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High-Modulus Wholly Aromatic Fibers: Introduction to the Symposium and Historical Perspective*

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ABSTRACT

Recently research workers at the laboratories of Monsanto Co. and DuPont Co. independently discovered organic fibers having specific tensile moduli greater than twice that of E-glass fibers. These fibers tend to have tensile strengths of at least 12 g/den and elongations-to-break of about 4%. Prior to the present discoveries, polyvinyl alcohol, polyethylene, rayon, and aromatic polyurea fibers had been made with specific moduli either equal to or approaching that of E-glass fibers; that work is reviewed briefly in the context of the recent advances. It was obvious on the basis of that early work that organic fibers which combined moduli at the 500 g/den level along with good thermal properties would have substantial utility for reinforcement applications where the density of glass and metal fibers is a drawback and where the very low extensibility of graphite fiber limits its usefulness.

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*Contribution from the Chemstrand Research Center, Inc., a subsidiary of Monsanto Company.

In the quest for thermally stable fibers based on aromatic polymers, there had been observed a high correlation between the proportion of para-oriented aromatic units in a given polymer and the tensile modulus of a well-drawn fiber made from the polymer. Effort at Monsanto Co.'s Chemstrand Research Center to make fibers composed mainly of para-oriented aromatic units culminated in the class of high-modulus organic fibers known generally within Monsanto as the X-500 class of fibers.

The Symposium as a whole is concerned with the polymer chemistry, polymer morphology, and fiber properties of several such X-500 class high-modulus fibers. Additionally, both rigid and flexible composite applications of certain polyamide-hydrazide fibers, a subgroup of the X-500 class, are reported.

Quite apart from the observed macroscopic tensile moduli of fibers, there has been considerable effort in the past on the part of a number of workers to determine the "theoretical" or limiting modulus of a given fiber either by calculations based on bond force constants of chain-forming bonds or by observation of the modulus of polymer crystallites within the fiber. That research, starting with the pioneering work of H. Mark and K. H. Meyer in the mid-1930s, is also reviewed in the Introduction to the Symposium.

INTRODUCTION TO THE SYMPOSIUM

Organic fibers with specific moduli greater than twice that of either E-glass fibers or drawn wire have been made quite independently in at least two different laboratories, those of Monsanto [1a] and DuPont [1b]. As Lord Snow recently put it regarding another major discovery: "...it was in the air" [2]. It may be that the discovery of such very-high-modulus organic fibers has also been made independently by others, but this is beginning to appear less and less likely because of the absence of literature or patents indicating such. (See page 41 for Note Added in Proof.)

The discovery of very-high-modulus organic fibers represents a major advance in polymer and fiber science. From an applications point of view, as we shall see in this Symposium, the discovery is quite like a quantum jump in the technology of organic fibers and, indeed, even to those of us concerned more with fiber science per se, there is a strong feeling of having opened up one of the most significant fiber fields yet. Not since the introduction of nylons 66 and 6, polyethylene terephthalate, and the acrylic fibers decades ago has a class of fibers been discovered which has such significant practical implications.

Examples of the types of polymers which have yielded these high modulus fibers are shown in Fig. 1. Their most significant structural feature is that they are composed essentially of only para-oriented aromatic units except for the linking groups. Among the characteristic physical features of such wholly para-oriented aromatic polymers are their very high melting points and generally very poor solubility, properties making fabrication of fibers most difficult. None of these polymers can be melt spun; they must be spun from a solution.

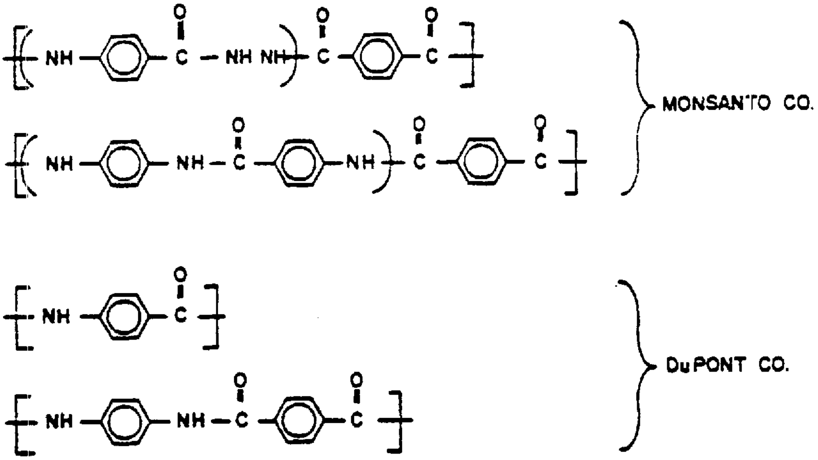


FIG. 1. Types of polymers which have yielded high-modulus organic fibers. In the case of the polyterephthalamide of 4,4'-diaminobenzanilide (the second formula), 10% of a comonomer was used.

The high-modulus aromatic fibers under discussion in this Symposium are specifically ones that have been made with specific tensile moduli greater than about 600 g/den (if you think like a fiber scientist), or Young's extensional moduli of $\approx 11 \times 10^6$ lb/in.^2 (if you think like an engineer) (Table 1). [Note: When physicists express

TABLE 1. Tensile or Young's Extensional Moduli of E-Glass and High-Modulus Wholly Para-Oriented Aromatic Fibers

	Moduli expressed in		
Fiber type	Textile units (weight basis) g/den	Specific modulus (weight basis) in. × 10^{-7}	Engineering units (cross-sectional basis) lb/in.^{2} × 10^{-6}
High-modulus aromatic fiber	>600	>21	>11
E-Glass fiber [3]	326	11.4	10.5
Steel wire	280	~10	~28

modulus on a cross-section or volume basis, they generally express it in dynes/cm^2 or kg/mm^2, in this case respectively, ~7.6 × 10^{11} dynes/cm^2 and 7.7 × 10^3 kg/mm^2. Engineers frequently express specific properties in inches; 600 g/den is 21 × 10^7 in. (The density of the high-modulus aromatic fibers is 0.052 lb/in.^{3}). Throughout this paper, however, modulus will almost always be expressed as lb/in.^{2} or g/den in view of 1) the fact that this symposium is not primarily concerned with the theoretical aspects of modulus, and 2) the fact that the papers to follow in the symposium will also use these units. Thus the reader will not need to resort to the use of conversion factors in referring from one paper to the other. Useful conversion factors, however, are:

	g/den	lb/in.^{2}	kg/mm^2	dynes/cm^2
g/den		density × 1.280 × 10^4	density × 8.995	density × 8.818 × 10^8
lb/in.^{2}	$\frac{7.813 \times 10^{-5}}{\text{density}}$		7.031 × 10^{-4}	6.890 × 10^4

To convert from g/den or lb/in.^{2} to another set of units, multiply by the factor indicated in the proper column.]

In addition to very high moduli, these fibers have very high tensile strength. The Young's modulus of virgin E-glass fiber is approximately 325 g/den or 10.5 × 10^6 lb/in.^{2} [3]; the Young's modulus for steel is ~280 g/den (28 × 10^6 lb/in.^{2}) (Table 1).

It is obvious that insofar as tensile modulus is concerned, one is dealing with potential substitutes for glass fibers and steel wire for various reinforcement applications, especially for those applications in which weight for a given tensile stiffness is a consideration. Glass fibers are now used in very large poundages for both rigid reinforced plastics and for tires and other flexible composites where rigidity and dimensional stability of the reinforcing fiber are prime requisites. Steel is being used increasingly for radial tires and has recently shown promise for the belts of bias/belted tires. Unlike glass, however, steel is not widely used for rigid reinforced plastics.

Glass fiber production was 467 million lb in 1970, up almost 300 million lb from 1960 [4] (Table 2). Usage in just one application, the belts of tires, has grown from essentially nothing in 1965 to around 45 million lb in 1970, and its use in tires is projected to be 115 million lb in 1975 [5]. More than 93% of new cars in 1968 had bias tires without glass belts, whereas 85% of the 1970 cars were delivered with belted tires, usually glass-belted ones [6].

TABLE 2. Textile Glass

Total production	Millions of pounds
1960	177
1970	467
1975	>700 (estimated) [4]
Volume by end use estimated for 1970	
Tire cord	45 [5]
	115 (1975 estimate) [5]
Reinforced plastics	~300
Other	~120

As valuable as glass fiber has proven to be, it has some serious shortcomings: low abrasion resistance leading to surface defects which weaken the filaments dramatically; relatively high sensitivity to the action of water on its surface, requiring over-designing of products exposed to water; less than desirable electrical properties, precluding the fabrication of completely satisfactory radomes, electrical housings, panels, and the like (especially true where moist environments are a factor); different coefficient of thermal expansion from those of the polymers generally used for composite matrices, leading to separation at the fiber surfaces; and poor compatibility of the glass fiber surface with organic polymers, making it difficult to achieve excellent adhesion of glass to the matrix polymers. Additionally, E-glass fibers have a relatively low ratio of modulus to density (i.e., low specific modulus), resulting in rather heavy composites for a given stiffness. The positive features of glass are: moderately low cost, isotropic properties, and relatively little change in modulus and strength up to 200°C.

Although steel is making increasingly strong inroads on both synthetic organic and glass fibers for tires, it almost certainly will not prove to be the ideal general purpose tire cord fiber. Its disadvantages are related largely to difficulties experienced in tire manufacture because of the high bending stiffness associated with the much higher filament diameters of steel fibers compared with those of either glass or organic fibers. Also, manufacturers must install much new capital equipment to make tires with steel fibers.

A very significant feature of the high-modulus organic fibers is that in the manufacture of such fibers from a single given polymer composition, one can trade modulus for extensibility, hence the energy required to rupture the fiber. This trade-off of modulus for extensibility is shown in Fig. 2. Fibers of the all-para-oriented aromatic type have a substantially higher initial modulus at any given elongation-to-break than conventional fibers. G. Raumann and the writer found that the expression, $M_i = 1000E_b^{-0.58}$, where M_i is the initial extensional modulus in g/den and E_b is the elongation-to-break, fits the modulus-extensibility trend observed

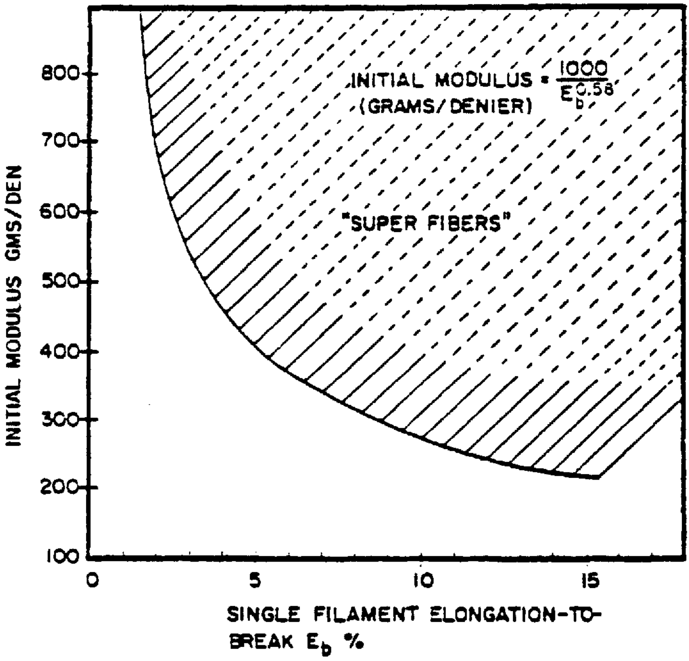


FIG. 2. Modulus vs elongation-to-break for "super-fibers."

for these types of fibers. (The fit was made for the lower levels of modulus observed at any given elongation-to-break. "Super-fibers" would indeed seem to be an appropriate expression for this new and very versatile class of fibers. In the case of glass and steel fibers, one cannot trade off modulus for extensibility to any great degree. It is not hard to visualize that the modulus-extensibility trade-off capability of the high-modulus organic fibers will result eventually in their being the fibers of choice for tires.

In the case of tire cord it is quite likely that one can sacrifice some of the ultimate modulus achievable in a given fiber to gain extensibility, hence energy-to-rupture, and still have sufficient stiffness to insure good treadwear. With regard to the usefulness of the high-modulus organic fibers for rigid reinforced products, on the other hand, very probably the highest modulus achievable will be desired.

It has been an article of faith with a number of us that if glass with its deficiencies can carve out such a large market, it is a virtual certainty that high-modulus organic fibers which overcome most of those deficiencies will have a great future in the reinforced rubber and reinforced plastic fields. Also indicating that the high-modulus organic fibers have potential commercial significance is the work reported recently in papers by Hannell [7] and Draves and Lee [8], which disclose very substantial application work toward the use of a high-modulus organic fiber for the belts of tires.

In spite of their good features, however, high-modulus organic fibers are not without a set of deficiencies and peculiarities of their own, not the least of which is cost, especially that cost associated with low volume production (<50 million lb/year). At high volume production the high-modulus organic fibers should be quite competitive with glass because of their much higher specific tensile strengths and specific moduli. For use in rigid reinforcement applications, one significant physical deficiency of the high-modulus aromatic fibers will have to be taken into account: weak transverse properties. As in the case of graphite fibers, the high modulus and high strength properties are in the fiber direction only. We have long lived with this situation as regards the strength of organic fibers and can confidently expect to do so with regard to modulus in the future. The anisotropic nature of such fibers will be dealt with quite extensively by Zaukelies and Daniels [9] in a later paper in the Symposium. The deficiencies of high-modulus organic fibers will be discussed further by the writer in the paper appearing later in the Symposium that describes the properties of an aromatic polyamide-hydrazide fiber [10].

The Symposium has been organized to tell a rather complete story, with one particular fiber acting as the vehicle through which much of the story is told. That particular fiber is a wholly para-oriented aromatic polyamide-hydrazide with the structure shown by the first formula in Fig. 1. This fiber type is representative of one subclass of Monsanto Textile Co.'s X-500 class of high-modulus organic fibers.

The story is structured as follows:

Historical perspective,
Polymer chemistry involved in this field.
Properties in detail of one particular fiber that was carried through early development stages.
Morphology—some x-ray and electron diffraction characterization.
Application studies
  a) Weaving of fabrics.
  b) Evaluation in rigid composites.
  c) Evaluation in the belts of belted, bias tires.
  d) Application to ballistic protection,
Exploratory work for high-modulus fibers based on copolymers.

HISTORICAL PERSPECTIVE

In order to put these recent discoveries in perspective, two different aspects of past art will be discussed: 1) What has been said about the upper limiting moduli possible for perfect crystals of some linear polymers, and 2) the discoveries and observations made by fiber scientists along the way to the recent discoveries discussed in this Symposium.

The Ultimate Extensional Young's Moduli Possible for Fibers of Organic Polymers

Two quite different approaches have been used to estimate the ultimate tensile modulus that could be obtained for a fiber of a given polymer; one is based on calculations and the other more on the direct observation of fibers. In the case of the calculated moduli, the theorist estimated what the limiting tensile modulus would be by determining the stress necessary for stretching the polymer chain longitudinally. In stretching the chain, the atoms making up the backbone of the chain must be displaced in the direction of the stress. Such displacement can be accommodated by 1) straightening out the molecule into something approximating a planar zigzag conformation, 2) widening the angles made by the chain-forming bonds, and 3) actually lengthening the chain-forming valence bonds themselves. Then, in order to estimate the overall force to stretch the chain, a rational means of coupling the calculated individual forces is required. Early workers generally assumed planar zigzag conformations for C—C—C and C—O—C catenations and assumed the molecules to be in a regular crystal habit as evidenced by x-ray diffraction.

The basic approach was described nicely by H. Mark [11] in 1936 (Fig. 3): "If we want to increase the distance between A and C by 10 percent we have the two possibilities: we can increase the angle α by $d\alpha$ and keep $\underline{a}$ constant or we can increase $\underline{a}$ by $\underline{da}$ and keep α constant." Fairly obviously, to increase $\underline{a}$, that is stretch bond $\underline{a}$, in order to increase the distance between atoms A and C will require a much greater force than to separate A from C by spreading the angle 2α. Based on Mark's work [11], the modulus for a straight-chain hydrocarbon would be approximately six times greater if bond stretching only were involved than if only bond angle bending were involved, 2800 g/den vs 450 g/den (Table 3).

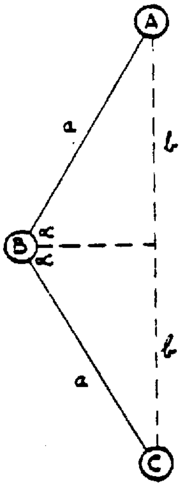


FIG. 3. After H. Mark [11].

TABLE 3. Elastic Moduli for Chain Axial Direction of Linear Polymers Calculated from Force Constants of Chain Bonds

	Elastic moduli			
	Engineering units (lb/in.^{2} × 10^{-6})	Textile units[a] (g/den)	Author and year	Ref.
<u>Natural and Carbochain Polymers</u>				
Cellulose	11.2-17.5	550-835	Meyer and Lotmar, 1936	12
	8.2	400	Treloar, 1960	16
Straight-chain hydrocarbon	5.7-35.6	450-2800	Mark, 1936	11
Polyethylene	49.3	3900	Mizushima and Simanouti, 1949[b]	17a
	26.4	2060	Treloar, 1960	20
<u>Condensation Polymers</u>				
Polyhexamethylene adipamide (nylon 66)	22.8	1440	Lyons, 1958	19
	28.4	1780	Treloar, 1960	20
Polyethylene terephthalate	21.2	1140	Lyons, 1958	19
	17.6	950	Treloar, 1960	20

[a] Crystallographic densities were used in conversions from engineering units to textile units, i.e., to specific property units.

[b] This value was first calculated from the lowest frequency Raman lines for crystalline paraffins.

Thus one sees the magnitude of the need to couple these forces properly in order to arrive at the proper overall force to separate A and C, and thus obtain the elastic modulus. Simple series coupling seemed to be the generally accepted manner.

The second approach to determining the limiting extensional modulus of a fiber from a given polymer is based on the assumption that the modulus would be the same as that of the individual crystallites making up the crystalline portion of the fiber. In 1958, more than 20 years after the pioneering work of Mark [11] and of Meyer and Lotmar [12], Dulmage and Contois [13] showed that one could determine the modulus of the crystallites of oriented films on the basis of comparison of the x-ray diffraction pattern of an oriented film under stress with that of the unstressed film. The film specimen is mounted in a stretching clamp in an x-ray diffraction apparatus in a manner permitting measurement of the 2θ values of meridional reflections. The change in spacing of meridional reflections with stress is a measure of the extension of the crystal lattice. The extension of the macroscopic specimen itself is also measured and the ratio of the extension of the crystallites to that of the speciman as a whole is computed. It is assumed both the amorphous and crystalline regions bear the load equally and, thus, that a simple series coupling of the two resistances to deformation applies. Consequently the modulus of the crystalline phase is equal to the specimen modulus times the ratio of the specimen strain to the crystallite strain.

Sakurada et al. [14a, 14b] extended this technique to fibers. Moreover, these workers varied the applied stress, which permitted them to plot stress-strain curves for the deformation of the crystalline regions, and thus to obtain the crystallite moduli directly. They assumed, as did Dulmage and Contois, that a series model applied for the stress to the crystalline and amorphous regions. Sakurada et al., however, did demonstrate experimentally the reasonableness of the series model assumption.

In Table 3 are given the elastic moduli of a number of fibers based on the approach of calculating the modulus using force constants of bond stretching and bond angle bending pioneered by Mark [11] and Meyer and Lotmar [12] in 1936. Crystallite moduli obtained from x-ray diffraction measurements of oriented films and fibers are listed in Table 4. The results of these two methods are compared in Table 5; in Table 5 the results of these two methods are also compared with commonly observed macroscopic moduli for the fibers themselves.

TABLE 4. Elastic Moduli Determined from Crystal Lattice Extensions Observed by X-ray Diffraction Measurement[a]

	Engineering units (lb/in.^{2})	Textile units (g/den)
Cellulose	19.4	1010
Polyvinyl alcohol[b]	36.3	2100
Polyethylene[b]	34.1	2660
Polyethylene terephthalate[c]	10.8 (19.9[d])	580 (1170[d])
5 GS Polyester[e]	0.6[d]	~32
Polycaproamide (nylon 6)[b]	3.6	230
Polypropylene (isotactic)[f]	6.0	520
Polystyrene (isotactic)[f]	1.7	—

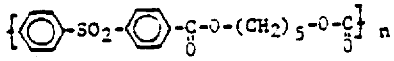
[a] Sakurada and co-workers [14a, b].

[b] Planar zigzag.

[c] Nonplanar, not fully extended.

[d] Dulmage and Contois [13].

[e] 5 GS is



[f] Helical.

Meyer and Lotmar [12] calculated that the elastic modulus for the cellulose crystal in the chain axial direction would be between 550 g/den (11.2 × 10^6 lb/in.^{2}) and 835 g/den (17.6 × 10^6 lb/in.^{2}) (Table 3) using the Meyer and Mark [15] model of the cellulose unit cell and available spectroscopic data. Meyer and Lotmar concluded that the higher value calculated was likely to be more correct since it was in better agreement with the measured dynamic modulus of ~600-800 g/den (~11-15 × 10^6 lb/in.^{2}) for dry flax (Table 6). Treloar [16], in a more refined treatment using a staggered ring conformation rather than the planar one used by Meyer and Lotmar, calculated an elastic modulus much lower than that observed for dry linen fibers, viz.,

TABLE 5. Comparisons of Moduli: (A) Calculated from Bond Force Constants, (B) Determined from Measurement of Lattice Extensions, (C) Measured for the Macroscopic Fiber; Compared on a Cross-sectional Basis (lb/in.^{2} × 10^{-6})

Fiber	Moduli calculated from force constants of chain bonds	Moduli determined from observed lattice extensions	Tensile moduli observed for conventional fibers
Cellulose	11.2-17.5[a]	19.4[b]	1.9-2.1[h]
	8.2[c]		
Polyhexamethylene adipamide (nylon 66)	22.8[d]		0.4-0.7
	28.4[c]		
Polyethylene	26.4[c]	34.1[b]	
	49.3[e]		
Polyethylene terephthalate	21.2[d]	19.9[f]	0.9-1.9
	17.6[c]		
Polyvinyl alcohol		36.3[b]	1.7-3.5
Graphite fiber	140-145[g]		35-65

Compared on a Weight Basis (g/den)			
Cellulose	550-835[a]	1010[b]	100-140
Polyvinyl alcohol		2100[b]	100-200
Polyhexamethylene adipamide (nylon 66)	1440[d] 1780[c]		30-50
Polyethylene terephthalate	1140[d] 950[c]	1070[f]	50-110
Graphite fiber	~5500[g]		1600-2600

[a] Meyer and Lotmar [12].
[b] Sakurada, Ito, and Nakame [14b].
[c] Treloar [16, 20].
[d] Lyons [19].
[e] Mizushima and Simanouti [17a].
[f] Dulmage and Contois [13].
[g] Value determined from graphite whiskers.
[h] Regenerated fibers.

TABLE 6. Moduli of Some Natural,[a] Regenerated, and Synthetic Fibers

	Modulus	
	g/den	10^6 lb/in.^{2}
Natural		
Jute, native	450	9
Ramie, native	350-500	7-10
Hemp, dry	520	10
Flax, native	600-800	11-15
Regenerated		
Viscose rayon, wet	10	0.2
"air" dry	90	1.7
at -50°C	120	2.3
Rayon, polynosic, "oven" dry[b]	250	4.8
Synthetic		
Nylon 66 (high tenacity)	50	0.7
Polyethylene terephthalate	110	1.9

[a] Meyer and Lotmar [12].
[b] Man-Made Textiles [43].

400 g/den (8.2×10^6 lb/in.^{2}) vs ~600-800 g/den (~11-15×10^6 lb/in.^{2}) observed for dry flax. Treloar suggested this serious discrepancy might be due to neglect of secondary forces in the calculation. All in all, however, the differences between calculated values and observed values are not disquieting. The fact that calculations from bond stretching and bond angle bending force constants for cellulose are in pretty good agreement with observation—even less than observed in the case of Treloar's value—coupled with the fact that the observed crystallite modulus is only slightly greater than the higher calculated values, inspires confidence in the reasonableness of these approaches to estimating theoretical Young's moduli of other fibers. Even so, the credulity of the scientist is tested by the estimations of the theoretical moduli of some synthetic fibers

obtained by this method. But before discussing that, flax will be considered further.

It probably is a surprise to many synthetic fiber scientists to find that the elastic modulus of flax (Table 6) is six to eight times greater than that of either conventional viscose rayon, a regenerated cellulosic fiber, or polyethylene terephthalate fiber, a "high-modulus" synthetic fiber. Indeed, the modulus of flax is greater than that of E-glass fiber, even on a cross-sectional basis, and, moreover, it is about the same as moduli of many of the synthetic fibers only recently discovered and under discussion in this symposium. One could well ask, "If there already existed natural organic fibers with specific Young's moduli twice that of E-glass fibers, why all the fanfare concerning these recent discoveries in the synthetic organic fiber field?" The natural high-modulus fibers almost certainly have not been widely used primarily for two reasons: 1) they exhibit a substantial fall-off in tensile properties with elevated temperatures and in moist environments, and 2) they are staple fibers and would not prove useful for those reinforcement applications which require continuous filament yarn. Continuous filament yarn is needed, for example, for tire cord, filament-wound structures, and continuous filament laminate composites, products for which high-modulus fibers are finding increasingly wide usage. In addition to being made in the form of continuous filament yarns, the wholly aromatic high-modulus organic fibers discussed in this Symposium are truly thermally resistant fibers; the tensile property fall-off with increased temperature and humidity is quite small by comparison with that of the cellulosic fibers. (The tensile property behavior of the high-modulus aromatic fibers with respect to temperature and moisture is discussed in detail in a later paper in this Symposium [10].)

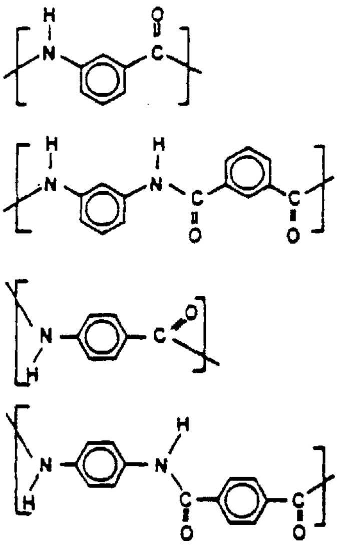
Quite possibly polyethylene is the most interesting fiber to discuss in the light of its observed crystallite modulus and its "calculated" modulus, 2700 and 2000-4000 g/den, respectively. The 4000-g/den calculated value was first arrived at by Mizushima and Simanouti [17a] who ascribed the lowest-frequency Raman lines of crystalline paraffins to longitudinal vibrations of the chains acting as if they were rods. This, of course, provides a more direct way to calculate the modulus than from force constants of bonds, and the method should be regarded as a quite separate and distinctive way to determine the limiting modulus of a fiber. (Actually this method based on Raman spectroscopy does not fit well in either the "calculated" or "observed" category. Some workers include data obtained by way of Raman spectroscopy along with values for moduli calculated from force constants while others include such data with "observed" moduli. In this connection it should be pointed out that modulus data obtained from calculations based on inelastic neutron scattering measurements likewise fit neither the "calculated" nor "observed" modulus category [21].) Mizushima and Simanouti noted that the lowest-frequency lines found for the solid state were absent in the liquid state in the case of cetane, $C_{16}H_{34}$ (the highest methylene homolog they studied), showing the absence of the extended molecular form in the liquid state. They also noted that their modulus for solid paraffins was comparable to that of diamond (34×10^{11} dynes/cm^2 vs 80×10^{11} dynes/cm^2 for diamond [21]). Interestingly, the crystallite modulus "observed" by Sakurada et al. [14] for polyethylene is almost one-third that of diamond—23.5×10^{11} vs 80×10^{11} dynes/cm^2.

Thus we see that by three independent methods of estimating the upper limit for the elastic modulus of polyethylene fiber or film, the theoretical modulus is indicated to be 20 to 40 times higher than found for highly drawn polyethylene fiber. That polyethylene has the potential of being made into a fiber with a modulus in the same order of magnitude as that of diamond is indeed very exciting. Even the extremely interesting high-modulus film-fibrils of polyethylene discovered by Blades and White [18a] have elastic moduli almost a power of magnitude lower than the 3000-4000 g/den range that appears possible based on observation of the x-ray diffraction and Raman spectra behavior of crystalline polyethylene.

Very interestingly, the elastic modulus of another planar zigzag molecule, polyvinyl alcohol, as determined from crystallite lattice stretching is essentially the same as that of polyethylene (Table 4). This provides substantial evidence according to Sakurada et al. [14] that interchain cohesion has no significant influence on the lattice extensibility in the chain direction.

Lyons [19] and Treloar [20] extended the calculations of the limiting Young's moduli of fibers moduli of synthetic polymers to those of condensation polymers, choosing two of the most important commercial fibers for treatment: polyhexamethylene adipamide (nylon 66) and polyethylene terephthalate (Table 3). In the case of nylon 66 the calculated moduli for the crystals were 30-40 times greater than generally observed for spun and drawn fiber; for polyethylene terephthalate the calculated moduli were on the order of 10 times greater. A polyethylene terephthalate with a modulus of just 3 times greater than conventional highly drawn fiber would have a specific modulus greater than that of E-glass. Both workers calculated a substantially higher limiting modulus value for nylon 66 than for polyethylene terephthalate. The crystallite elastic modulus of polyethylene terephthalate determined from lattice extension was also found to be relatively low [13].

Quite recently Fielding-Russell [22] calculated the theoretical moduli of a) the polyisophthalamide of m-phenylenediamine, b) the corresponding polytherephthalamide of p-phenylenediamine, c) poly-m-benzamide, and d) poly-p-benzamide (Fig. 4). (The aromatic polyamide fiber Nomex is almost certainly made of the polyisophthalamide of m-phenylene diamine.) The two wholly para-oriented polymers have been spun to very high modulus fibers as discussed in the beginning of this article [1b]. Fielding-Russell's calculations indicated, of course, that high elastic moduli would be possible for the wholly para-oriented polyamide fibers, reporting a value of 1500 g/den (29 × 10^6 lb/in.^{2}). Observed macroscopic moduli up to



CALCULATED ELASTIC MODULI	
LBS/IN^2 X10^{-6}	GMS/DEN
18.4	950
18.4	950
29.0	1500
29.0	1500

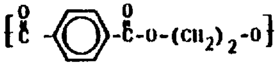
FIG. 4. Elastic moduli of wholly aromatic polyamides calculated from force constants of chain bonds [22].

~1000 g/den (19 × 10^6 lb/in.^{2}) have been reported [1b]. Fielding-Russell calculated the theoretical modulus of the meta analogs to be 950 g/den (18.4 × 10^6 lb/in.^{2}), almost two-thirds that calculated for the para-oriented fibers. It is noted, however, that moduli greater than about 150 g/den have not been reported for the meta fibers. The point is that whereas almost two-thirds of the calculated modulus of one of the wholly para-oriented polymers has been realized, no more than one-sixth of the calculated modulus for the long-studied analogous meta fiber [poly-(m-phenylene isophthalamide)] has been realized. This once again points up the fact that the inherency of high modulus as determined from calculations from force constants leaves much to be desired as a guide as to which polymer the researcher should pick in his quest for a high-modulus fiber. Indeed, the limiting modulus predicted for polyethylene is appreciably higher than even Fielding-Russell's limiting value for the wholly para-oriented aromatic polyamides.

It would be of considerable interest to know in the case of the para-oriented polyamides what is the crystal modulus based on lattice extension. If found to be high like the calculated modulus, then one could reasonably hope to increase the modulus significantly by more sophisticated spinning; if the crystallite modulus is relatively low, basic morphological changes probably would have to be effected by the spinning process, a much more difficult task.

It is quite clear that the ultimate modulus possible for a polymer crystal in the chain direction, and consequently the limiting modulus for the corresponding fiber, is highly dependent on how nearly the polymer molecules are fully extended. Any deviation from the fully extended state such as results from helical conformation or from forces preventing full extension of the polymer chains in the crystalline state has been found to result in much lower crystal moduli than otherwise possible [13]. This is seen for isotactic polypropylene [14a], isotactic polystyrene [14b] (Table 4), and an experimental polyester based on 4,4'-sulfonyldibenzoic acid and pentamethylene glycol (code-named 5GS) [13] (Table 7). Dulmage and Contois [13] determined that for the 5GS polyester there was a 15% contraction of the chains in the fiber identify period from that calculated for the fully extended state. Consistent with this they found the crystallite modulus to be only 3% of that determined for polyethylene terephthalate, a chemically similar fiber (Table 7). Even polyethylene terephthalate was found to have some contraction of its fiber identity period from the theoretical value for fully extended

TABLE 7. Relationship between Contraction of Fiber Identity Period (FIP) and Observed Modulus of Polymer Crystal[a]

Polymer	Calculated FIP[b] (Å)	Observed FIP (Å)	FIP Contraction (%)	Crystal modulus determined from lattice distortion (lb/in.^{2} × 10^{-6})
	10.9	10.75	1.5	19.9
	18.9	16.0	15	0.6

[a] After Dulmage and Contois [13].
[b] Fiber identity period calculated for fully extended chain molecule.

chains, thus explaining its relatively low crystallite modulus compared with that of nylon 66 or those of polyethylene and polyvinyl alcohol.

Dulmage and Contois [13] considered what would be the effect on the macroscopic modulus resulting from increasing the degree of crystallinity of the specimen for each polyethylene terephthalate and 5GS fiber employing the series model for coupling the moduli of the crystalline and amorphous portions. For the limiting crystallite moduli they used those obtained from observation of the lattice extensions for the crystalline regions of the respective polymers; for the amorphous phase the same low value of 0.3 lb/in.^{2} was used in the case of each fiber. As seen in Fig. 5, the effect on the macroscopic modulus by increasing the degree of crystallinity from 20 to 80% would be relatively small for both fibers. On the other hand the effect on the macroscopic modulus resulting from increasing the degree of crystallinity from 90 to 100% would be very great for polyethylene terephthalate (and other fibers with high crystallite moduli). For polyethylene terephthalate the modulus would be expected to rise from ~3 to 20 lb/in.^{2} (170-1100 g/den) with the increase in crystallinity from 90 to 100%. As discussed below, this picture is almost certainly too simple because it does not take into account the changing nature of the amorphous phase with increasing orientation of the film or fiber.

The upper limit of the macroscopic modulus theoretically possible for fibers has been considered strictly on the basis of a 100% crystalline specimen with the c axis of the crystals being parallel with the fiber axis (explicitly in the case of the investigation of moduli by the x-ray technique and implicitly in the case of moduli derived from force constants, since the crystallographic cross-sectional area of the molecule is employed in the calculation). In practice, however, obtaining essentially single crystal fibers is most unlikely. Thus some consideration needs to be given to the relative contribution of the amorphous phase to the modulus with increasing specimen crystallinity (as evidenced by Bragg reflections) and specimen orientation. As the proportion of well-oriented crystallites builds up to relatively high levels, it is quite unlikely that the modulus of the amorphous component would remain unchanged since such amorphous material is for the most part increasingly organized along the c axis. In fact, evidence for such has been obtained by Dulmage and Contois [13]. They calculated that the modulus of the amorphous phase of a film of polyethylene terephthalate having a degree of crystallinity of 47% would, based on density, be about twice that indicated by the graph in Fig. 5.

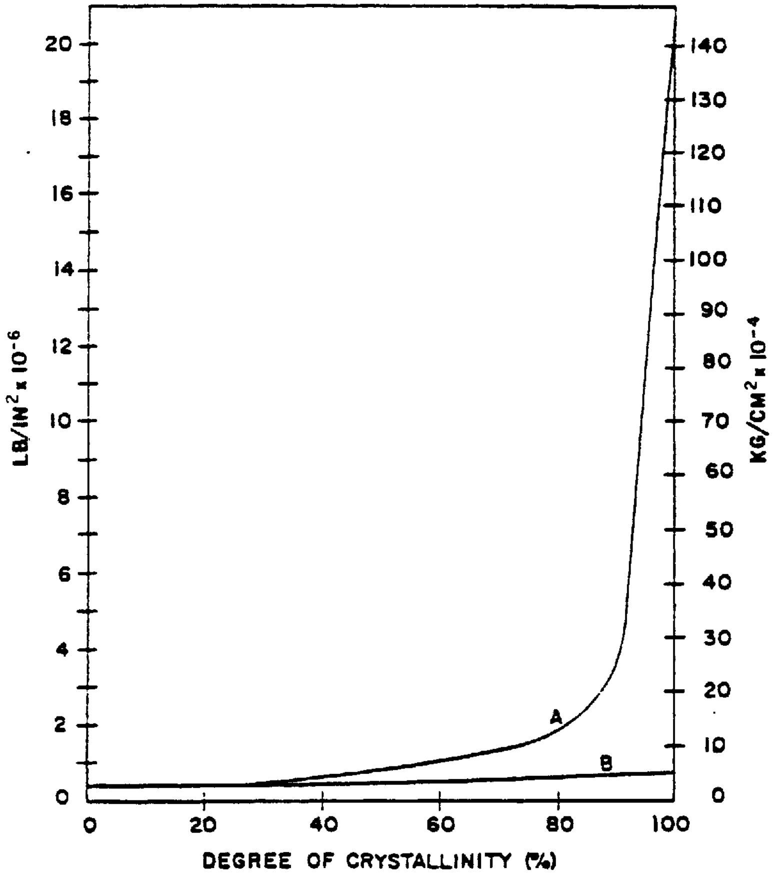


FIG. 5. The dependence of the elastic modulus on the degree of crystallinity for the series model. For Polymer A the modulus of the crystalline regions is 19.9 × 10^6 lb/in.^{2}, and for Polymer B it is 0.6 × 10^6 lb/in.^{2}. For both curves the modulus of the amorphous phase is assumed to be 0.3 × 10^6 lb/in.^{2}. [A is polyethylene terephthalate; B is the poly(pentamethylene glycol) ester of 4,4'-sulfonyldibenzoic acid.] After Dulmage and Contois [13].

Indeed, it is not difficult to imagine that moderately high moduli could be obtained in the absence of any appreciable three-dimensional crystallinity (i.e., well-defined Bragg reflections) provided that the molecules tend to be fully-extended (planar zigzag or equivalent), that the chains do not tend to fold, and that they are very well oriented along the fiber axis. Such a phenomenon would be more likely to show up for the quite stiff, predominately para-oriented aromatic polymers than for the more flexible aliphatic polymers. The aromatic polymer molecules could be expected to organize preferentially along the c axis of the fiber upon drawing the fiber, in part because of the little likelihood of chain-folding; their bulkiness and their high glass transition temperatures, however, could make the attainment of good three-dimensional crystalline order difficult in some instances even though a rather high degree of longitudinal order might well be possible.

Another aspect of the amorphous contribution to the specimen or macroscopic modulus concerns the relationship of the fiber's glass transition temperature to that temperature at which the measurement of modulus is made. Generally, as the temperature of a polymer is lowered, the more the various molecular motions of the chains are frozen out. Linear polymers without side-chain groups or oxygen in the main chain tend to have no identifiable relaxations below about 100°C. In fact, polyethylene terephthalate with a methylene sequence length of only two shows its γ-transition at 240°C, almost 100°C higher than that of the corresponding polymer from decamethylene glycol, clearly showing the freezing out of a given relaxation at higher temperatures as molecular constraints are imposed. Woodward, Sauer, and co-workers [23a-e] have shown that unoriented linear polymers without large side groups or chain-oxygen show the greatest increase in elastic modulus upon being cooled from room temperature to 4.2°K. Even so, the increase is only 2- to 4-fold, with the highest elastic modulus value at 4.2°K for any unoriented linear polymer studied being that of linear polyethylene, 1.5×10^6 lb/in.^{2} (~120 g/den) [23e].

To the extent that relaxations would be frozen out at room temperature for unoriented high-modulus aromatic fibers with glass transition temperatures (α-transitions) in the 400-500°C range, and to the extent that one could expect any β- or γ-transitions temperatures to be elevated substantially (or be nonexistent because of the aromatic nature of the polymer chain), a fair question is: Can one expect such a fiber at room temperature to be quite like the more conventional aliphatic polymers at 4.2-100°K with regard to elastic modulus, and if so, what does this imply in the way of the contribution of the amorphous phase to the specimen modulus? On the basis of the discussion above and in the absence of a strong orientation effect in the polymer, one would not expect the modulus of the amorphous phase at ~25°C to be more than three to four times what the amorphous phase modulus would be at temperatures approaching the 400-500°C glass transition temperatures. There is no reason to expect the former modulus to be unusually high. As a matter of fact, it turns out that the sonic modulus at room temperature of an unoriented fiber of wholly para-oriented polyamide-hydrazide was in the order of 0.93 lb in.^{2} [25], somewhat less than that reported for linear polyethylene and nylon 66 at 77°K (1.4 and 1.3 lb in.^{2}, respectively) [23e]. Thus it appears that at room temperature the amorphous phase of that high-modulus aromatic fiber is not yet quite like aliphatic linear polymers at temperatures below 100°K, and that one can say that either all the possible relaxations are not frozen out at room temperature for unoriented molecules of the all-para polyamide-hydrazide, or that, if they are frozen out, a high-modulus amorphous phase is not a consequence. Consistent with the interpretation that not all possible relaxations are frozen out at room temperature is the fact that the polyamide-hydrazide fibers referred to above shows a significant loss factor when poorly oriented ($\tan \delta = 0.03$ at room temperature) and further, the loss factor is somewhat affected by moisture in the sample [10]. It seems quite likely that further investigation will show that all possible relaxations are not frozen out, especially when the fiber contains absorbed moisture, and that even if the temperature of the unoriented fiber is lowered to 4.2°K, the elastic modulus will not be dramatically increased.

Now, of course, the next question is: What contribution does the amorphous phase make at room temperature when the fiber is highly oriented? It is the writer's feeling that it will prove to be very significant, but that in essence the question devolves into one of orientation of the chains with respect to the c axis as indicated earlier and that really the discussion is moot. The significant question will prove not to be one of amorphous vs crystalline contribution, but one of correlating some distribution of c axis orientation of the molecular chains with modulus, recognizing that the limiting specific modulus would result from a fiber composed of fully extended macromolecules oriented perfectly along the c axis of the fiber.

Many of the considerations of estimating the limiting moduli possible for polymers have also been reviewed recently by Holliday and White in a paper entitled, "The Stiffness of Polymers in Relation to Their Structure" [21]. The reader interested in greater detail concerning some aspects of estimating the modulus possible for a given polymer is referred to that review, especially if his interest centers on estimating moduli from Raman or inelastic neutron scattering spectroscopy.

Advances in the Attainment of Higher Modulus in Organic Fibers Prior to the Recent Discoveries Reported in this Symposium

Discussion will now turn to those experimental findings over the past 15 years which have indicated that one might expect to obtain fibers with very much higher Young's moduli than generally associated with fibers from synthetic polymers. It can be stated at the outset, however, that until recently only the achievement of very high modulus in the case of graphite from polyacrylontrile ($>70 \times 10^6$ lb/in.^{2}) had given a strong indication that with synthetic fibers one might achieve moduli approaching those calculated from force constants of chain bonds or from lattice elongations. Even so, the network nature of graphite made it a rather poor example on which to base strong hope for obtaining exceedingly high modulus fibers in the case of simple linear polymers.

While it is true that para-oriented aromatic fibers of the type discussed in this Symposium do indeed represent a major advance, it is also true that some significant accomplishments along the line of substantially increased moduli had been made earlier with several different fiber types. Characteristically, such successes resulted from the combination of special polymers and relatively sophisticated spinning techniques.

Moseley and Parrish [24a] made significant progress toward the development of high modulus fibers in the late 1950s (Fig. 6). Indeed, in both the United States and in the Belgian patent application [24b] corresponding to their parent U.S. patent application, only those fibers having an "initial" modulus of at least 180 g/den and a tenacity of at least 9 g/den were claimed. Moreover, the polymers had glass transition temperatures of at least 180°C. These polymers were composed either of wholly aromatic units or combinations of cycloaliphatic and aromatic units; the cyclic units were joined by amide or urea linkages.

In general the polyurea fibers had initial tensile moduli of 250-300 g/den, but one aliphatic-aromatic polyurea fiber was reported to have an initial modulus of 415 g/den, a value substantially greater than they reported for any of the other fibers studied (Fig. 6). Unfortunately, that polyurea was found to have rather poor thermooxidative

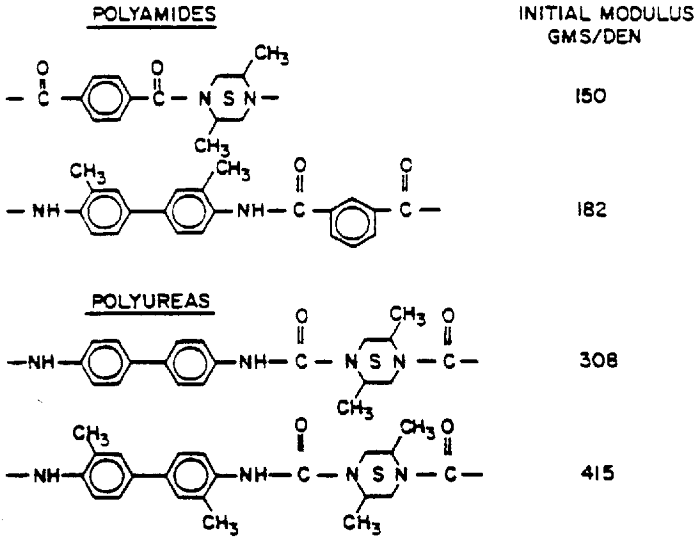


FIG. 6. Significant early work in making relatively high-modulus fibers from condensation polymers (Ref. 24b; see also Ref. 24a).

stability [25], making it unsuitable for many applications. The moduli of the polyamide fibers ranged up to 182 g/den. Interestingly, in the case of every fiber that Moseley and Parrish demonstrated to have a modulus greater than 180 g/den, at least one ring component of the polymer repeat unit contained one or more methyl groups (Fig. 6). Characteristically, cycloaliphatic and aromatic polymers with such lateral methyl groups have quite high glass transition temperatures, a property indicated by Mosely and Parrish as closely related to the propensity of cycloaliphatic-aromatic and wholly aromatic polymers to yield high-modulus fibers. Seemingly, the steric hindrance to rotation resulting from such substitution aids the polymer in aligning itself more nearly to a fully extended conformation upon orientation. Quite possibly the methyl groups on the aromatic and cycloaliphatic rings are a substantial hindrance to chain folding, a structural feature not considered to be consistent with high modulus. Bach and Hinderer [26] found that although methyl substitution on the phenylene rings of an aromatic polyamide with only para-orientation did not afford better tensile modulus than that generally obtainable with unsubstituted wholly para-oriented aromatic polymers, such substitution could permit the fabrication of a polymer whose unsubstituted parent polymer was too insoluble for fabrication of fiber. Further, they found that moduli greater than 600 g/den could be achieved with a polymer of lower density than those not so-substituted.

Noteworthy in the work of Moseley and Parrish was the absence of any wholly aromatic fiber in which all of the aromatic units were para-oriented. This omission, of course, is not at all surprising in the light of the great difficulties that fiber scientists have had through the years of fabricating fibers having high proportions of para-oriented units because of the inherent low solubility and very high high-melting nature of such polymers [27-29]. The general trend of higher moduli with fibers of wholly para-oriented aromatic polymers was recently reviewed by the writer [30]. An indication of what lay in store for those engaged in aromatic fiber research was provided by the work reported by Preston and co-workers [31] and by Frenkel et al. [32a, 32b]. The former workers reported initial moduli as high as 250 g/den for fibers of the polyterephthalamide of 4,4'-diaminobenzanilide (Fig. 7). In the case of this polymer a sufficient degree of tractability for fiber formation was achieved by using an unsymmetrical diamine which provided a copolymeric effect, thus yielding a reasonably soluble

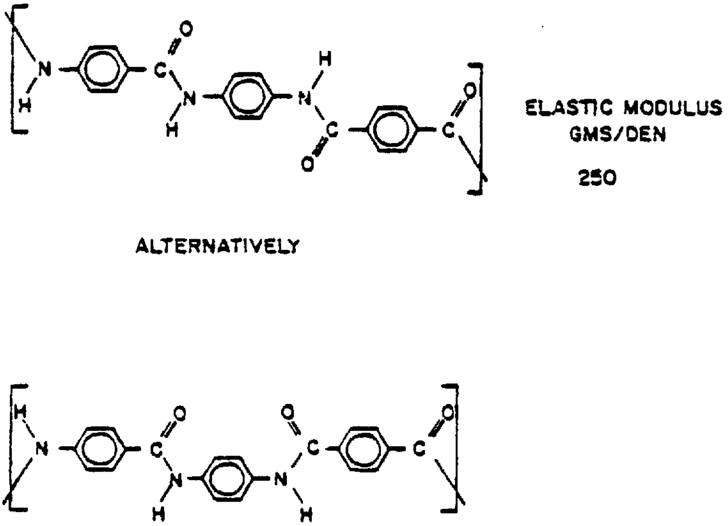


FIG. 7. Polyterephthalamide of 4,4'-diaminobenzanilide [31].

all-para, wholly aromatic polymer. Frenkel and co-workers obtained a modulus of ~300 g/den with the polypyromellitimide of 1,4-bis(4-aminophenyleneoxy)-benzene (Fig. 8), a polymer structurally similar to a wholly para-oriented aromatic polyamide (Fig. 7). As can be seen, however, from the structural formula of Frenkel's polyimide, there is a substantial difference between it and the wholly para-oriented polyamide shown in Fig. 7. In the polyamide, the —CONH— link, while not linear itself, nevertheless permits two sequential phenylene units to be oriented in the same direction, whereas in the polyimide, the phenylene between the two ether groups is necessarily not oriented in the direction of the chain as a unit. This short-range disruption of c-axis orientation, however, does not seem to affect greatly the propensity of the polymer to yield a relatively high modulus fiber. More serious disruption to the c-axis organization potential, as in the case of the chemically similar polypyromellitimide derived from oxydianiline, on the other hand, leads to low modulus fibers (Fig. 8) [33]. As Preston and co-workers have noted [34], in the case of the pyromellitimide of oxydianiline with its one ether linkage per polymer repeat unit, a substantial proportion of the chain cannot be aligned with the remainder of the chain because the alignment of the polymer can be brought back to the same angle only at every other repeat unit. Apparently this degree of disruption to longitudinal alignment results in a type of packing of all-para polymers not amenable to being straightened out sufficiently toward the fully extended conformation upon drawing in order to yield high-modulus fibers.

The work of Frenkel et al. indicates that heterocycles as well as hydrocarbon aromatic rings can be expected to lead to high-modulus fibers when incorporated in the polymer chain. Additional evidence was supplied by Frazer and Wilson [35] and later by Imai [36], each of whom obtained moduli greater than 200 g/den for poly(phenylene oxadiazoles) in which the ratios of p-phenylene to m-phenylene were 50:50 and 75:25, respectively (Fig. 9). Also, Preston, Black, and DeWinter [37] reported a modulus of greater than 200 g/den for a polybenzoxazole-imide (Fig. 9). That heterocycle-containing fibers can indeed lead to very high-modulus fibers will be shown later in the Symposium in papers co-authored by Preston and the writer [34, 38].

While this Symposium is concerned with wholly aromatic fibers which are characterized by their high glass transition temperatures and thermal stabilities (as well as their high tensile moduli), it is important to note in passing that the fiber scientist's ability to

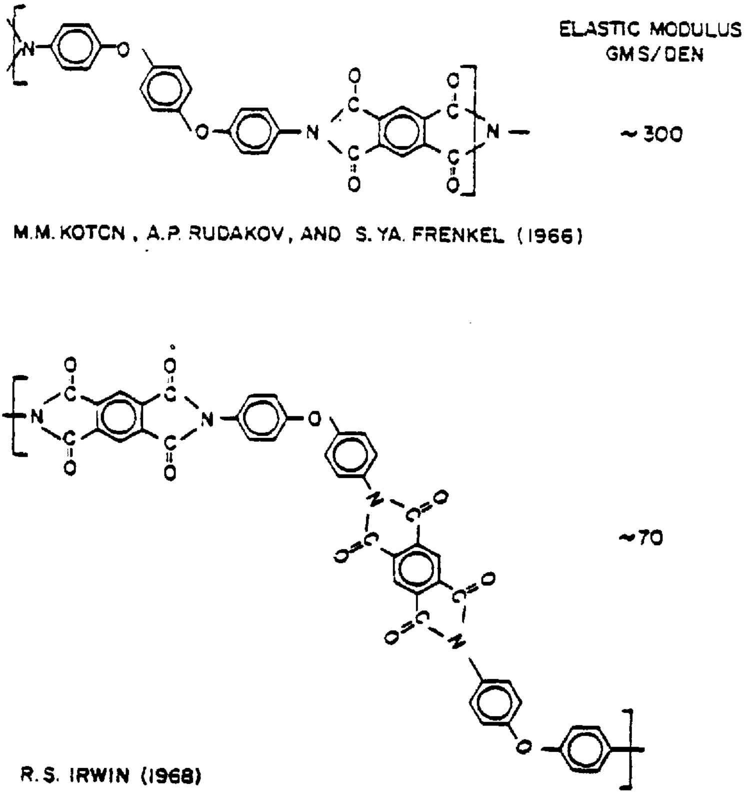


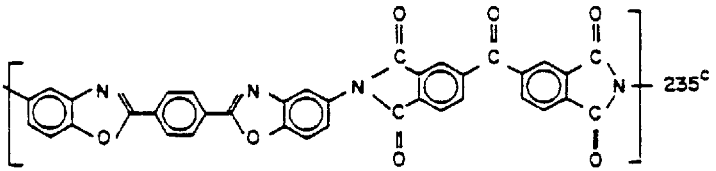
FIG. 8. Effect of aromatic ether linkages on extending aromatic polymer chains.

make fibers of appreciably higher moduli than normally observed from organic polymers has not been restricted to aromatic polymers, albeit the results have been considerably more spectacular in the case of aromatic fibers. It was seen that fibers with relatively low glass transition temperatures such as polyethylene and polyvinyl alcohol have the potential for high moduli on the basis of both force constant calculations and observations of lattice extensions (Tables 3 and 4).

In 1964 Black and Cox reported high-strength steroregular polyvinyl alcohol fibers with initial tensile moduli up to 225 g/den [39, 40], measured after equilibration at 65% relative humidity (RH) at 70°F (standard conditions for measurement of tensile

50 % PARA, 50 % META ALTERNATING COPOLYMER

75 % PARA, 25 % META RANDOM COPOLYMER



[a] A.H. FRAZER AND D.R. WILSON, 1969.

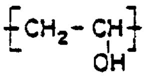
[b] Y. IMAI, 1970.

[c] J. PRESTON, W. DeWINTER AND W.B. BLACK, 1969

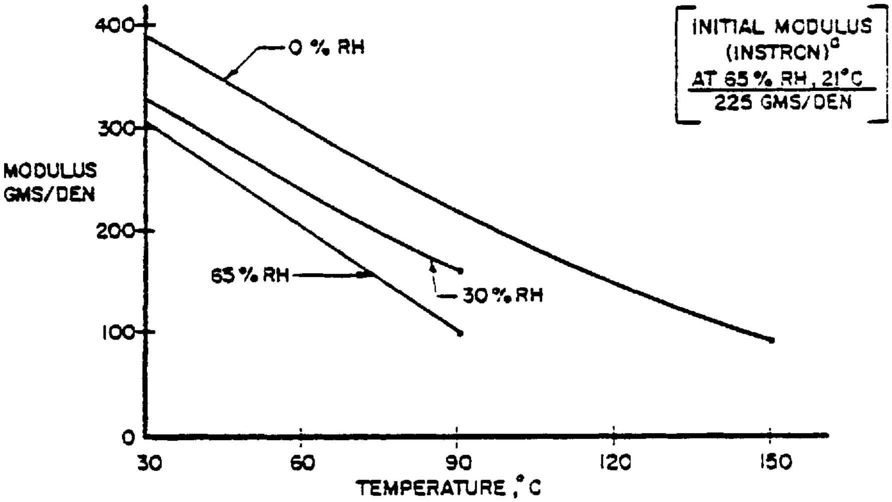
FIG. 9. Some relatively high-modulus fibers of polymers containing heterocycles.

properties of textile fibers). Sonic moduli as high as 387 g/den were observed when measured at 0% RH by Black et al. [41]; the sonic moduli were only around 300 g/den, however, when measured at 65% RH (Fig. 10). It was remarked [39] that such fibers approach glass in tensile properties and that one could expect their use to reinforce plastics. Soon after this report, Zwick and Bochove [42] published similar results with several highly linear and stereoregular polyvinyl alcohols. As yet, however, moduli above 600+ g/den do not appear to have been observed for polyvinyl alcohol fibers.

In mid-1964 Courtaulds Ltd. announced a very high strength polynosic rayon. In addition to having high strength, this fiber had a tensile modulus in the neighborhood of 300 g/den [43] (Table 8). As in the case of the stereoregular polyvinyl alcohol



$$\left[CH_2-\underset{\displaystyle OH}{CH}\right]$$



aW. B. BLACK AND P. R. COX, 1964

FIG. 10. Variation of the sonic modulus (W. B. Black, P. R. Cox, and W. H. Howard, Monsanto Co. data) of high-modulus syndiotactic polyvinyl alcohol fiber with temperature and relative humidity.

TABLE 8. High-Modulus Rayons

	Initial modulus	
	g/den	lb/in.^{2}
Fortisan (standard conditions)	261[a]	5.0×10^5
Coutaulds[b] polynosic high-modulus rayon ("oven dry")	250	4.8×10^6
("air dry")	235	4.3×10^6

[a] Measurement made by Monsanto Co.
[b] Man-Made Textiles [43].

fibers, the modulus, however, was substantially lower under conventional test conditions than under "oven dry" conditions. Fortisan (Table 8) is another example of a rayon with a modulus approaching that of E-glass on a specific property basis.

Like polyvinyl alcohol, polyethylene has been obtained with moduli much greater than found for the usual organic fibers. Blades and White [18a] extruded hot methylene chloride solutions of linear polyethylene under relatively high pressure into the ambient atmosphere. Continuous extrudate consisting of a three-dimensional network of film-fibrils resulted from the exploding of bubbles of the vaporizing methylene chloride in the polymer matrix. As "spun" such extrudates were relatively weak and had very low tensile moduli, but they could be processed like textile yarns. Upon stretching in hot ethylene glycol 6.7 times, ribbonlike yarns with moduli up to 429 g/den resulted (Table 9). Although these striking results may have come as no great surprise to the theorist, the results must have been very satisfying nevertheless. In addition to having very high moduli, such yarns were exceedingly strong, tenacities up to 23 g/den being observed; elongations-to-break as low as 5.9% were also reported. (While the 429 g/den modulus for polyethylene with a density of ~0.96 g/cm^3 is much higher than that of E-glass on a weight basis, it translates to only about 5.2 × 10^6 lb/in.^{2}, a value appreciably less than that of E-glass on a cross-sectional basis. For most wholly aromatic all-para aromatic fibers on the other hand, 430 g/den would be the equivalent of ~7.5-8.0 × 10^6 lb/in.^{2}).

It is quite possible that the polyethylene films to be discussed by V. I. Selikhova for Zubov et al. [18b] at the International Symposium on Macromolecules (Helsinki, July 2-8, 1972) will prove to

TABLE 9. High-Modulus Polyethylene Film-Fibrils[a]

	Initial modulus	
	g/den	lb/in.^{2}
Film-fibril yarn as extruded	3.7	-
Above yarn drawn 6.7 times	429	5.2 × 10^6[b]

[a] Blades and White [18a].
[b] Assumed density of 0.96 g/cm^3.

have high moduli. These workers report that highly drawn films of linear polyethylene after being heated at 270°C under a pressure of 100×10^3 lb/in.^{2} become "practically fully crystalline" (density and melting point are 0.996 g/cm^3 and 144°C, respectively). Accompanying the increase in density and melting point is an increase in the crystallite length from around 300 Å to at least 1000 Å, i.e., the molecules tend to become considerably more fully extended.

We have seen then that theorists by both a calculation method (based on force constants of chain-linking bonds) and two experimental methods (measurement of lattice extension of crystallites and a method based on Raman spectral lines for longitudinal motion of a polymer chain) indicated it was conceivable that one could obtain certain synthetic fibers with very much higher moduli than had been observed macroscopically. We have seen also that two such fibers, polyvinyl alcohol and polyethylene, predicted to be capable of quite high modulus, have since been obtained with moduli several times greater than those seen earlier for these fibers. On the other hand we have not seen such a trend for those fibers for which the molecules in the crystalline portions do not lie in fully extended conformations, e.g., isotactic polypropylene with its helical conformation. One can certainly reasonably ask, nevertheless, whether it would be possible to effect a change in morphology during or subsequent to fiber formation in the case of some of the polymers which "inherently" yield low-modulus fibers, in order to permit a higher than predicted modulus to be obtained. Certainly polymorphs are known for polymers, so it would seem possible.

This introduces us indirectly to the last aspect of high modulus fibers to be considered in this introduction to the Symposium: fiber fabrication, i.e., spinning and drawing. No paper in this Symposium will deal directly with the subject of fiber spinning of the high-modulus organic fibers. Characteristically, synthetic fiber companies are reluctant to disclose the details of how fibers are spun, especially so when dealing with those processes associated with new products. Further, production potential is somewhat inextricably tied to spinning process art. Nevertheless, some general considerations can be discussed here.

How great a part do fiber spinning techniques play in achieving moduli much greater than normally observed? The answer is implicit in my statement to the effect that synthetic fiber manufacturers do not talk freely about spinning processes. Spinning and drawing techniques are indeed very important to achieving high-modulus fibers, but the problem encountered is really a broader one than the terms spinning and drawing generally connote.

It is noted that all of the high-modulus fibers discussed have been obtained from solutions of the respective polymers, even including the high-modulus polyethylene fibers prepared by Blades and White. (Polyethylene, of course, is easily extruded as a melt.) It is the writer's opinion that the researcher has more control over a polymer when in solution than as a melt. He can, for example, minimize interchain forces until that morphological condition is reached during spinning which lends itself to further operations (e.g., drawing and annealing) for maximizing the Young's modulus of fibers. This implies that, in spinning, every step from a static solution of the polymer all the way to the final highly oriented fiber is potentially critical to achieving the maximum modulus possible for a given polymer. Frank [44] has provided us with an excellent commentary on the potential importance of shear vs extensional flow as it might pertain to the modulus of fibers, reviewing in his discourse the work of Pennings and co-workers concerning the tendency of solutions of polyethylene to crystallize at higher than normal temperatures under certain flow conditions. Pennings' fibrous crystals have the "shish-kebab" character seen by a number of researchers. Shishkebab crystals are reported to have a central thread of fully extended molecules, a molecular arrangement discussed earlier as being critical to obtaining high modulus.

Looking at the solution spinning processes further along, one is faced with determining what degree of orientation of the molecules should be sought during the process of solvent removal in order to obtain the maximum (or desired) modulus in the final product. Does he want a relatively high orientation (and perhaps concommitant crystallization) or does he want to defer orientation as much as possible, preferring to align the molecules during a later spinning step which might be better suited to yielding more fully aligned and extended molecules? There is a body of evidence that argues against permitting crystallization to occur prior to obtaining high orientation. Moseley and Parrish [24] were quite explicit regarding the adverse effect of obtaining crystallinity prior to achieving high orientation for achieving high tenacity and high modulus stating, "Furthermore, the drawing must be accomplished before crystallization of the polymer occurs." Certainly crystallization of polymers into any type of crystallites that would tend to be intractable toward allowing the molecules to be fully extended is undesirable insofar as achieving high modulus is concerned. It appears that chain folding is undesirable and perhaps not tolerable, but this is yet to be determined.

In conclusion, two properties of the high-modulus wholly aromatic fibers in addition to modulus deserve mention once again: high strength and thermal stability. In fact, the combination of these two properties along with high modulus set the high-modulus wholly aromatic fibers even further apart from the more conventional fibers than if high modulus had been achieved at the expense of tenacity [44] or without significant thermal stability.

While this Symposition has been limited to wholly aromatic fibers because there was nothing known to the writer indicating that a specific Young's modulus in the order of twice that of E-glass fibers had been achieved with other classes of synthetic polymers, it was explicitly limited because wholly aromatic fibers have come to be almost synonymous with fibers for which properties change relatively little with temperature and humidity. As we have seen, the modulus of aliphatic polymers tends to be very temperature sensitive and frequently very sensitive to moisture as well.

ACKNOWLEDGMENTS

I am indebted to Dr. Jack Preston for many pertinent criticisms and suggestions concerning the experimental fiber work reviewed, and for his assistance to insure that a reasonably balanced presentation of such work was portrayed. I am grateful to Dr. D. A. Zaukelies for helpful discussions concerning the theoretical aspects of fiber moduli reviewed, and to Dr. R. Buchdahl for stimulating discussions concerning the amorphous phase of high modulus fibers.

In a different context, I would like to express my appreciation to Dr. Preston for his encouragement and generous assistance with regard to organizing this Symposium.

REFERENCES

[1a] J. Preston, U.S. Patent 3,484,407 (1969) to Monsanto. J. Preston, U.S. Patent 3,584,046 (1971) to Monsanto. B. K. Daniels, J. Preston, and D. A. Zaukelies, U.S. Patent 3,600,269 (1971) to Monsanto. J. Preston, U.S. Patent 3,632,548 (1972) to Monsanto.

[1b] A. H. Frazer, U.S. Patent 3,536,651 (1970) and 3,642,707 (1972) to DuPont. F. M. Logullo, U.S. Patent 3,595,951 (1971) to DuPont. S. L. Kwolek, U.S. Patent 3,600,350 (1971) to DuPont. South African Patent 68/8181 (1968) to DuPont. West German Offenlegungsschrift 1,929,694 (1970) to DuPont. S. L. Kwolek, U.S. Patent 3,671,542 (1972) to DuPont.

[2] C. P. Snow, Review of Einstein: The Life and Times, by Ronald W. Clark, Life Magazine, 71(8), 14 (1971).

[3] Ind. Eng. Chem., 58(3), 21 (1966).

[4] Chem. Eng. News, September 6, 1971, p. 19A.

[5] Ibid., October 5, 1970, p. 13.

[6] Time Magazine, April 26, 1971, p. 92.

[7] J. W. Hannell, Polym. News, 1(1), 8 (1970).

[8] C. Z. Draves and Z. S. Lee, Rubber World, July 1971, p. 41.

[9] D. A. Zaukelies and B. K. Daniels, J. Macromol. Sci.—Chem., A7(1), 000 (1973).

[10] W. B. Black, J. Preston, H. S. Morgan, G. Raumann, and M. R. Lilyquist, J. Macromol. Sci.—Chem., A7(1), 137 (1973).

[11] H. Mark, Trans. Faraday Soc., 32, 144 (1936).

[12] K. H. Meyer and W. Lotmar, Helv. Chim. Acta, 19, 68 (1936).

[13] W. J. Dulmage and L. E. Contois, J. Polym. Sci., 28, 275 (1958).

[14a] I. Sakurada, Y. Nukushina, and T. Ito, J. Polym. Sci., 57, 651 (1962).

[14b] I. Sakurada, T. Ito, and K. Nakamae, Bull. Inst. Chem. Res., Kyoto Univ., 42, 77 (1964).

[15] K. H. Meyer and H. Mark, Aufbau der hochpolymeren organischen Naturstoffe, Akademische Verlag, Leipzig, 1930.

[16] L. R. G. Treloar, Polymer, 1, 290 (1960).

[17a] S. Mizushima and T. Simanouti, J. Amer. Chem. Soc., 71, 1320 (1949).

[17b] T. Shimanouchi (sic), M. Asahina, and S. Enomoto, J. Polym. Sci., 59, 93 (1962).

[18a] H. Blades and J. R. White, U.S. Patent 3,081,519 (1963) to DuPont.

[18b] Yu A. Zubov, V. I. Selikhova, M. B. Konstantinopolskaja, F. F. Sukhov, N. F. Bakeev, A. V. Kruykov, V. A. Sokolsky, and G. P. Belov, Preprints of the International Symposium on Macromolecules, Helsinki, July 2-8, 1972, Vol. 4, Section No. III-62, p. 333.

[19] W. J. Lyons, J. Appl. Phys., 29, 1429 (1958).

[20] L. R. G. Treloar, Polymer, 1, 95, 279 (1960).

[21] L. Holliday and J. W. White, Pure Appl. Chem., 26, 545 (1971).

[22] G. S. Fielding-Russell, Text. Res. J., 41, 861 (1971).

[23a] J. M. Crissman, A. E. Woodward, and J. A. Sauer, J. Polym. Sci., A3, 2693 (1965).

[23b] C. W. Deeley, J. A. Sauer, and A. E. Woodward, J. Appl. Phys., 29, 1415 (1958).

[23c] A. E. Woodward, J. M. Crissman, and J. A. Sauer, J. Polym. Sci., 44, 23 (1960).

[23d] J. A. Sauer, L. J. Merrill, and A. E. Woodward, J. Polym. Sci., 58, 19 (1962).

[23e] J. A. Sauer and R. G. Saba, J. Macromol. Sci.—Chem., A3(7), 1217 (1969).

[24a] W. W. Moseley, Jr., and R. G. Parrish, U.S. Patent 3,318,849 (1967) to DuPont.

[24b] Belgian Patent 569,760 (1958) to DuPont.

[25] J. Preston, W. B. Black, and W. L. Hofferbert, Jr., J. Macromol. Sci.—Chem., A7(1), 67 (1973).

[26] H. C. Bach and H. E. Hinderer, Polym. Preprints, 11(1), 334 (1970).

[27] J. Preston, J. Polym. Sci., Part A-1, 4, 529 (1966).

[28] W. B. Black and J. Preston, "Fiber-Forming Aromatic Polyamides," in Man-Made Fibers. Science and Technology: Vol. 2 (H. F. Mark, S. M. Atlas, and E. Cernia, eds.), Wiley (Interscience), New York, 1968, p. 297.

[29] J. Preston, U.S. Patent 3,225,011 (1965) to Monsanto.

[30] W. B. Black, Trans. N.Y. Acad. Sci., [II] 32(7), 765 (1970).

[31] J. Preston, R. W. Smith, W. B. Black, and T. L. Tolbert, J. Polym. Sci., Part C, 22, 855 (1969).

[32a] M. M. Koton, A. P. Rudakov, and S. Ya. Frenkel, Vestn. Okad. Nauk SSSR 36(8), 56 (1966).

[32b] N. A. Adrova, M. J. Bessonov, L. A. Laius, and A. P. Rudakov, Polyimides, Technomic Publishing Co., Stamford, Conn., 1970, p. 178.

[33] R. S. Irwin, U.S. Patent 3,415,782 (1968) to DuPont.

[34] J. Preston, H. S. Morgan, and W. B. Black, J. Macromol. Sci.—Chem., A7(1), 325 (1973).

[35] A. H. Frazer and D. R. Wilson, Appl. Polym. Symp., 9, 89 (1969).

[36] Y. Imai, J. Appl. Polym. Sci., 14, 225 (1970).

[37] J. Preston, W. B. Black, and W. DeWinter, Appl. Polym. Symp., 9, 145 (1969).

[38] J. Preston, W. B. Black, and W. L. Hofferbert, Jr., J. Macromol. Sci.—Chem., A7(1), 45 (1973).

[39] W. B. Black and P. R. Cox, Preprints of the Annual Meeting, Textile Research Institute, New York, March 1964.
[40] W. B. Black, U.S. Patent 3,329,754 (1967) to Monsanto.
[41] W. B. Black, P. R. Cox, and W. H. Howard, Data from Monsanto Co.
[42] M. M. Zwick and C. van Bochove, Text. Res. J., 34, 417 (1964).
[43] Man-Made Textiles, 41(481), 28 (1964).
[44] F. C. Frank, Proc. Royal Soc. Ser. A, 319, 127 (1970).

Note Added in Proof: In January 1971 a thermally stable organic fiber, Vniivlon N, with modulus values as high as 930 g/den, was reported anonymously by the All-Union Research Institute of Artificial Fibers, USSR [Khim. Volokna, 13(1), 76 (1971)]. No information was provided, however, concerning the chemical composition of the polymer other than that the polymer was a thermally stable aromatic one. Whether this fiber resulted from an independent discovery cannot be determined.