# Chain Folding in Thermotropic Polyesters

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ABSTRACT: Certain thermotropic liquid crystalline copolyesters containing ca. 10 mol % isophthaloyldiphenyl units provide high molecular weight fibers having the apparently contradictory characteristics of high macromolecular alignment in the axial direction and high initial modulus, coupled with stretchability far beyond levels usual for such materials (up to 40%, versus 2–5%). This phenomenon is defined in terms of copolymer composition, types, and ranges and physical conditions of fiber formation. Experimental observations accord with a model for the nematic melt whereby a significant proportion of the isophthaloyldiphenyl units exist in a resonance-stabilized, 180°-folded conformation which allows the intervening extended, linear segments to adopt good parallel alignment. Under extensional forces such a structure can undergo unfolding if the intermolecular cohesion is not excessive, which serves as the basis for high levels of elongation. The associated modest levels of fiber strength are the result of lowered effective length of the folded chains in comparison with the completely extended conformation.

## Introduction

Aromatic polyesters, capable of adopting a minimum-energy, rodlike conformation in the fully extended state and with moderate rotational energy barriers opposing reversion to less extended conformations, are, in principle, capable of providing liquid crystalline, thermotropic melts.[1] As a practical measure, to ensure that melting occurs below thermal decomposition temperatures (roughly 375 °C), modifications such as copolymerization or asymmetrical ring substitution, to introduce controlled, along-chain irregularities of structure, are usually necessary. Thermotropic melts consist of a microdomains or aggregates, within which the extended macromolecules are arranged in parallel. In the absence of any applied stress, the domains are mutually oriented at random to each other.

Modest levels of stress such as shear flow relative to a solid surface or elongational flow when a melt extrudate is pulled away from a die, as in fiber spinning, cause the domains to become mutually oriented in the direction of stress. The individuality of domains disappears in favor of a macroassembly of extended, well-oriented macromolecules. Removal of applied stresses permits the melt to revert to its original structure of randomly oriented domains. However, the relaxation time for this to occur is relatively long so that rapid cooling can capture the highly oriented structure produced by applied stresses. This is the essence of melt-spinning of thermotropic melts to well-oriented fibers, wherein applied extensional loads can be shared more or less equally by most of the macromolecules to give the characteristic combination of high extensional modulus (i.e., resistance to elongation), low extensibility or elongation at break, and high tensile strength. High orientation may be measured by wide-angle X-ray analysis.

Tensile strength also depends on degree of polymerization, but asymptotically tends toward some limiting value in the region of ca. 100 repeat units for aramids and other aromatic condensation polymers. With comparatively stiff copolymers (compared with aliphatics), such as thermotropic aromatic polyesters, melt viscosities are excessively high at molecular weight levels needed for high strength. Fibers are thus extruded at considerably lower molecular weights and high molecular weight levels subsequently attained by post-heat treatment of the fibers at temperatures approaching the softening points.[2] Thermotropic polyesters are usually prepared by reaction of carboxylic acid with acetate groups, so that fiber heat strengthening is accompanied by expulsion of acetic acid as byproduct. The practicability of such solid-phase polymerization in thermotropic polyester fibers depends on the characteristic absence of length change during the process.

A linear thermotropic polyester chain can accommodate a minor amount of nonlinear (or bent) comonomer components without significant diminution of mechanical properties. In fact, for a typical composition[3], 1,4BE/2,-6NG/T (60/20/20) [consisting of 60 mol % 4-hydroxybenzoic acid (1,4BE), 20% 2,6-naphthalenediol (2,6NG), and 20% terephthalic acid (T)], replacement of part of the 2,6NG by resorcinol initially results in higher tensile strength in the heat-treated fiber product[1,4] as shown in Table I. Inevitably, however, progressive diminution of rodlike conformation, as illustrated by progressively increased amounts of copolymerized resorcinol in Table I, causes sequentially loss in modulus, increase in elongation at break, loss in tensile strength, and eventually disappearance of liquid crystallinity in the melt.

Table I illustrates the contrast between well-aligned fiber assemblies of more or less rod-shaped macromolecules, as characterized by anisotropy or liquid crystallinity in the melt precursor, and closely similar compositions with diminished capability for rodlike conformation or optimal chain alignment. The former show combinations of high modulus and low elongation, and the latter show low modulus and high elongation. The former may or may not show high tensile strength, depending on the molecular length. The transition from former to latter type with changing composition is quite abrupt. In thermotropic polyesters the combination of high modulus and high elongation has not been reported and is unlikely, based on a consideration of structure as described above.

A much broader range of oriented, high molecular weight polymer assemblies, transcending polymer types, method of fiber formation, and orientation, liquid crystallinity or otherwise in precursor melt or solutions, is represented in the stress–strain curves in Figure 1. This shows a clear division of polymers into two classes depending on their ability or otherwise to provide oriented assemblies of

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**Table I. Effect of Tensile Properties of 1,4BE/2,6NG/T (60/20/20) Fibers When the 2,6NG Is Progressively Replaced by Resorcinol**

| resorcinol, % | tenacity, GPA | elongation, % | modulus, GPa | melt anisotropy |
|---|---|---|---|---|
| 0 | 1.8 | 3.5 | 53 | + |
| 5 | 2.3 | 4.7 | 49 | + |
| 10 | 2.3 | 6.3 | 36 | + |
| 20 | 1.0 | 20.0 | 5 | - |

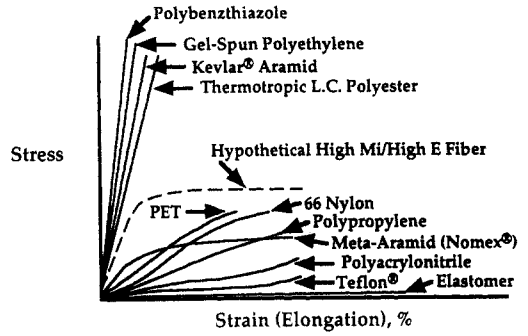



**Figure 1.** Stress–strain curves of various fibers, showing two groups: (a) high modulus and low elongation; (b) low modulus and high elongation.

extended, approximately rodlike macromolecules in parallel:

1. Stiff but not tough: combinations of high modulus (above ca. 40 GPa) and low break elongation (below ca. 10%).

2. Tough but not stiff: combinations of low modulus (below ca. 15 GPa) and high elongation (above ca. 15%). Very few, if any, polymers show intermediate behavior, i.e., high stiffness and high toughness. (In this discussion, the term toughness, in terms of ability to withstand flexural or extensional deformations, may be roughly assessed in terms of elongation at break as is customary for practically all high molecular weight fibers.) The polymeric fibers closest to the category include highly-drawn poly(1,3-phenyleneisophthalamide)[5] and polyamide hydrazides,[6] having modulus/elongation of 17.5 GPa/14% and 50.6 GPa/12%, respectively. The hyperbolic relationship between elongation and modulus for poly(1,4-hydroxybenzoate) fibers has been illustrated by Ciferri and Ward.[7]

This paper discusses a novel category of thermotropic copolyesters compositions which provide fibers having a unique combination of high molecular alignment and high modulus, with unusually high elongation.

## Nomenclature

The shorthand notations for monomers and polymers in this paper are based on a comprehensive, self-consistent system used in these laboratories for many years. This system allows codes to be easily created for new or unfamiliar materials and, with a little practice, chemical structures to be understood from the code without reference to a tabulation of codes and structures.

Shorthand designations for the basic diols, diacids, or hydroxy acids underlying the aromatic polyesters discussed here are created by combinations of the following elements.

1. Cyclic in-chain components

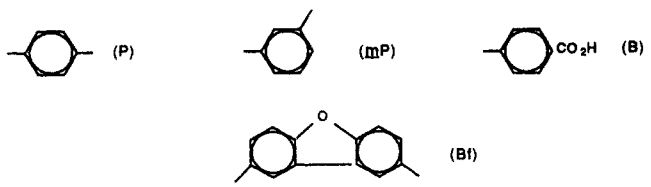
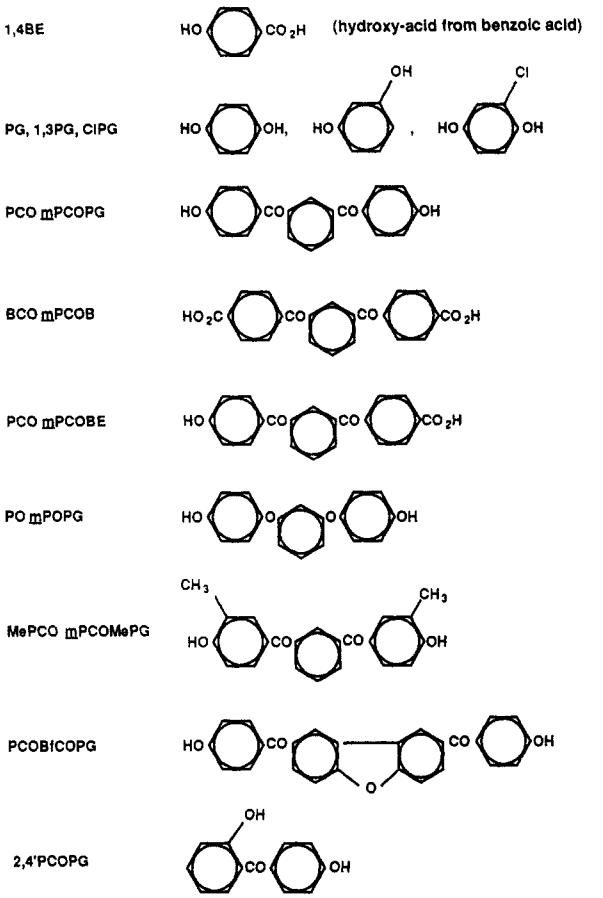



**Chart I**




2. Ring substituents are written immediately in front of the ring code (e.g., ClP, MeP).

3. Ring bridging groups, ethers or carbonyls, are written as O or CO.

4. In the monomer code a terminal G indicates a diol (G = glycol, from aliphatic chemistry), B is a diacid, and E is a hydroxy acid (E = self-esterifier).

Although we have endeavored to describe each code when first mentioned in the text, Chart I shows the application of the above principles to specific examples. (A few very common monomers, viz., isophthalic acid and terephthalic acid, are simply referred to as I and T, according to common usage.)

Polymer compositions are then written in terms of constituent diols, diacids, or hydroxy acids, separated by a diagonal slash to indicate random copolymers or a hyphen to indicate entirely AA–BB character. Molar proportions are in parentheses (e.g., 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) and PhPG/PCO*m*PCOPG(80/20)-T).

## Experimental Section

**Materials. 4,4'-Isophthaloyldiphenyl Diacetate (PCO*m*-PCOPG Diacetate).** A mixture of isophthalic acid (49.8 g, 0.3 mol) and phenol (59.1 g, 0.63 mol) in HF (500 mL) was placed in an autoclave at 0 °C, purged with nitrogen and then pressurized at 30 psi with $BF_3$ during 6 h. Water (ca. 300 mL) was added carefully to decompose the red $BF_3$ complex, and the mixture was combined with excess water (ca. 1 L). The dark brown crude diol (82 g, 86%) was isolated by filtration, dried, and acetylated without purification by acetic anhydride (300 mL) with 6 drops of sulfuric acid at 100 °C for 3.5 h. Cooling grave crude diacetate, mp 181–187 °C, in 46% yield, subject to improvement by concentrating the acetic anhydride solution. Recrystallization from chloroform gave mp 191–192 °C.

In an alternate synthesis anisole was condensed with isophthaloyl chloride with $AlCl_3/CH_2Cl_2$ and then demethylated with HBr/AcOH to give free diol (PCO*m*PCOPG), mp 141–144 °C, in

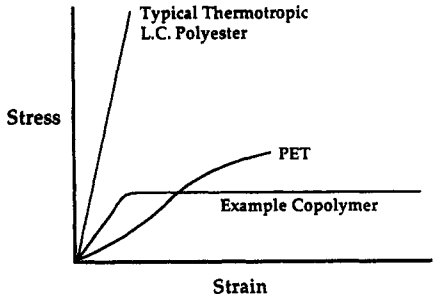



**Figure 2.** Stress–strain curve of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) fibers in comparison with poly(ethylene terephthalate) (PET) and a typical thermotropic liquid crystalline polyester.

60% yield. Acetylation by acetic anhydride (threefold volume ratio) with sulfuric acid at reflux gave diacetate, mp 192–196 °C, in 92% yield.

The HF/$BF_3$ was used for other carbonyl monomers in this study. In many cases the $BF_3$ may be omitted.

**4,4'-Isophthaloyldi-3-cresyl diacetate (MePCO*m*PCOMePG diacetate),** mp 208.5–211 °C, was obtained in 81% overall yield.

**3,4'-Diacetoxy-3'-methylbenzophenone (3,4'-MePCOPG diacetate),** mp 120.5–122 °C, was obtained in 91% yield.

**2,4'-Diacetoxybenzophenone** was prepared by R. K. Siemionko, DuPont.

**Bis(4-hydroxybenzoyl)benzofuran (PCOBfCOPG),** mp 302–304 °C, was converted to diacetate, mp 177–179 °C.

**Bis[4-hydroxy-3-(methylbenzoyl)-4-phenyl] ether (MePCOPOPCOMePG),** mp 208–211 °C, gave diacetate, mp 147–150 °C, after recrystallization from $CCl_4$.

**[4-(3-Hydroxybenzoyl)phenoxy]-4-phenol (*m*PCOPOPG).** 3-Hydroxybenzoic acid 4-phenoxyphenol were condensed in HF/$BF_3$ to form diol, mp 118–120 °C, which was converted to diacetate, mp 67–70 °C after crystallization from methanol.

**4-[3-(4-Hydroxybenzoyl)benzoyl]benzoic acid (PCO*m*PCOBE)** was synthesized by R. A. Clement, DuPont.

**1,3-Phenylenedioxydi-4-phenol (PO*m*POPG).** A mixture of 4-methoxyphenol (558 g, 3.83 mol, 50% excess), 1,3-dibromobenzene (300 g, 1.28 mol), KOH (143 g, 2.55 mol), and copper powder (18 g) was heated with stirring for 5 h. Water distilled off via a Vigrex column during the first hour. The cooled mixture was poured into a stirred solution of 215 g of KOH/3 L of water. The bottom layer was taken up in methylene chloride, the mixture was washed with water, methylene chloride was distilled off, and the residue was fractionally distilled to provide the dimethoxy compound as a yellow oil, bp 204–206 °C/0.4 mm, mp 74–82 °C. Demethylation with $Ac_2O$/HBr gave diol, mp 131–134 °C. The diacetate melted at 109–112 °C.

Polymerization, spinning, and heat-strengthening methods for 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) and related high-elongation polymers are described in ref 8 and are applicable to thermotropic liquid crystalline polyesters in general.

Liquid crystallinity (or anisotropy) was established by observation of a bright field when a specimen of polymer solution between microscope slides and between cross polarizers, was viewed through a microscope. Isotropic solutions under these circumstances give a dark field.

## Results

Certain aromatic polyesters containing close to 10 mol % of isophthaloyldiphenol (PCO*m*PCOPG) may be extruded as anisotropic melts through a spinneret to form well-oriented (~20° by wide-angle X-ray analysis), moderately crystalline, but weak and brittle fibers. Heating under zero tension at temperatures approaching the melt temperature increases the tensile strength to useful levels, together with an unprecedented combination of high elongation and high modulus. The stress–strain curve of such a material is compared in Figure 2 with that of a typical high-strength liquid crystalline polyester and a typical flexible, random coil polymer [poly(ethylene terephthalate)], respectively.

The first example of such characteristics was for 1,4-hydroxybenzoic acid (1,4BE)/hydroquinone (PG)/PCO*m*PCOPG/terephthalic acid (T) (60/10/10/20) as shown in Table II. Heat-treatment reduced the orientation angle from 18 to 12°, while improving the already-significant degree of crystallinity, and gave elongation-to-break and initial modulus up to 20% and 35 GPa. The optimal combinations of elongation and modulus are highly sensitive to PCO*m*PCOPG content. In the copolymer system under discussion, an increase in PCO*m*PCOPG level from 10 to 12 mol % (with compensating decrease in PG level) produces an increase in elongation (from 20 to 35%) and a reduction in modulus (from 28 to 18 GPa). With 17% PCO*m*PCOPG, in 1,4BE/PCO*m*PCOPG/T (66/17/17), as shown in Table II, elongation is as high as 60% with modulus 16 GPa but tensile strength is starting to drop. At high levels of PCO*m*PCOPG, the polymer melt temperature drops too low for effective heat strengthening. When PCO*m*PCOPG content is lowered from 10 to 8% as in 1,4BE/PG/PCO*m*PCOPG/T (60/12/8/20), there is a significant increase in polymer melting point which seems to arise from an incidence of blockiness in the copolymer and consequent nonoptimal melt flow/extrusion uniformity.

Substitution of chlorohydroquinone (ClPG) for PG as in 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) significantly improved uniformity of melt flow and fibers therefrom. Presumably, ClPG is more miscible with the polymerisate than PG and thus copolymer randomization is improved. This composition has a significantly higher fiber elongation (40%) compared with the PG case (Table II).

The extent of break elongation afforded by PCO*m*PCOPG copolymers may be quite variable, depending on the upper limit of fiber heat-treatment temperature, as illustrated by the variability in the stress–strain curves for 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) shown in Figure 3. (Frequently, the tenacity of break is slightly lower than the tenacity maximum; i.e., the fiber can be stretched with negligible additional applied tension beyond some early maximum. In some such cases the extension beyond maximum tenacity was not recorded, e.g., in the cases of 292 and 275 °C heat treatments (Figure 3).) A detailed analysis of fiber-spinning conditions for the same copolymer showed that there is indeed an upper heat-treatment temperature where break elongation becomes maximal (Figure 4). This temperature is ca. 10 °C below the initial flow temperature, which may be determined by direct observation on a hot stage. The heat treatment limit varies according to polymer composition. Elongation is also sensitive to other changes in extrusion variables. Figure 4 shows that it is reduced by reduction in melt viscosity, as may be achieved by increasing the temperature of the melt. It is also lowered by increasing "spin-stretching", which is the elongational shear rate at which the extrudate is drawn away from the spinneret orifice. Certain combinations of conditions favoring low elongation and correlating with high stress applied to the polymer chains during extrusion can produce stress–strain curves for this same polymer tending away from the convex shapes of Figure 3 and toward the linearity associated with conventional thermotropic polyester fibers [characterized by very low elongation (2.0–3.5%) and higher levels of modulus (45 GPa)]; tenacity is still rather limited (8 GPa). In other words, the polymer acts like a conventional thermotropic polyester with rather poor long-range mo-

**Table II. Properties of Thermotropic Copolyester Fibers Based on 4-Hydroxybenzoic Acid (1,4BE), Terephthalic Acid (T), and PCO*m*PCOPG**

| composition | tenacity, GPa | *E*, % | modulus, GPa | orientation angle (WAX), deg | $\eta_{inh}$, dL/g |
|---|---|---|---|---|---|
| 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) | | | | | |
| as extruded | 0.03 | 0.5 | 3.3 | | 1.92 |
| heat treated | 0.63 | 40 | 35 | | |
| 1,4BE/PG/PCO*m*PCOPG/T (60/10/10/20) | | | | | |
| as extruded | 0.15 | 0.8 | 3.3 | 18 | 1.43 |
| heat treated | 0.58 | 20 | 28 | 12 | |
| 1,4BE/PCO*m*PCOPG/T (66/17/17) | | | | | |
| heat treated | 0.43 | 60 | 16 | | 1.31 |
| typical thermotropic, e.g., 1,4BE/3,4′PCOPG/T (60/20/20) | | | | | |
| heat treated | 3.07 | 3.2 | 43 | | |

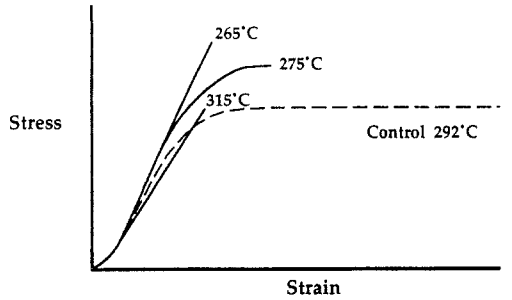



**Figure 3.** Effect of heat-strengthening temperature on stress–strain behavior of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) fibers.

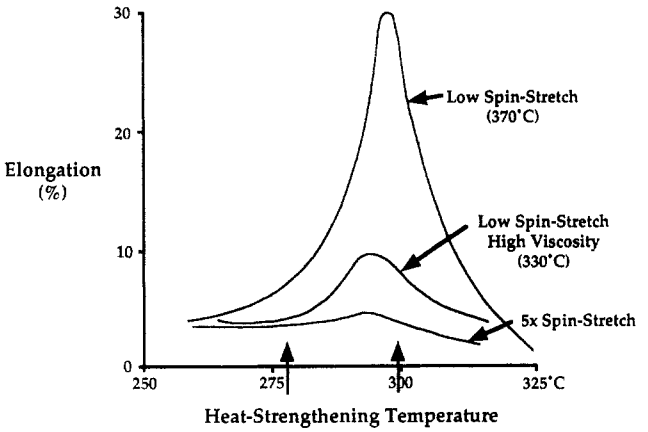



**Figure 4.** Effects of degree of spin stretching, melt viscosity, and heat-strengthening temperature on elongation at 21 °C for 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) fibers.

lecular orientation but with fairly high short-range orientation. This suggests the polymer may be capable of two quite different types of basic fiber structure.

Tensile properties of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) measured at elevated temperatures show a pronounced increase in elongation and drop in modulus at increasing temperatures (Figure 3 and Table III). The maximum rate of change occurs approximately at the glass transition temperature (111 °C), although it is not known if there is significance in this correlation. Even in cases where elongation at 21 °C is quite low (cf. Figure 4) due to nonoptimal process conditions, the elongation at 150 °C can approach or exceed 100%. By contrast, elongation of conventional high-strength thermotropic polyester fibers, already low at 21 °C, drops even lower at higher temperatures (Figure 5).

Fibers of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) processed and heat-treated under optimum conditions for

**Table III. Comparison of Stress–Strain Properties of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) at Elevated Temperatures with Those of a Typical High-Strength Liquid Crystalline Copolyester, ClPG/MePCOPG(75/25)-T**

| | 1,4BE/ClPG/PCO*m*PCOPG/T | | | ClPG/MePCOPG-T | | |
|---|---|---|---|---|---|---|
| test temp, °C | tenacity, GPa | *E*, % | $M_i$, GPa | tenacity, GPa | *E*, % | $M_i$, GPa |
| 21 | 0.5 | 10 | 26 | 2.2 | 4.4 | 47 |
| 100 | 0.4 | 34 | 19 | | | |
| 150 | 0.2 | 66 | 2.2 | 1.1 | 2.8 | 35 |
| 200 | 0.1 | 56 | 1.6 | | | |

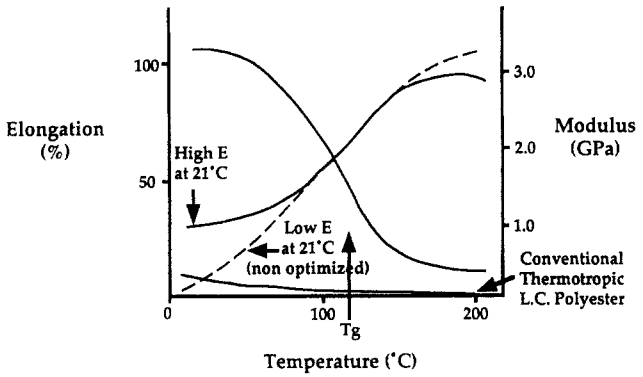



**Figure 5.** Change in modulus and elongation of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) fibers with increasing temperature.

**Table IV. Average Recovery Properties of 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) Fibers at 21 °C**

| elongation, % | work recovery, % | tensile recovery, % | stress decay, % |
|---|---|---|---|
| 1 | 59 | 78 | 14 |
| 2 | 37 | 65 | 19 |
| 3 | 23 | 47 | 21 |
| 5 | 13 | 32 | 20 |
| 10 | 8 | 20 | 16 |

high elongation (Figure 4) could be stretched up to 10–15% through a tube containing hot nitrogen to provide a large drop in elongation (to ca. 2.5%), a modest increase in modulus (by ca. 30%), and a minor increase in tenacity. When the same fibers were deformed by elongating to a specific moderate level for a specific length of time, they did not recover their original dimensions when the stress was removed; i.e., they retained a percentage of the original deformation as measured in terms of deviation of "tensile recovery" and "work recovery" (Table IV) from 100%. The decay of originally applied stress is also shown in Table IV. The applied elongation in relation to the stress–strain curve is shown in Figure 6, which indicates yielding at

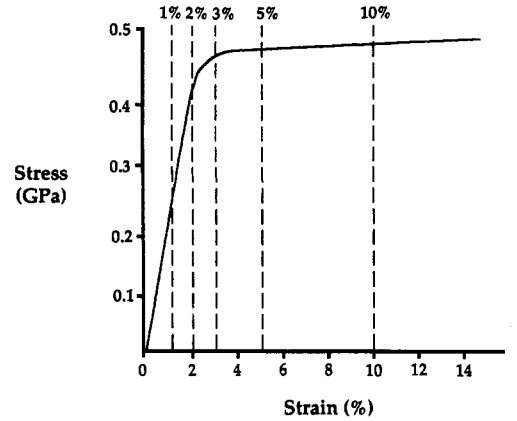
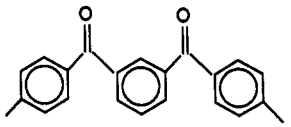



**Figure 6.** Relationship of recovery measurements (Table IV) to stress–strain profile.

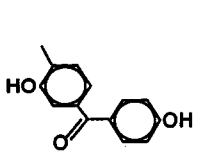
2–3%. Beyond ca. 5% elongation, the material acts as though it were ductile, showing very little propensity to regain its original dimensions.

The high-elongation phenomenon appears to be unique to copolymers containing the PCO*m*PCOP unit:

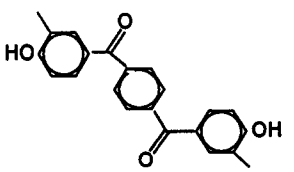


In 1,4BE/ClPG/T/PCO*m*PCOBE (60/12/14/14), where PCO*m*PCOBE is the hydroxy acid analog of PCO*m*PCOPG, and the composition conformationally closely analogous copolymers previously discussed, fiber tenacity/elongation/modulus of 5.8 GPa/18%/34 GPa was obtained. As before, the stress–strain curve was extremely sensitive to extrusion conditions and changes in the diketone content. Similar copolymers containing the diacid analog (BCO*m*PCOB) of PCO*m*PCOPG such as 1,4BE/ClPG/T/BCO*m*PCOB (60/20/10/10) had convex fiber stress–strain curves but not the pronounced bend therein associated with high-elongation fiber discussed previously. It is not clear why a diacid monomer, apparently affording the same conformational possibilities as the corresponding diol, as a copolymer constituent should, in fact, lead to appreciable differences in polymer properties. However, other instances of this have been noted in past work on thermotropic polyesters. For example, isophthaloyl units appear to confer significantly diminished chain flexibility compared with resorcinol residues.

The uniqueness of the PCO*m*PCOP residue, as a diketone wherein the carbonyls are separated by a *m*-phenylene ring, for high elongation/high modulus may be inferred from comparison with closely related copolymers based on (a) a monoketone, 3,4′-MePCOPG, and (b) a diketone, MePCOPCOMePG, wherein the carbonyls are separated by a *p*-phenylene ring.



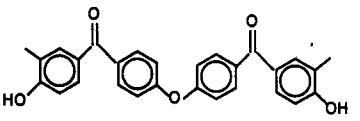
(3,4′MePCOPG)



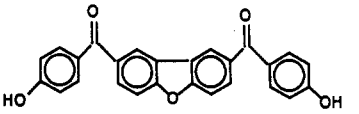
(MePCOPCOMePG)

(The methyl substituents were incorporated to ensure a homogeneous polymerisate and randomness in the copolymer.) Table V shows these units lead to the usual low elongation/high modulus and approximately linear stress–strain curves of conventional thermotropic polyesters. The lowered strength of the MePCOPCOMePG-containing copolymers compared with the 3,4′-MePCOPG-containing copolymers may be attributed to reduced long-range chain linearity as affected by the pronounced crank shape or lateral displacement of the diketone units.

Diketone diols wherein the separation of the carbonyl groups is larger than a *m*-phenylene unit are not conducive to high elongation/high modulus fiber properties.



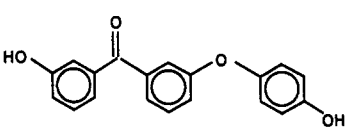
(MePCOPOPCOMePG)



(PCOBfCOPG)

Thus, 1,4BE/PG/MePCOPOPCOMePG/T (60/10/10/20) exhibits a gently convex stress–strain curve with limited tenacity and rather low elongation and modulus typical of a liquid crystalline melt polymer wherein the perfection of chain extension is tempered by a low concentration of nonlinear flexible units (0.86 GPa/7.6%/18 GPa). PCOBfCOPG represents the MePCOPOPCOMePG structure (excluding the methyl substituents) stiffened as shown by formation of a central furan unit which formally resembles the *m*-phenylene unit in the disposition of the bonds to carbonyl groups. 1,4BE/PG/PCOBfCOPG/T (60/10/10/20) did not provide homogeneous melts but good fibers were obtained by replacement of PG by resorcinol (1,3PG). These again provided linear stress–strain curves, and increased stiffness was represented by a higher modulus (41 GPa) and lower elongation (2.1%). This is quite different from 1,4BE/1,3PG/PCO*m*COPG/T (60/10/10/20), which shows moderately good fiber chain alignment (29°), coupled with elongation of 25% and modulus of 14 GPa. The latter relatively low value reflects the nonlinearity in the polymer chain imposed by the 1,3PG.

The criticality of carbonyl as the flexible linkage in the present context is affirmed by the contrasting properties of analogous copolymers containing PO*m*POPG, the ether analog of PCO*m*PCOPG. Thus, 1,4BE/PG/PO*m*POPG/T (60/10/10/20) had a linear stress–strain curve with tenacity/elongation/modulus of 1.0 GPa/7.6%/37 GPa. The mixed ether ketone, *m*PCOPOPG, likewise had conventional properties.



(mPCOPOPG)

AA–BB type copolyesters, as distinct from those based on 4-hydroxybenzoic acid (AB type), containing PCO*m*PCOPG provided high-elongation fibers only in a few cases. Thus, PhPG/PCO*m*PCOPG(80/20)-T, from phenylhydroquinone (PhPG) and containing 10 mol % PCO*m*PCOPG, formed weak fibers which nevertheless gave 19% elongation after heat treatment (Table VI). Again properties were highly sensitive to heat-treatment conditions and to preparation of isophthaloyldiphenyl units. With ClPG or MePG (chloro- and methylhydroquinone, respectively) in place of PhPG the heat-treated fibers did

**Table V. Heat-Strengthened Fiber Properties for Copolymers Containing Monoketone Units and/or Isomeric Diketone Units**

| | tenacity, GPa | elongation, % | modulus, GPa |
|---|---|---|---|
| 1,4BE/3,4'MePCOPG/T (60/20/20) | 2.6 | 3.1 | 84 |
| 1,4BE/MePCOPCOMePG/T (60/20/20) | 1.4 | 4.6 | 33 |
| 1,4BE/PG/MePCOPCOMePG/T (60/10/10/10) | 1.4 | 3.5 | 41 |
| 1,4BE/ClPG/PCO*m*PCOPG/T (60/10/10/20) (from Table II) | 0.6 | 40 | 35 |

**Table VI. Tensile Properties of Selected AA–BB Type Copolyesters Containing Isophthaloyldiphenyl Units**

| | tenacity, GPa | elongation, % | modulus, GPa |
|---|---|---|---|
| PhPG/PCO*m*PCOPG(80/20)-T | | | |
| as spun | 0.4 | 3.3 | 22 |
| heat treated | 0.6 | 19 | 22 |
| ClPG/PCO*m*PCOPG(80/20)-T | | | |
| heat treated | 0.7 | 8 | 29 |
| MePG/PCO*m*PCOPG(80/20)-T | | | |
| heat treated | 0.6 | 7 | 20 |
| PCO*m*PCOBE/ClPG/T (43/43/14) | | | |
| heat treated | 0.5 | 19 | 21 |

not provide high elongation, but from the convex shape of the stress–strain curves, it was concluded that there was an inherent tendency to provide high elongation, which could be realized at elevated temperatures. However, one ClPG-T copolymer with the hydroxy acid PCO*m*PCOBE had an elongation of 19%.

## Discussion

The ability of certain thermotropic polyester fibers, as assemblies of axially aligned, parallel macromolecules, to undergo a high degree of elongation under applied extensional forces is discussed in terms of a hypothesis which invokes 180° folding of chains in the longitudinal direction. This is consistent with experimental observations and, in the absence of any alternative hypothesis, unique. It was beyond the scope of this project to seek experimental confirmation by direct structural investigations.

The combination of high strength, low elongation, and high modulus associated with conventional thermotropic polyester fibers is a consequence of a high degree of axial alignment of fully extended, linear macromolecules. Applied extensional forces therefore cause primarily bond stretching or widening of bond angles. A small amount of copolymerized nonlinear or flexible units in an otherwise rodlike composition such as 1,4BE/ClPG/T normally causes mild lowering of tenacity and modulus and increased elongation up to ca. 7%. Contrary to expectation, the incorporation of 10 mol % PCO*m*PCOP or PCO*m*POBE can produce elongation as high as 40% at 21 °C and higher at elevated temperatures. This is associated with quite modest levels of tenacity (ca. 0.6 GPa) and fairly high moduli (ca. 24 GPa). Questions arise as to the mechanism whereby this occurs; the unique role of the isophthaloyldiphenyl unit within a narrow concentration range; the extreme weakness of the as-spun fibers before heat-strengthening, even though inherent viscosity measurements indicate substantial levels of molecular weight; the high criticality of processing conditions, especially heat-strengthening temperatures; absence of shrinkage during heat-treatment of high-elongation fibers; high levels of chain orientation, especially after heat-strengthening, as measured by wide-angle X-ray.

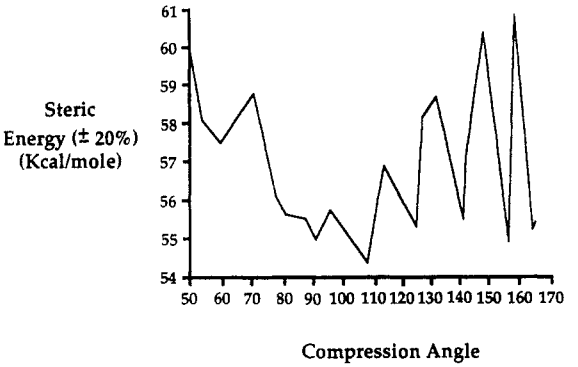
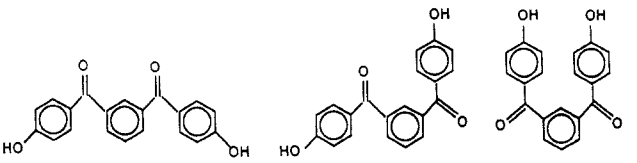
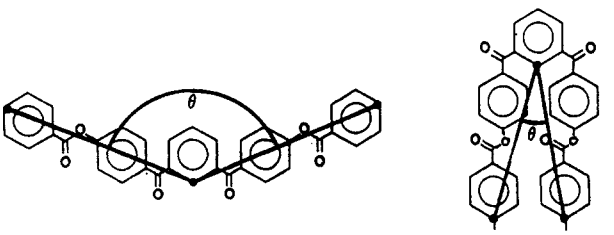



**Figure 7.** Computer-generated profile of energy level of successive conformations of isophthaloyldiphenyl-containing segment as compression angle is varied (ca. 170° represents complete folding).

An initial consideration of alternative conformations of the isophthaloyldiphenyl unit in terms of resonance structures shows several, quite different, resonance-stabilized possibilities. Thus, PCO*m*PCOPG may be written




A more precise determination of conformational possibilities of this unit as a component of polymer chains is derived from the application of the MM2 energy minimization molecular modeling program.[9,10] In these it has been assumed that interactions between adjacent macromolecules are absent; i.e., they are assumed to exist in a hypothetical gas phase. In a segment of macromolecule containing the isophthaloyldiphenyl unit, as shown below, the angle $\theta$ is varied systematically between the most extended and most folded conformations.




The computer-calculated minimum energy for intermediate values of $\theta$ is plotted against "compression angle", defined as $(180° - \theta)$ in Figure 7. Examples of intermediate configurations are shown in Figure 8. The highest compression angle in Figure 7 (ca. 165°) corresponds to complete folding, i.e., total reversal of chain segment direction, as indicated in the structural formula. This conformation is stabilized relative to adjacent minimum energy conformations by a significant energy barrier of ca. 6 kcal/mol. Various additional energy minima at intermediate energy levels are separated by comparable energy barriers of 3–6 kcal/mol (Figure 7) which reflect the conjugative interaction of carbonyl groups with adjacent aromatic rings. In the most extended minimum energy conformation, $\theta = 120°$ and stabilization is little more than 1.5 kcal/mol; i.e, fully extended chains are far from rectilinear and would not be expected to pack well

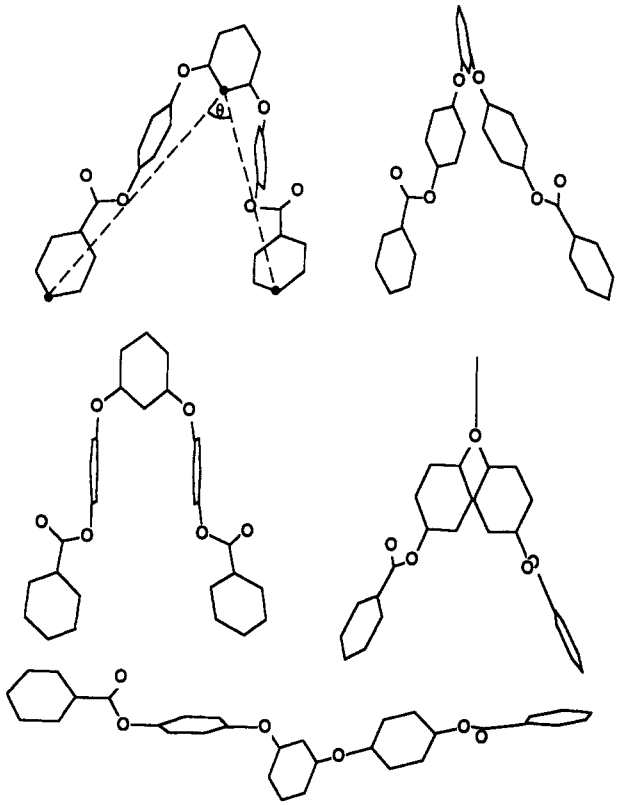
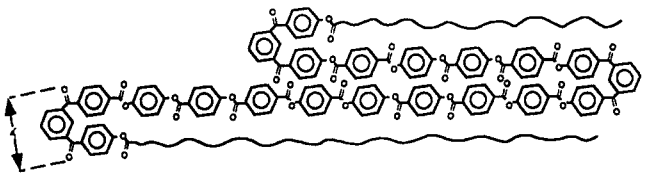


**Figure 8.** Examples of computer-generated conformations for 1,3-phenylenedioxydiphenyl segments. Conformations of isophthaloyldiphenyl segments, used for construction of Figure 7, are analogous.



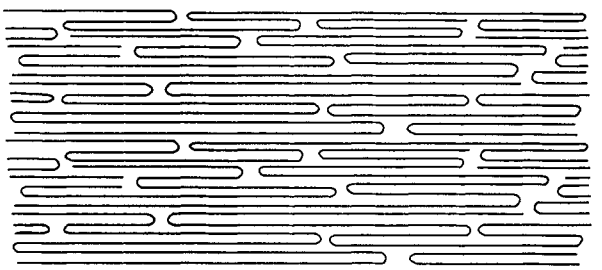


**Figure 9.** Representation of folded chain structure in nematic melt.

as a thermotropic melt. The molecular segments under discussion, if the macromolecules were in isolation, would adapt a distribution throughout the available energy minima proportional to their relative energy levels; however, as minor components of an otherwise highly thermotropic system, their preferred conformation is dictated by thermodynamic equilibration toward parallel chain alignments as a nematic melt for greatest packing efficiency. The conformation which best conforms with such a preferred melt structure would appear to be the 180° folded state. All other stable conformational possibilities require deviations from linearity in the macromolecule. Figure 9 is a representation of the nematic melt state wherein macromolecular segments are maintained in excellent parallel array as a result of 180° folding of the otherwise nonlinear isophthaloyldiphenyl units.

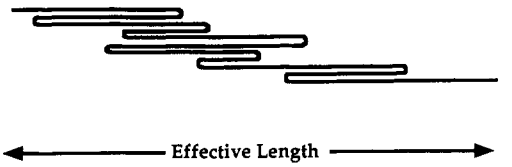



**Figure 10.** Effective length of folded macromolecule.

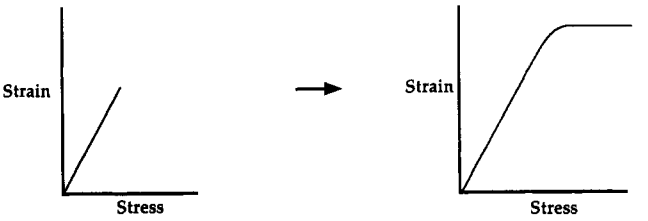
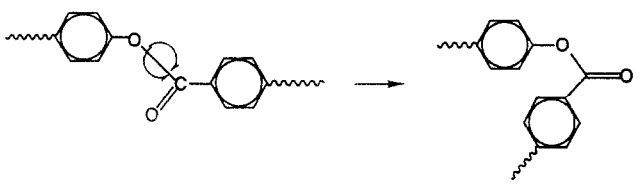



**Figure 11.** Stress–strain curves of 1,4BE/ClPG/PCO*m*P-COPG/T (60/10/10/20): (a) as-spun; (b) heat-strengthened. The tenacity, elongation, modulus, and orientation angle are (a) 0.05 GPa, 1.6%, 34 GPa, and 16° and (b) 0.6 GPa, 27°, 30 GPa, and 12°.

When nematic domains as represented in Figure 9 are extruded through a spinneret under moderate shear forces, it is expected that 180° folds will be largely retained and high segmental orientation in the axial direction will occur. This structure is, of course, captured in the fiber when the melt solidifies. The inherent viscosity (1.0–2.0 dL/g) of the polymer, as extruded, is comparable with that of conventional thermotropic polyesters and represents $M_n$ of roughly 10 000; this indicates a molecular length sufficient to sustain a tensile strength in the range 0.35–0.70 GPa. With folded chains, however, the effective molecular length (Figure 10), which is a major determinant of tensile strength, is considerably abbreviated, and tensile strengths usually lie in the low 0.3–1.2-GPa range. As-spun fibers are brittle because of the combination of low tenacity and low elongation to break as shown in Figure 11.

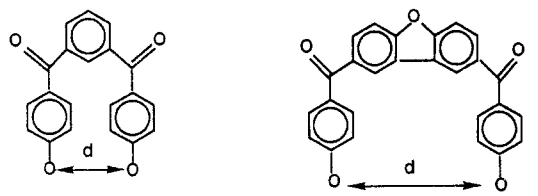
Heat treatment of as-spun fibers under conditions usual for thermotropic polyesters, i.e., where the combination of elevated temperature and enhanced segmental mobility of polymer chain segments facilitated considerable molecular weight growth, caused a preferred increase in fiber toughness, a combination of increased tenacity and, more particularly, elongation, with some improvement in orientation. The increase in effective length of the chains raises tenacity to or beyond the yield point (Figure 11); beyond this, practically no additional tension is needed for elongation, i.e., ductile behavior. The high sensitivity of capability to elongate with heat-treatment temperature indicates that the latter contributes also to some kind of reordering of the folded structure (Figure 9). Flory[11] has suggested that this could well be some degree of growth and redistribution of ordered regions containing aligned straight segments and enriched concentrations of folded segments.

When tensional forces are applied to such an assembly of parallel, folded chain, the initial resistance to stretching is of similar order to that of fully extended parallel chains. Hence, a folded-chain structure possesses a relatively high initial modulus. When the yield point is exceeded, the only logical explanation for the high observed degree of elongation is unfolding of chains, presumably involving a peeling process. Aromatic polyesters are by no means stiff, rigid chains; the energy involved in altering conformation as shown below, which migh depict part of a peeling process, is only 11 kcal/mol. This is energy of rotation about a C(O)–O bond.

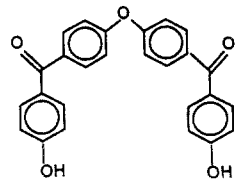


The criticality of the ca. 10 mol % level of concentration of PCO*m*PCOPG or PCO*m*PCOBE units in providing the maximal combination of modulus and elongation may well relate to the average length of the intervening straight segment of 9 repeat units. Straight-segment length undoubtedly influences total cohesion between chains and the facility with which unfolding can occur. At lower levels of PCO*m*PCOPG, say 8%, the somewhat longer straight segments (~11.5 repeat units) have higher overall cohesion such that unfolding cannot occur as readily and high elongation does not appear. At higher levels of PCO*m*PCOPG, beyond 10%, increased disorder lowers cohesion and modulus but gives higher elongation. For example, 1,4BE/PCO*m*PCOPG/T (60/17/17) had tenacity/elongation/modulus of 0.43 GPa/60%/16 GPa. Capability of unfolding is also influenced by the actual chemical nature of the straight segments, as it influences degree of cohesion. Thus, whereas PhPG/PCO*m*PCOPG/T (40/10/50) provides elongation of 20% and a relatively low modulus of 19 GPa, the analog wherein PhPG is replaced by ClPG or MePG shows low tendency or potential for high elongation in the stress–strain curve. The large increase in elongation when measured at elevated temperatures obviously is a result of reduced intermolecular cohesion.

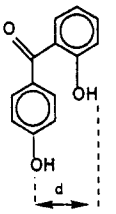
It is probably significant that, for the formation of relatively stable 180° folds which retain their conformation through extrusion, the spacing *d* between the phenoxy units in the 180° folded conformation is close to the interchain distance, as is obvious by inspection of the following structure and in Figure 9.



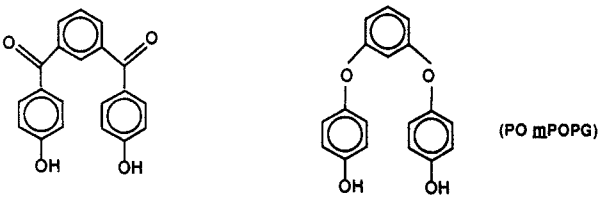
The analog of PCO*m*PCOPG, dibenzofuranoyldiphenol (PCOBfCOPG), provides 180° folding but the *d* spacing is much greater than the interchain distance. Polyesters containing 10 mol % of this unit, typified by 1,4BE/1,3PG/PCOBfCOPG/T (60/10/10/20) behaves like a conventional thermotropic polyester with a near-linear stress–strain curve and no evidence of high elongation. It is tempting to argue that the large *d* spacing prevents formation of stable folds to that the polymer exists in extended form in the melt, but there is an alternative possibility that the dibenzofuran unit is sufficiently large as to hinder ease of peeling. In this context it was noted that substitution of biphenylene units in otherwise high-elongation compositions seems to prevent high elongation. A close analog of PCOBfCOPG, oxydibenzoyldiphenol,



also failed to facilitate high elongation in various copolyesters; however, here there is no special stabilizing influence for the 180° folded structure as shown. Attempts to assess compositions with a very small *d* spacing, as shown for 2,4′-dihydroxybenzophenone, were thwarted by inadequate melt homogeneity as needed for preparation of good fibers.



The importance of some degree of resonance stabilization in the 180° folded conformation of the PCO*m*PCOPG unit, in relation to folding in the thermotropic melt and high elongation, may be inferred by comparison with analogous polymers containing the ether analog of PCO*m*PCOPG (PO*m*POPG), which is capable of adopting a geometrically very similar 180° folded conformation.




Thus, 1,4BE/ClPG/PO*m*POPG/T (60/10/10/20), in contrast with the PCO*m*PCOPG analog, provides an as-spun fiber tenacity commensurate with that of conventional thermotropic polyesters (0.35 GPa), an essentially linear stress–strain curve with no evidence of high elongation ($E$ = 4.6%) after heat treatment and a rather higher tenacity (0.90 GPa) and modulus (33 GPa). These properties are characteristic of fully extended polymer chains wherein tenacity and modulus are limited by the combination of a nonlinear unit flanked by rather flexible carbonyl groups.

Process conditions which are not conducive to the formation of a highly extensible structure include high extensional shear (rate at which the still-molten, incipient fiber is stretched as it is pulled away from the spinneret), high functional shear (as provided by extrusion orifices of increased length), and high melt viscosity (either the result of higher molecular weight or of temperature lowering) as shown in Figure 4. These conditions all tend in the direction of higher extensional forces on individual macromolecules and it seems reasonable to conclude that 180° folding is thereby diminished. Under such conditions, 1,4BE/PG/PCO*m*PCOPG/T (60/10/10/20), as an example, provides tensile properties typical of a conventional thermotropic polyester and indeed similar to those of the unfolded PO*m*POPG analog discussed above:

| | tenacity, GPa | elongation, % | modulus, GPa |
|---|---|---|---|
| 1,4BE/PG/PCO*m*PCOPG/T (60/10/10/20) | | | |
| folded | 0.63 | 40 | 35 |
| nonfolded | 1.00 | 2.5 | 56 |
| 1,4BE/PG/PO*m*POPG/T (60/10/10/20) | 0.90 | 4.6 | 33 |

The recovery properties, discussed earlier, indicate that high-elongation fibers are prediposed to acquire a permanent deformation if stretched beyond the yield point.

The question arises as to what fiber tensile properties can be achieved by actually drawing these fibers at elevated temperatures. Contrary to expectations of high drawability suggested by Figure 5, heat-treated 1,4BE/PG/PCO*m*PCOPG/T (60/10/10/20) could be drawn by a maximum of 50%, at 300 °C, to provide a level of properties approaching those of the "nonfolded" fiber in the above table. Very high temperatures of up to 300 °C apparently did not permit unfolding significantly beyond that achieved in the 21–100 °C region. If all isophthaloyldiphenyl units were folded at 180° and present at a 10 mol % level, and assuming a degree of polymerization of ca. 100, which is fairly common for aromatic condensation polymers, there would be 10 folds per chain, which might be construed as the basis for up to 10-fold elongation uder applied tension. The much smaller elongations observed, of ca. 50% under the most favorable conditions, suggest that a relatively small fraction of the isophthaloyldiphenyl groups present are actually folded at 180°.

## References and Notes

(1) Irwin, R. S. *Mater. Res. Soc. Symp. Proc.* **1991**, *227*, 293.
(2) Luise, R. R. U.S. Patent 4,183,895, 1980.
(3) Calundann, G. U.S. Patent 4,184,996, 1980.
(4) Irwin, R. S. U.S. Patent 4,188,476, 1980.
(5) Hare, W. A. DuPont, unpublished information.
(6) Morgan, H. S. U.S. Patent 3,796,693, 1974.
(7) Ciferri, A.; Ward, I. *Ultra-High Modulus Fibers*; Applied Science Publishers: London, 1979; p 221.
(8) Irwin, R. S. U.S. Patent 4,381,389, 1983.
(9) Allinger, N. L.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 8127. Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, DC, 1982.
(10) Molecular modeling was performed by W. P. Gerred and J. J. Turner, DuPont.
(11) P. J. Flory, private communication.