

## Fibers from Aromatic Copolyamides of Limited Order\*

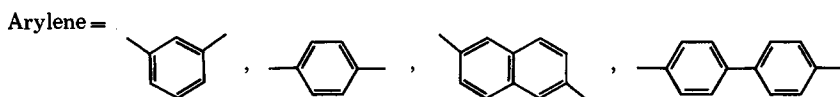
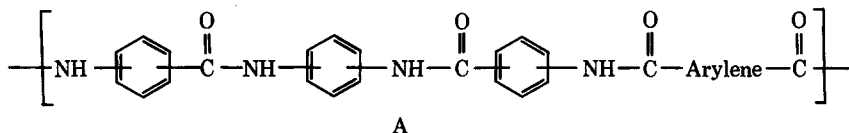
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### Synopsis

Fibers were spun from six different, wholly aromatic copolyamides of limited order. Tensile properties of the fibers were obtained at standard conditions and, for selected fibers, at elevated temperatures and after heat-aging at 300°C in air. The dry-heat shrinkage determined up to 400°C on selected fibers was relatively low; zero-strength temperatures ranged from 375°C to 495°C. Resistance to numerous chemical reagents was determined for one of the fibers and found to be comparable to that of the fibers from other wholly aromatic polyamides. Resistance to ultraviolet light appeared to be of the same order as that of unstabilized nylon 66.

### INTRODUCTION

Previous papers in this series<sup>1-3</sup> have described the thermal properties of fibers from ordered aromatic copolyamides (A):



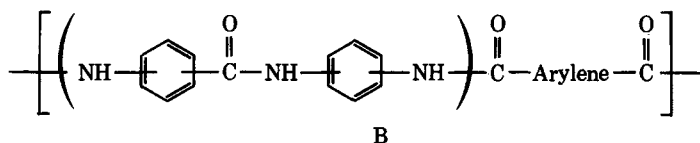
Because of the regularity of structure in the repeat units of such polymers, their properties resemble those to be expected from homopolymers, and meaningful structure-property correlations, particularly as regards thermal properties, may be drawn.

For copolyamides of limited order (B),<sup>4</sup> it is a much more difficult matter to correlate properties with structural units because of the lack of regularity in the polymer repeat unit. The "copolymeric effect" produced by the

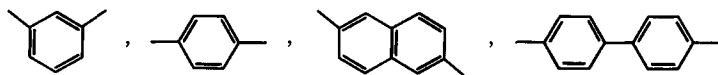
\* Part XV in a series on New High Temperature Polymers.

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Arylene =



random head-to-head and head-to-tail segments in B has a pronounced effect on thermal properties; e.g., when B contains only meta-oriented phenylene rings; a polymer having a melting point of about 290°C is obtained, while A containing all meta-oriented phenylene rings in the ordered arrangement has a melting point of about 400°C. However, as pointed out earlier,<sup>5</sup> when B contains only para-oriented phenylene rings, the fiber produced therefrom has as high a melting point and decomposition point as has been reported for any polyamide.

In the present work, we wish to report the properties of several fibers derived from aromatic copolyamides of limited order; the polymers used for these fibers have a thermal behavior which lies between the extremes shown by the polymer having all meta-oriented phenylene rings and that having all para-oriented ones.

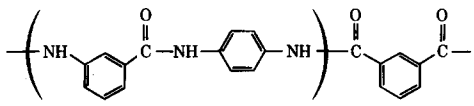
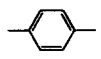
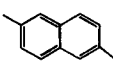
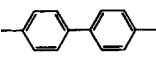
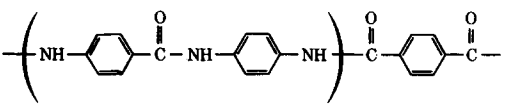
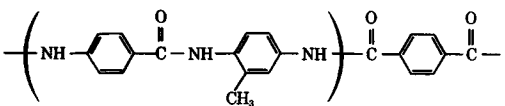
## RESULTS AND DISCUSSION

The structures of the various polymers used for the preparation of fibers are shown in Table I. Unless otherwise noted, the inherent viscosities given in Table I are those corresponding to the polymers from which the fibers of this report were prepared. Although the molecular weights of the several polymers were not determined, the rather high inherent viscosity values (2.0 to 4.7) obtained imply that the polymers are of high molecular weight. The fact that the viscosities were determined in concentrated sulfuric acid lends all the more credibility to such a supposition. Then, too, there is the evidence that fibers of high tensile strength, such as those reported here, are prepared only from relatively high molecular weight polymers.

### Fiber Properties

Strong, highly lustrous and well-collapsed fibers were obtained by spinning from the amide-type solvents, e.g., dimethylacetamide (DMAc), hexamethylphosphoric triamide (HPT), and N-methylpyrrolidone (NMP), used as the polymerization media for the various polymers. In general, the solutions of polymer contained dissolved lithium chloride, which was present prior to the preparation of the polymer or was produced by the neutralization of by-product HCl with LiOH. The physical properties of the several fibers are given in Table II. Although fibers were spun by

TABLE I  
Aromatic Copolyamides of Limited Order

Polymer no.	Structure :	Inherent viscosity *
I		2.1
II		2.7
III		2.4
IV		2.0
V		4.7
VI		3.5

\* Determined at 30°C for a solution of 0.5 g polymer dissolved in 100 ml concentrated sulfuric acid.

either the wet- or dry-spinning methods, the former method generally gave superior results and was the method of choice. Hot-drawing of the fibers obtained from either spinning process resulted in improved fibers, i.e., fibers of higher tensile strength and modulus. For fiber I, which contains a

TABLE II  
Fiber Properties\* of Aromatic Copolyamides of Limited Order

Properties	I	II	III	IV	V	VI
Tenacity, g/den <sup>b</sup>	5.7	5.3	4.3 <sup>c</sup>	2.7 <sup>d</sup>	6.2	4.3 <sup>d,e</sup>
Elongation, %	22.8	19.7	40.9 <sup>c</sup>	9.7 <sup>d</sup>	3.4	12.0 <sup>d,e</sup>
Initial modulus, g/den	77	84	97 <sup>c</sup>	85 <sup>d</sup>	236	203 <sup>d,e</sup>
Moisture regain, <sup>f</sup>	7.0	—	—	—	—	—
Density, g/cc	1.32	1.29	—	1.29	—	—

\* Single filament properties for unboiled-off fibers at 21°C and 65% relative humidity. Unless otherwise noted, the various fibers were hot-drawn to the maximum at about 300°C.

<sup>b</sup> Deniers of the fibers, in den/fil., are: I, 6.9; II, 4.6; III, 1.2; IV, 19.7 (bundle); V, 11.5; VI, 26.3 (bundle).

<sup>c</sup> As-spun fiber, i.e., not hot-drawn.

<sup>d</sup> Properties determined for a bundle of as-spun fibers.

<sup>e</sup> Properties of hot-drawn fiber (23.8 bundle denier): tenacity, 5.0 g/den; elongation, 1.9%; initial modulus, 361 g/den.

<sup>f</sup> Equilibrium moisture at 21°C and 65% relative humidity.

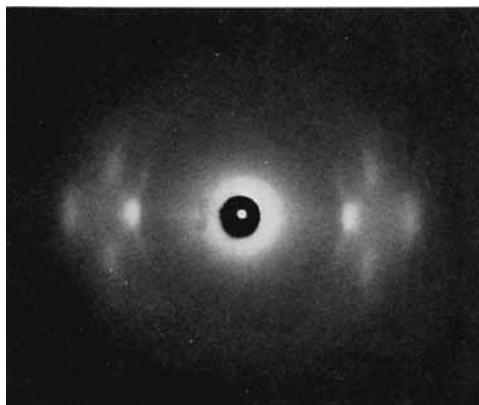


Fig. 1. X-Ray diffraction pattern of fiber I hot-drawn ( $1.7\times$ ) at  $350^{\circ}\text{C}$ .

higher proportion of meta-oriented phenylene rings than the other fibers of Table II, hot-drawing was required to convert the amorphous, as-spun fiber (i.e., a fiber which has received orientation during spinning because of stretching in the gel state but has not been further oriented by stretching at an elevated temperature) to a crystalline fiber (Fig. 1).

The color of the fibers I–IV was white, while that of fibers V and VI was a pale yellow, a color often associated with fibers containing all para-oriented rings. The densities (1.29–1.32) of fibers from polymers I, II, and IV are somewhat low compared to those (1.35–1.37) of fibers from ordered polymers containing comparable ring structures. This phenomenon could be the result of poorer packing for the copolymers of limited order, which can contain segments of polymer in the head-to-head and head-to-tail arrangement.<sup>4,5</sup>

Although the fiber properties of V from polymer of very high molecular weight ( $\eta_{inh} > 8$ ) were reported earlier,<sup>5</sup> the fiber properties of V from a lower molecular weight polymer (and in the range usually observed) are given in Table II.

#### Fiber Properties at Elevated Temperatures

Only the tensile properties for fiber I were determined at an elevated temperature. At  $300^{\circ}\text{C}$ , the tenacity and initial modulus of fiber I were found to be 1.7 g/den and 40 g/den, respectively, at an elongation of 20%. These values are comparable to those of many commercial textile fibers at room temperature.

The high zero-strength temperatures for fibers V and VI (Table III) indicate that these fibers, too, should have excellent tensile properties at elevated temperatures. (Note: Fiber from polymer V, having an exceptionally high inherent viscosity, was reported earlier and it indeed did show high strength at high temperatures: 2.5 g/den at  $300^{\circ}\text{C}$ ; 2.0 g/den at  $400^{\circ}\text{C}$ ; and 1.0 g/den at  $450^{\circ}\text{C}$ .)<sup>5</sup>

TABLE III  
Dry-Heat Shrinkage and Zero-Strength Temperatures

Fibers	Shrinkage, <sup>a</sup> %			Zero-strength temp., <sup>b</sup> °C
	300°C	350°C	400°C	
I	7	32	73	375
V	—	—	2	495
VI	—	—	—	405

<sup>a</sup> The length of the fiber was redetermined after it was placed on a heated metal surface of the indicated temperature.

<sup>b</sup> Temperature at which the fiber breaks under a load of 0.1 g/den when heated at 5°C/min in nitrogen.

The dry-heat shrinkage values for fibers I and V are given in Table III; these indicate that these fibers possess considerable dimensional stability to very high temperatures.

#### Fiber Properties After Heat-Aging

The retention of tensile strength (Table IV) by fiber I after heat-aging at 300°C in air can be considered to be only fair relative to other aromatic polyamides containing *p*-phenylene rings. Probably the poor packing referred to earlier may account for this behavior. On the other hand, the elongation of fiber I after the heat soak at 300°C in air is surprisingly good, despite a nearly 50% drop after 72 hr, and compares favorably with other aromatic polyamides in this regard. The heat-aging data for fiber II (Table IV) indicates poorer thermal stability for II than for I, although in terms of per cent retention of tensile strength, elongation, and modulus it would appear to be comparable to fiber I. But it must be pointed out that a fiber of higher initial strength than that of II given in Table IV might be expected to drop to about the same final tensile strength as observed for II after heat aging; almost certainly the per cent retention of strength would not be so high for a fiber having a high initial tensile strength.

TABLE IV  
Tensile Properties of Fibers After Heat-Aging in Air at 300°C<sup>a</sup>

Time, hr	<i>T/E</i> <sup>b</sup>	
	I	II
0	5.7/22.8	2.4/14.7 (71) <sup>c</sup>
4	—	2.3/14.6 (65) <sup>c</sup>
8	3.0/23.0	—
17	—	1.8/11.7 (57) <sup>c</sup>
36	2.6/16.0	—
40	—	1.4/6.3 (56) <sup>c</sup>
72	2.4/13.0	—

<sup>a</sup> Tested at 21°C after the heat soak.

<sup>b</sup> *T/E* = tenacity, g/den; elongation-to-break, %.

<sup>c</sup> Initial modulus (g/den).

### Chemical Resistance

The chemical resistance (Table V) for fiber I in a variety of solvents and reagents, like that of several other fibers from wholly aromatic polyamides,<sup>2,3</sup> is rather good. It is very possible that even better retention of tensile strength might be observed for the fiber of polymer I of higher molecular weight than that of the polymer used in the test. The relatively low tensile strength (3.5 g/den instead of the 6–8 g/den) of the test specimen may also mean that this fiber is less crystalline and hence more vulnerable to penetration by solvents.

TABLE V  
Chemical Resistance for Fiber I<sup>a</sup>

Reagent	Strength, %	Temp., °C	Tensile strength retained after 10 hr exposure, %
Stoddard solvent	100	25	95
Tetrachloroethylene	100	25	94
Sodium hydroxide	10	60	80
	50	25	77
	50	60	failed
Sulfuric acid	10	60	106
	50	60	80

<sup>a</sup> From polymer of  $\eta_{inh} = 1.1$ ; original tensile strength, 3.5 g/den.

### Resistance to Ultraviolet Light

The resistance (Table VI) of fiber I to degradation by ultraviolet light (Fade-Ometer) is comparable to that of several other fibers from wholly aromatic polyamides; i.e., the ultraviolet light stability of fiber I is of the same order of magnitude as that of unstabilized nylon 66. The rapid drop in elongation, i.e., embrittlement, is characteristic of degradation of fibers from wholly aromatic polymers in general, although it is not clear whether the polymer undergoes chain scission or crosslinking which results in the embrittlement of the fiber.

TABLE VI  
Retention of Tensile Properties for Fiber I Exposed to  
Ultraviolet Light (Fade-Ometer)

Time, hr	$T/E^a$
0	7.9/7.6
20	5.3/4.8
40	4.1/3.6
80	2.7/2.1

<sup>a</sup>  $T/E$  = tenacity, g/den; elongation, %; values are based on bundle breaks; total denier of bundle, 68.0.

### Viscosity Studies For Polymer V

Viscosity measurements on a series of samples having the structure V were determined in concentrated sulfuric acid at 30°C. The Huggins constant was determined to be  $k' = 0.535$ , where  $k'$  is defined by

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2C.$$

The relationship between  $[\eta]$  and the inherent viscosity for a 0.5% solution of V is given in Figure 2; the  $[\eta]$  values of the several samples of V in concentrated sulfuric acid at 30°C were 1.70, 3.21, 5.10, 6.30, 9.20, and 13.2.

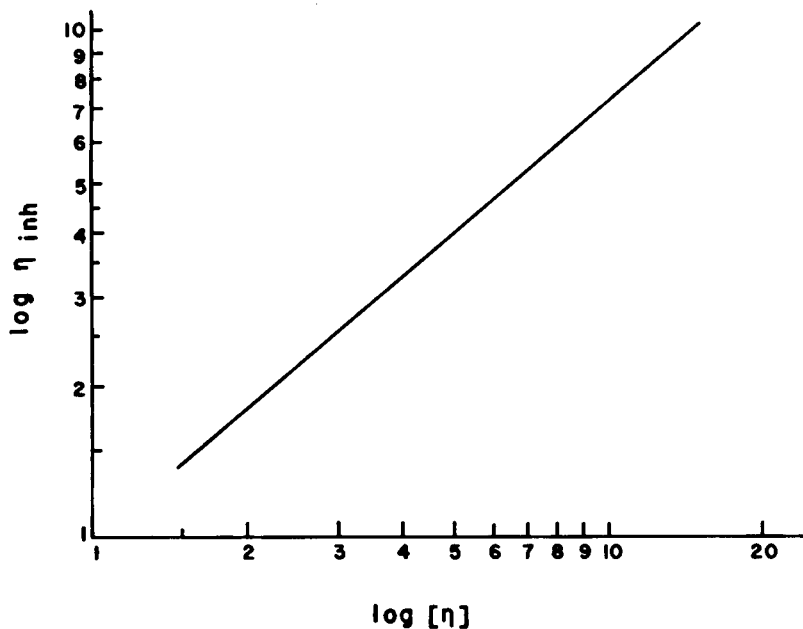


Fig. 2. Intrinsic viscosity-inherent viscosity relationship for polymer V in concentrated sulfuric acid (0.5 g polymer in 100 ml solvent) at 30°C.

### EXPERIMENTAL

Polymers were prepared<sup>4</sup> by the low-temperature solution polycondensation method and spun from solution.

Tensile properties were obtained on single filaments with an Instron tester (gauge length, 1 in.; rate of extension, 100%/min). In the elevated temperature tests, fibers were held at the indicated temperatures for 1 min, then broken at that temperature. In the heat-aging test at 300°C, fibers were exposed in the relaxed state for the indicated periods of time and broken at room temperature.

The authors wish to express their appreciation to the late Mr. H. S. Morgan for spinning of the various fibers and to Messrs. R. W. Bullard and W. L. Smith for expert technical assistance in the preparation of intermediates and polymers. The cooperation and assistance of Dr. T. L. Tolbert in supervising the preparation of selected compositions is gratefully acknowledged, as is the determination of the viscosity data and the inherent viscosity-intrinsic viscosity relationship by Dr. W. B. Witmer.

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Received May 16, 1972

Revised June 13, 1972