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High Modulus Wholly Aromatic Fibers. III. Random Copolymers Containing Hydrazide and/or Carbonamide Linkages

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High Modulus Wholly Aromatic Fibers. III. Random Copolymers Containing Hydrazide and/or Carbonamide Linkages

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ABSTRACT

Several random copolymers composed largely of p-phenylene rings connected by hydrazide and/or carbonamide linkages yielded fibers exhibiting the high tensile strengths and the very high moduli characteristic of the fibers from wholly or partially ordered polyamide-hydrazides having only p-phenylene rings. The random copolymers showed the expected improved spinning performance relative to that of the all para-oriented polyamide-hydrazides and certain polyamides containing only para-oriented phenylene rings.

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*Deceased, June 1, 1972

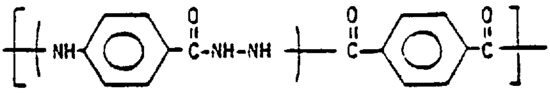
Undoubtedly the improved spinnability of the random copolymers over that observed for all-para-oriented ordered or partially ordered copolymers is attributable to better solubility.

A copolyterephthalamide based on a 90/10 mole % mixture of 4,4'-diaminobenzanilide (DBT) and p-aminobenzhydrazide gave a fiber having a tenacity, elongation, and initial modulus of 17.4 g/den, 3.7%, and 698 g/den, respectively, whereas the polyterephthalamide of 4,4'-diaminobenzanilide alone under similar spinning conditions yielded a fiber with only 5.0 g/den tenacity, 2.9% elongation, and 240 g/den initial modulus. In another example, the copolyterephthalamide based on DBT substituted with 10 mole % p-phenylene-2,2'-bis(5-aminobenzoxazole) was spun to fiber having the following tensile properties: 9.3 g/den tenacity, 2.1% elongation, and 793 g/den initial modulus.

INTRODUCTION

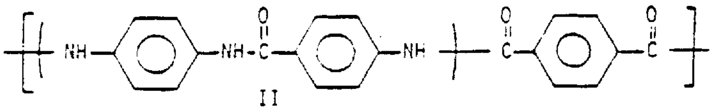
Previous papers [1-3] in this series have pointed out the requisite structural features of polymers intended for the preparation of fibers having very high initial moduli coupled with high tenacities. The most salient feature cited were those of 1) wholly aromatic ring structures having all para-orientation (or other rodlike structure) and 2) hydrogen bonding from $-\overset{\overset{\displaystyle O}{\|}}{C}-$ and $-NH-$ in various combinations, e.g., $-\overset{\overset{\displaystyle O}{\|}}{C}-\ NH-$, $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH-\overset{\overset{\displaystyle O}{\|}}{C}-$, $-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$, and $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$.

A polymer [4-7] which fulfills these requirements and has been found to yield fibers [6, 7] having very high tensile strength and



I

modulus is I. Other polymers previously reported [8-12] which possess some or all of the required structural features for the special fibers are:



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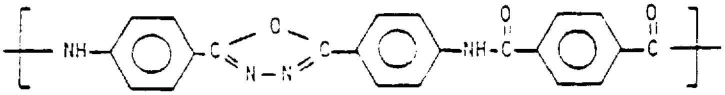
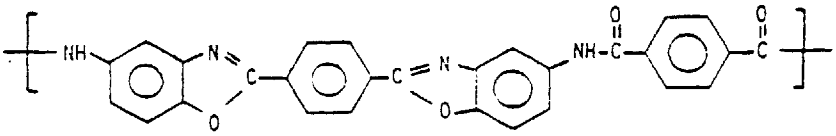


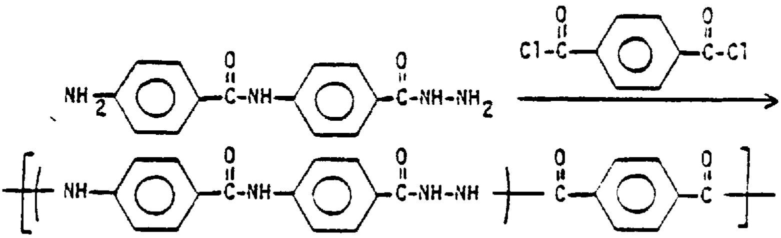
III



IV

In this report the tensile properties of a substantial number of random copolymers composed largely of p-phenylene rings connected by hydrazide and/or carbonamide linkages are discussed. The fibers are generally characterized by the very high moduli found for wholly or partially ordered polyamide-hydrazides having only p-phenylene rings. Various random copolymers derived from selected combinations of the moieties found in Polymers I-IV are listed in Tables 1-3. The tensile properties of fibers from these copolymers are given in Tables 4-6. Other random copolymers along with their fiber properties are given in Tables 7-9.

A polymer (V) which combines the structural features of Polymers I and II was produced using the same type of polycondensation reaction (Eq. 1) employed for Polymer I; fiber from V also was found to exhibit high tenacity and high initial modulus properties (Table 7).



V

(1)

DISCUSSION AND RESULTS

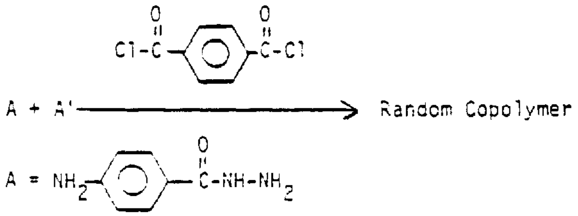
Polymerization

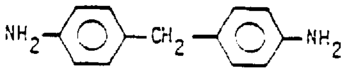
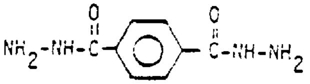
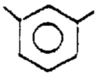
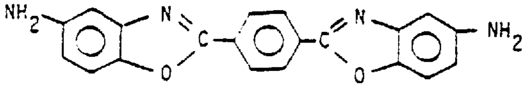
The copolymers discussed are of the random type as opposed to completely ordered copolymers, or copolymers of limited or partial order. Two AA monomers are mixed in an amide-type solvent and reacted with a stoichiometric amount of a BB monomer. Under such conditions it is possible, indeed in some cases even likely, that when the functional groups of the AA monomers have different rates of reactivity toward the BB monomer, that block copolymers are produced. But it is outside the scope of the present study to elucidate the exact nature of the polymers obtained. Only the relative proportions of the two AA monomers, referred to here as the A monomer and the A' monomer, will be given in describing the compositions of the various random copolymers I-XVII (Tables 1-3).

$$\underset{\text{(AA monomers)}}{\text{Monomer A} + \text{Monomer A}'} \xrightarrow{\text{BB monomer}} \text{random copolymer} \qquad (2)$$

The AA monomers are taken from diamines, dihydrazides, and aminobenzhydrazides; the BB monomer for the most part is terephthaloyl chloride. The amide solvents employed are chosen from N,N-dimethylacetamide (DMAc), N-methylpyrrolidone (NMP), or mixtures of these solvents. These solvents contain up to 7% dissolved lithium chloride.

TABLE 1. Random Terephthalamide Copolymers from p-Aminobenzhydrazide and Various Diamines and Dihydrazides[a]



No.	Diamine or dihydrazide, A'	Molar ratio of A/A'	η_{inh}
VI		9:1	4.8[b]
VII		9:1	5.9[b]
VIII	"	7:3	4.5[b]
IX		7:3	4.8[c]
X	"	1:1	2.6[c]
XI		9:1	7.6[d]

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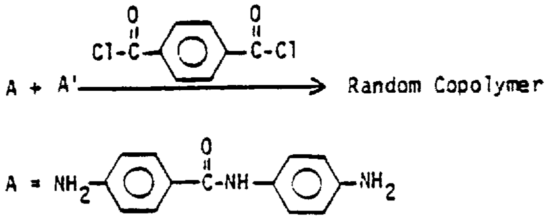
[a] Oxalyldihydrazide was also used as a monomer with A (9:1) but the polymer gelled prior to spinning.

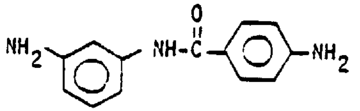
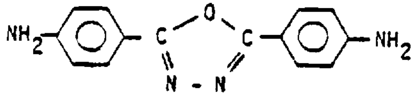
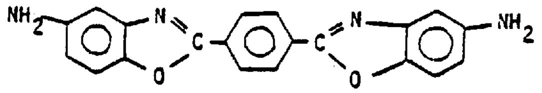
[b] Determined at 30°C on a 0.2% solution of polymer in dimethyl sulfoxide (DMSO).

[c] Determined at 30°C on a 0.5% solution of polymer in DMSO.

[d] Determined at 30°C on a 0.2% solution of polymer in DMAc containing 5% dissolved LiCl.

TABLE 2. Random Terephthalamide Copolymers from 4,4'-Diaminobenzanilide and Various Diamines



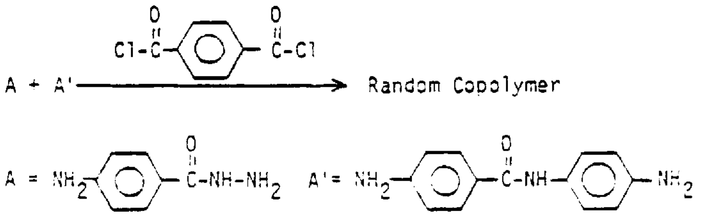
No.	Diamine A'	Molar ratio of A/A'	η_{inh}[a]
XII		9:1	4.5
XIII		9:1	8.8
XIV		9:1	6.5

[a] Determined at 30°C on a 0.2% solution of polymer in concentrated sulfuric acid.

Another terephthalamide, XVIII, was prepared by reacting 90% of the theoretically required amount of terephthaloyl chloride with p-aminobenzhydrazide and completing the polycondensation with the stoichiometric amount of 4,4'-methylenediphenylisocyanate. The derived polymer is a block copolymer containing predominately hydrazide, amide, and urea linkages; a small number of urylene linkages undoubtably are also present.

Still another set of terephthalamides, XIX and XX (Table 8), was prepared by reacting terephthaloyl chloride with solutions containing

TABLE 3. Random Terephthalamide Copolymers from p-Aminobenzhydrazide and 4,4'-Diaminobenzanilide



No.	Molar ratio of A/A'	η_{inh}[a]
XV	9:1	7.2
XVI	1:1	5.1
XVII	1:9	6.4

[a] Determined at 30°C on a 0.2% solution of polymer in DMAc containing 5% dissolved LiCl; a weighed sample of polymer in a solution of DMAc containing 5% dissolved LiCl was diluted with solvent to obtain the desired polymer concentration.

mixtures of m- and p-aminobenzhydrazide. Unlike the reaction of terephthaloyl chloride with either of the aminobenzhydrazides alone which yields partially ordered polyamide-hydrazides [2], the reaction of terephthaloyl chloride with the mixed aminobenzhydrazides produces a random copolymer, at least in the sense of a random distribution of m- and p-phenylene units along the polymer chain.

Likewise, the reaction of a mixture of terephthaloyl and isophthaloyl chlorides added simultaneously to p-aminobenzhydrazide in solution yields a random copolymer, XXI (Table 9), rather than a partially ordered copolymer as would be the case if either of the diacid chlorides alone was reacted with the p-aminobenzhydrazide. The random copolymer XXI also is not to be confused with the type of copolymer which can be produced by stepwise addition of one of the diacid chlorides followed by the other [2].

TABLE 4. Fiber Properties of Miscellaneous Polymers and Random Copolymers

Polymer	$T/E/M_i$[a] (den) WTB As-spun	 Hot-drawn
II $\eta_{inh} = 5.9$[b]	4.8/20.9/135 (7.2) 0.805	5.0/2.9/240 (6.3) 0.096
acid dope, $\eta_{inh} = 6.6$[b]	5.5/25.5/161 (5.8) 1.130	7.3/8.3/286 (5.6) 0.537
III $\eta_{inh} = 4.8$[b]	2.8/54.8/56 (28.9) 1.190	5.0/13.8/115 (20.3) 0.517
VI	5.4/56/122 (15.7) 2.294	14.0/5.8/443 (7.8) 0.538
VII	8.7/8.0/288 (4.6) 0.520	-
VIII	7.3/6.0/267 (6.3) 0.343	10.1/5.1/637[c] (78) 0.162
also	7.1/19.2/204 (13.3) 1.150	12.8/2.8/665[c] (37) 0.279
IX	8.5/6.6/254 (4.1) 0.408	12.8/3.0/541 (2.5) 0.235
X	-	7.5/4.3/243 (2.5) 0.235
XI	-	12.8/3.0/572 (6.1) 0.223
XII	4.5/33.9/115 (7.0) 1.295	9.0/3.3/373 (5.0) 0.204

(continued)

TABLE 4. Fiber Properties of Miscellaneous Polymers and Random Copolymers (Continued)

	$\frac{T/E/M_i^a}{(den)\ WTB}$	
Polymer	As-spun	Hot-drawn
XIII	$\frac{5.4/20.3/173}{(9.3)\ 0.892}$	$\frac{5.5/8.9/207}{(5.3)\ 0.340}$
		and $\frac{7.0/3.6/310}{(5.0)\ 0.150}$
XVIII $\eta_{inh} = 3.2^d$	$\frac{6.0/31/205}{(9.1)\ 1.499}$	$\frac{10.6/2.9/678}{(5.7)\ 0.243}$

[a] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

[b] Determined at 30°C on a 0.5% solution of polymer in concentrated sulfuric acid.

[c] Bundles used for test because of numerous fused filaments on hot-drawn sample.

[d] Determined at 30°C on a 0.2% solution of polymer in DMSO.

High orientation from hot-drawing of the random copolymers brings about crystallization of the fiber as desired, and yields fibers of high strength and high initial modulus. But highly regular polymers frequently crystallize in domains which cannot be oriented sufficiently, even with hot-drawing, to achieve high strength and modulus.

It is interesting to note that the copolymeric effect may be used to produce high strength and modulus for wholly para-oriented copolyamides while the same effect for aliphatic copolyamides, even in the case of isomorphous substitutions, leads to fibers of low strength and low initial modulus [13, 14]. In the case of isomorphous substitution in melt spinnable copolyamides, it was observed that higher elongations and higher compliance ratios (which are a measure of orientation) could be obtained [14]. The key difference between the present work and the former and the thing which accounts for the vast change in results observed is

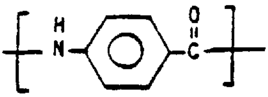
TABLE 5. Fiber Properties of Terephthalamide Copolymers XV-XVII

	$T/E/M_i$[a] (den) WTB	
Polymer	As-spun	Hot-drawn
XV	-	6.3/3.0/549 (5.6) 0.092
XVI	6.6/14.4/232 (11.2) 0.789	18.1/3.1/776 (4.6) 0.385
XVII	6.7/22.3/205 (12.1) 1.220	17.4/3.7/698 (5.9) 0.417

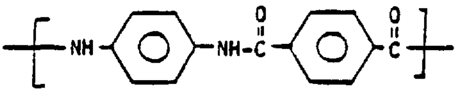
[a] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

that the wholly para-oriented aromatic polymers almost certainly tend to chainfold much less than such linear polymers as polyethylene and nylon 66. This permits the development of very high crystallinities for the wholly para-oriented aromatic fibers. Fibers of aliphatic homopolyamides rarely achieve crystallinities greater than 55-65% whereas fibers such as I have been observed with crystallinity indices as high as 97%.

Wholly para-oriented polyamides, such as II, can be spun from inorganic solvents, such as concentrated sulfuric acid [15]. And fibers of high strength and modulus have been reported by spinning polyamides, such as XXII and XXIII [16], from concentrated



XXII



XXIII

TABLE 6. Fiber Properties of Copolymer XIV

Conditions	T/E/M_i[a] (den) WTB
As-spun	5.9/36.5/158 (9.8) 1.700
Machine hot-drawn	6.9/2.1/500 (6.9) 0.126
Hand-drawn	8.5/3.2/502 (7.6) 0.186
	10.4/2.5/660 (7.1) 0.189
	9.3/2.1/793[b] (7.5) 0.169

[a] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

[b] One single filament break was observed (not counted in the average breaks) of $\frac{20.0/1.7/1450}{(3.4)\ 0.199}$

TABLE 7. Fiber Properties of Copolymer V[a]

T/E/M_i[b] (den) WTB	
As-spun	Hot-drawn
4.6/31.5/137 (12.9) 1.150	7.3/1.5/607 (8.7) 0.075

[a] Inherent viscosity = 3.12; determined at 30°C on a 0.2% solution of polymer in DMSO.

[b] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

TABLE 8. Random Terephahalamide Copolymers from p-Aminobenzhydrazide and m-Aminobenzhydrazide

Polymer	Ratio p-/m-	η_{inh} [a]	Conditions	T/E/M_i [b] (den) WTB
XIX	9:1	4.8	As-spun	8.5/6.6/254 (4.1) 0.408
			Hot-stretched (max)	12.8/3.0/541 (2.1) 0.294
XX	1:1	2.6	As-spun	1.5/16.6/21 (4.6) 0.083
			Hot-stretched (max)	7.5/4.3/243 (2.5) 0.235

[a] Determined at 30°C on a 0.5% solution of polymer in DMSO.

[b] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

TABLE 9. Fiber Properties of Copolymer XXI[a] from p-Aminobenzhydrazide and Mixed Acid Chlorides[b]

T/E/M_i [c] (den) WTB	
As-spun	Hot-drawn
8.3/13.8/254 (4.3) 0.910	11.5/4.5/474 (3.5) 0.360

[a] Inherent viscosity = 5.01; determined at 30°C on a 0.5% solution of polymer in DMSO.

[b] Terephthaloyl chloride and isophthaloyl chloride (4:1).

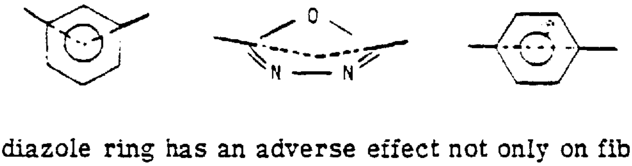
[c] Tenacity, g/den; elongation, %; initial modulus, g/den; denier per filament; work-to-break, g-cm/den-cm.

sulfuric acid solutions having certain minimum concentrations which lie above the critical concentration points [17]. It is quite inconvenient, however, to prepare polymers in organic solvents, isolate and dry them, then redissolve them in another solvent, e.g., concentrated sulfuric acid. Moreover, many polymers, and particularly those containing unsubstituted hydrazide linkages (the predominate linkage for most of the polymers of the type used in our work), are degraded by strong acid solutions.

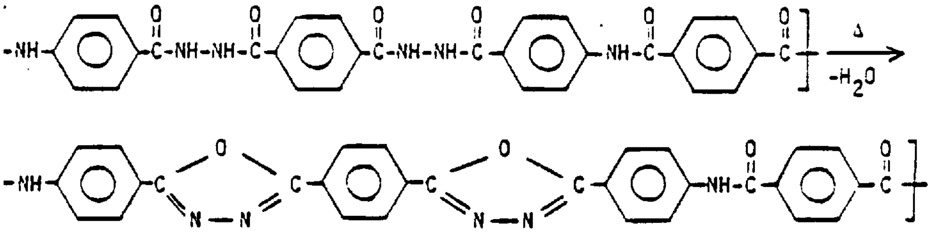
Fiber Properties as Related to Polymer Structure

Fibers obtained from II did not have as high strength or modulus as those obtained from I despite several similarities of structure in the respective polymers. The fact that the properties of fibers from random copolymers containing the moities from I and II are no lower in strength or modulus than those for II may be taken as evidence that the structure of II is inherently capable of yielding fibers of high strength and modulus. Indeed, it should be noted that two copolyamide fibers, XVI and XVII (Table 5), spun from random copolymers containing, respectively, 50 and 90 mole % of the units used for II, possess some of the highest strengths and moduli observed for fibers from organic polymers. These excellent properties may be attributed to the ability to orient these fibers to a much greater degree than was accomplished for fibers of the partially ordered fiber II.

It is somewhat surprising that fibers from the polyoxadiazole-amide III show no higher strength and modulus than they do, even when it is considered that the 1,3,4-oxadiazole ring is structurally less rodlike than a p-phenylene ring, being oriented at an angle somewhat between that of a m- and a p-phenylene ring. But the



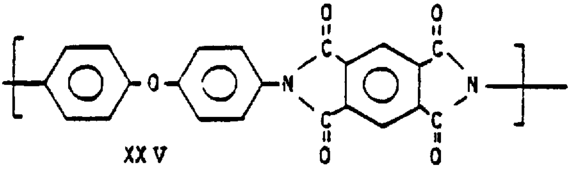
1,3,4-oxadiazole ring has an adverse effect not only on fiber from III, but also it prevents the attainment of high tensile strength and modulus in fiber from the random copolymer XIII which contains only 10 mole % of the units of III. Hot-drawing produces little increase in strength and modulus for the fiber of XIII although the elongation drops to one-half its previous value on successive hot-drawings (Table 4). Since the ordered polyamide-oxadiazole fiber produced from a wholly ordered polyamide-hydrazide was found



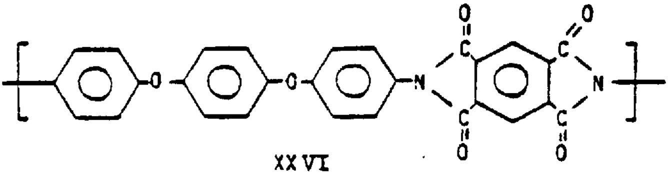
XXIV

(3)

to have high strength and modulus (560 g/den) [1], it seems likely that the 1,3,4-oxadiazole ring itself may not be a bar to the attainment of high-modulus fibers. The situation is not unlike that for fibers from the polypyromellitimides XXV and XXVI.



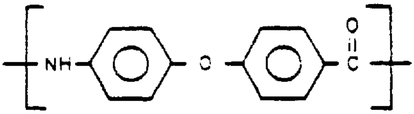
XXV



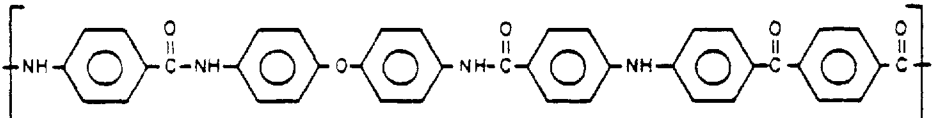
XXVI

Fibers obtained from the former polymer have achieved moduli of about 75 g/den [18] while fiber from the latter have been reported which obtain moduli of about 300 g/den [19]. A possible explanation for the fiber data above may be found in the restoration of symmetry afforded by two ether bridges or two 1,3,4-oxadiazole groups in the polymer repeat units, thus retaining an overall rodlike configuration in Polymers XXIV and XXVI but not in Polymers III and XXV.

The fact that fibers from polyamides such as XXVII [20] and XXVIII [21] exhibit rather modest tensile properties (T/E/M$_i$ for fiber from XXVII and XXVIII, respectively, 10.5/11/110 and 8.7/5.4/176) may be taken as further evidence of the necessity for symmetrical placement of linkages, such as ether bridges, in the polymer repeat unit of polymers intended for use in the preparation of high-strength/high-modulus fibers. If it is assumed that both XXVII and XXVIII are of a molecular weight suitable for the formation of good fibers, then it is not surprising that high-modulus fibers are not achieved because the η_{inh} values for the polymers were merely, 1.35 and 1.71, respectively. Polymers of only moderate molecular weight having extended chains in solutions can reasonably be expected to have η_{inh} values of at least 3 and more usually 6-8.



XVII

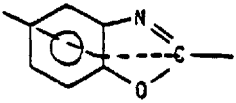


XXVIII

Despite the fact that all of the phenylene rings of VI (Table 1) are para-oriented, the presence of the $-CH_2-$ bridge in the diamine moiety prevents this segment of the polymer from assuming a rod-like configuration, i.e., the p-phenylene units separated by the methylene group cannot be both in a straight line and coplanar simultaneously. It may also be recalled that a $-CH_2-$ linkage has been shown to be isomeric with an $-O-$ linkage [14]. Hence arguments of the above type become relevant when there is but one $-CH_2-$ linkage in the polymer repeat unit.

Fiber of VI has excellent tensile strength and rather good initial modulus, the latter reflecting the influence of the $-CH_2-$ linkage in VI. That both strength and modulus are not materially lowered in the fiber can be explained by the fact that the effect of the relatively small substitution of diamine A' for A is more than off-set by a beneficial effect of random copolymerization, producing fiber of more nearly optimum properties for a given polymer composition. However, larger amounts of 4,4'-methylenedianiline can drastically reduce both strength and modulus (as has been demonstrated by the authors in an unpublished study) because of the effect on polymer structure referred to above.

Two fibers, XI and XIV, which show relatively high strength and quite high moduli are obtained from polymers containing benzoxazole units. Because the benzoxazole ring is not as rodlike as a p-phenylene ring, arguments concerning symmetry also probably can be applied



in the case of XI and XIV as well as for the polymers discussed above. Fibers XI and XIV are rather remarkable for the fact that they contain 10 mole % of the units corresponding to Polymer IV which was reported to be too insoluble for the preparation of fibers [12]. The fact that the tensile properties of fibers from XI are similar to those for fibers from I would argue that the fiber of IV, assuming that the intractability could be overcome, is inherently capable of yielding high-strength and high-modulus fibers.

Fiber of XIV again shows that the units of II are capable of producing high-strength and modulus fibers because XIV contains 90 mole % of II. Fiber of XIV was the only ultrahigh-modulus fiber of this report which contains only amide linkages produced by polycondensation, i.e., XIV contains no hydrazide linkages and the fiber of XIV shows that hydrazide linkages are not essential for the preparation of high-modulus fibers. The thermal stability of fibers of XIV would be expected to be higher than that of the polymers containing hydrazide linkages.

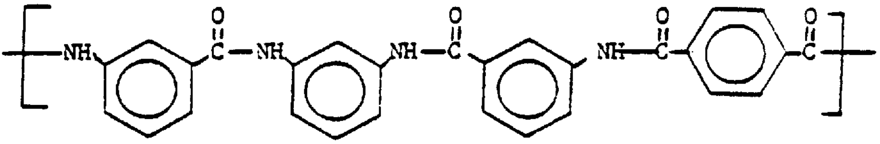
Although only a single break was obtained for the fiber of XIV showing a tensile strength of 20 g/den and a modulus of almost 1500 g/den, this result cannot be discounted out-of-hand, and it seems likely that optimization of spinning and hot-drawing (plus possibly heat-annealing) might see the attainment of such properties for a number of polymers of the type reported here.

The pronounced effect of m-phenylene rings in polymers intended for the preparation of high-modulus fibers has been noted earlier [1, 2]. However, it is somewhat surprising that the fiber of XII has only moderate tensile properties because one-half of the rings of the 10 mole % 3',4-benzanilide moieties in XII are meta-oriented, i.e., XII contains a mere 2.5 mole % m-phenylene rings. This is especially surprising in view of the fact that the relatively large amount of m-phenylene rings (15 mole%) in IX has a minimal effect in reducing the tensile properties of fiber from IX (Table 4). On the other hand, the 25 mole % meta-oriented rings in X produced a fiber having only modest strength and modulus.

Fiber of XVIII is prepared from a polymer which is an oligomer of I chain extended with 4,4'-methylenediphenylisocyanate (MDI). As explained earlier, the effect of the $-CH_2-$ bridge in XVIII might be expected to lower the tenacity and modulus of the derived fiber. The copolymeric effect introduced by the MDI moiety permits the fiber of XVIII to be drawn sufficiently to achieve a relatively high tenacity and a quite high initial modulus. A higher level of substitution of MDI for terephthaloyl chloride would undoubtably lead to a polymer which would have lower strength and modulus.

Fibers XIX and XX illustrate again the importance of using just enough meta-oriented rings to break up the order, but not so much as to interfere with the overall rodlike structure apparently required for high-strength and high-modulus fibers. Thus the fiber of XIX, which has 5 mole % m-phenylene rings, has a tenacity of 12.8 g/den and an initial modulus of 541 g/den at 3% elongation to break while the fiber of XX, which has 25 mole % meta-oriented rings, only possesses a tenacity of 7.5 g/den and an initial modulus of 243 g and 4.3% elongation to break. (Compare also Fibers IX and X.) It should be noted that the molecular weights of Polymers XIX and XX are probably comparable. The η_{inh} values for the wholly para-oriented polyamide-hydrazide, I, have been related to molecular weights and these values (Table 10) have tended to be rather high even at moderate weight-average molecular weights (from light-scattering measurements) [22]. The η_{inh} values for wholly aromatic polyamides high in their percentage of m-phenylene rings, e.g., XXIX, are considerably lower (Table 10) at comparable weight-average molecular weights.

In all of the foregoing fibers, terephthaloyl chloride only was used to introduce the diacid moiety of various polymers. Fiber was prepared from XXI which was obtained by substituting 20 mole % isophthaloyl chloride for a portion of the terephthaloyl



XXIX

TABLE 10. Inherent Viscosity and Weight-Average Molecular Weight [22]

Polymer	η_{inh}[a]	$\overline{M}_W$[b]
I	3.25[c]	29,700
	5.11[c]	44,000
	7.02	62,300
XXIX	1.74[d]	110,000
	2.95[d]	195,000

[a] Determined at 25°C for a solution of 0.1 g of polymer per 100 ml of solvent.

[b] From light-scattering measurements.

[c] DMSO.

[d] DMAc containing 5% dissolved LiCl.

chloride in a reaction which is essentially the same as that for Polymer I, the difference being a 10 mole % introduction of m-phenylene groups which are undoubtable randomly situated along the polymer chain. The net effect of the meta-substitution is reflected in fiber XXI by a slightly lower tenacity and initial modulus relative to the fiber of I with a comparable elongation to break. At comparable tenacities and moduli for Fibers I and XXI, the elongation and work-to-break (WTB) of XXI is considerably higher. Unfortunately, part of the gain in elongation and WTB are lost on heat-aging (Table 11) in air at 185°C after 2 days. The decrease in tensile properties of XXI upon heat-aging, however, was about the same proportionally as that for I.

TABLE 11. Heat-Aging of As-Spun Fiber XXI at 185°C in Air[a]

Time (days)	$\frac{T/E/M_i}{(\text{den})\ \text{WTB}}$
0	$\frac{8.3/13.8/254}{(4.3)\ 0.910}$
1	$\frac{7.2/12.6/217}{(4.3)\ 0.710}$
2	$\frac{7.4/9.9/224}{(4.2)\ 0.507}$
4	$\frac{7.0/9.7/218}{(4.2)\ 0.482}$
8	$\frac{6.7/7.7/217}{(4.3)\ 0.364}$
14	$\frac{6.8/8.0/224}{(4.3)\ 0.390}$

[a] An as-spun fiber of I, chosen for its high elongation, had initial tensile properties of $\frac{7.8/8.0/274}{(5.4)\ 0.470}$ but after 14 days at 185°C had tensile properties of $\frac{5.9/5.7/230}{(5.8)\ 0.256}$.

Fiber Toughness

Fibers of the type reported here, and for predominately wholly para-oriented polyamide-hydrazides in general, are remarkable for the fact that they possess specific strength comparable to that of glass fibers and specific moduli up to two and one-half times greater than that of E-glass fibers; toughness, as expressed by WTB values, is generally greater than that of glass fibers. Indeed, the higher elongation types of polyamide-hydrazide fibers derived from I have specific WTB values which range up to over

1.5 g-cm/den-cm (i.e., in the class with fibers of nylon 66); 0.2 g-cm/den-cm approaches the upper limit for E-glass fibers. This higher level of toughness might reasonably be expected to translate to higher abrasion resistance and higher resistance to fatigue.

EXPERIMENTAL

Aminobenzhydrazides were obtained from Gallard-Schlesinger; the preparation of 4,4'-diaminobenzamide and the heterocyclic diamines were described earlier [8, 23, 24]. The synthesis of 4-aminobenzamido-4'-benzhydrazide and the polymerization to prepare V are described below.

Methyl 4-Nitrobenzamido-4'-benzoate

To a solution at 0°C of 9.06 (0.06 mole) methyl p-aminobenzoate in 50 ml of DMAc was added 11.16 g (0.06 mole) p-nitrobenzoyl chloride. After 5 min the clear solution was allowed to warm to room temperature (RT); after 2 hr the turbid solution was poured into 250 ml of water and dried. Yield: 17 g; mp, 235-238°C.

Methyl 4-Aminobenzamide-4'-benzoate

A 15-g (0.05 mole) portion of the above product was reduced in 100 ml DMAc at 39 psi hydrogen pressure using 0.33 g 5% Pd on charcoal as catalyst. After 1 hr the reaction mixture was filtered and poured into 400 ml of water. The precipitate was collected and dried. Yield: 13 g; mp, 227-229°C.

4-Aminobenzamido-4'-benzhydrazide

A solution of 8.5 g (0.031 mole) of the above amine in 70 ml of isopropanol, 7 ml of water, and 14 ml of hydrazine (98%) was refluxed with stirring for 6 hr. The product was filtered, washed with 30 ml of ethanol, and dried. Yield: 7.5 g; mp, 273-276°C. (The melt resolidified and melted at 355-358°C.)

Polymerization

To a solution of 0°C of 8.10 g (0.03 mole) of 4-aminobenzamido-4'-benzhydrazide in 150 ml of DMAc containing 5% dissolved LiCl was added 6.0 g (0.03 mole) terephthaloyl chloride with stirring. After about 15 min the clear solution became quite viscous and was allowed to warm to RT. The solution was neutralized by the addition, with stirring, of 5.2 g of $Ca(OAc)_2$ slurried in 10 ml of DMAc containing 0.5 ml of water. The neutralized solution of Polymer V was heated to 50°C for 30 min then to 75°C for 30 min, and allowed to cool. The spinning dope (7% polymer solids) was degassed under vacuum and spun to clear lustrous fibers.

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. In the heat-aging tests fibers were exposed for the indicated periods of time and broken at RT.

CONCLUSIONS

Numerous random copolymers having highly rigid chains may be used to prepare high-strength/high-modulus fibers. As regards their initial modulus in relationship to their elongations, many of these fibers may be considered to be "super fibers" as defined by the expression initial modulus (g/den) equals 1000 divided by the elongation-to-break (%) raised to the 0.58 power. This expression defines a curve that had been fit to many modulus-elongation data points obtained for the X-500 class polyamide-hydrazides to describe the lower modulus-elongation limits for fibers that could reasonably be classed as "super fibers" [25, 3]. Figure 1 shows that the initial modulus of nearly all of the hot-drawn fibers of the various random copolymers studied here fall above the curve defined for super-fibers. Also the initial modulus of many high elongation, as-spun fibers from random copolymers fit the super-fiber curve as well as do their hot-drawn counterparts.

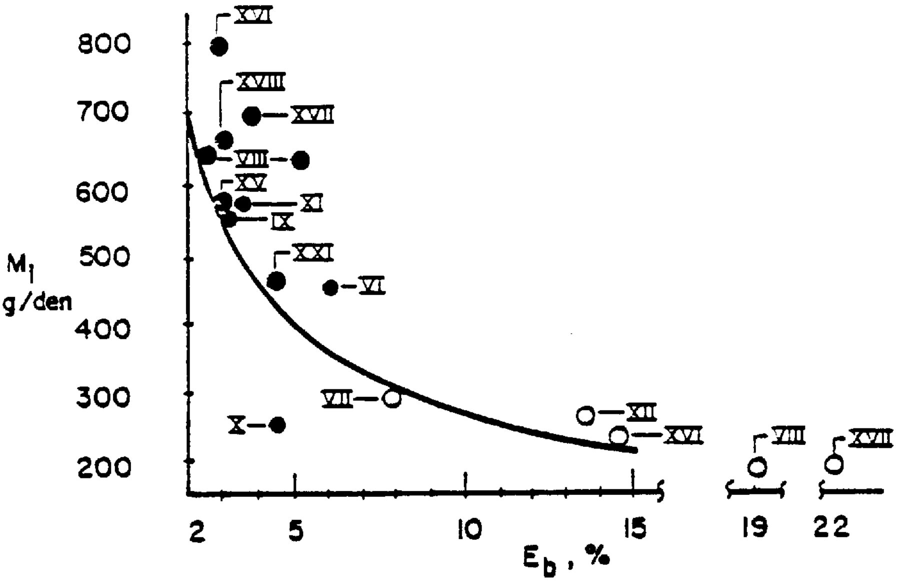


FIG. 1. Relationship of initial modulus and elongation-to-break for some as-spun and hot-drawn fibers of high modulus copolymers [3]. The curve is given by $M_i = 1000E_b^{-0.58}$, where E_b is elongation-to-break. (●) Hot-drawn fiber; (○) as-spun fiber.

It is of paramount importance to note that, when using the random copolymeric effect, one should employ just enough of a nonrodlike unit to break up the structural order of the polymer chains in order to achieve increased tractability but not so many of these units that there will be interference with the overall rodlike structure apparently required for high-strength and high-modulus fibers.

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