken at that temperature. In the heat-aging tests and the tests in various reagents, fibers were exposed for the indicated periods of time and broken at RT.

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