Pretreatment of Polystyrene Copolymer Beads.[5] A 1-L round-bottomed flask was charged with 400 mL of cyclohexane and 77 g (0.739 equiv) of polystyrene–2% divinylbenzene copolymer beads. The polymer was allowed to swell with stirring, for 24 h at 60 °C and then cooled to 0 °C. TMEDA (112 mL, 86.2 g, 0.742 equiv) was added, followed by *n*-butyllithium (0.731 equiv). After stirring for 1 h at room temperature, the slurry was heated to 60 °C for 8 h, at which point it was cooled to 0 °C and quenched with methanol. The usual workup afforded the material used in subsequent steps.[8]

General Procedure for the Preparation of Silylated Copolymer Beads. In a similar fashion, the pretreated beads (50.8 g, 0.48 equiv) were allowed to swell in cyclohexane (300 mL) at 60 °C for 24 h and then cooled to 0 °C. Following addition of the requisite amount of TMEDA and *n*-butyllithium (in a 1:1 molar ratio), the temperature was raised to 60 °C and the slurry stirred for 24 h. The lithiated polymer was cooled to 0 °C and excess chlorotrimethylsilane (twofold based on butyllithium) added. The usual workup afforded the silylated polymer (ν(KBr) 1250, 840 cm^{-1}). Analytical data are summarized in Table I.

General Procedure for Halogenation of PS-SiMe$_3$. A slurry of CH_2Cl_2 (75 mL) and silylated polystyrene (5 g) was allowed to swell at room temperature for 12 h. To the slurry was added a solution of the requisite amount of halogenating agent in CH_2Cl_2 (15 mL). After 8 h of stirring at room temperature, the usual workup afforded either partially brominated polymer or partially iodinated polymer, depending on halogenating agent. Analyses are summarized in Table II.

IR analysis showed partial loss of the silyl stretching frequencies. C–X stretching frequencies could not be readily discerned within the aromatic region.

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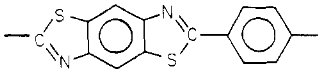
(7) At these levels, a change of 0.2% elemental composition leads to a change of approximately 1.0–1.5% in degree of functionalization calculated therefrom.
(8) Failure to pretreat the beads in this fashion resulted in consistent overhalogenation, probably due to extra vinyl groups in the polymer.[5]

Communications to the Editor

Mechanical Studies of High-Strength, High-Modulus Poly(*p*-phenylenebenzobisthiazole) Fibers

This work deals with the evolution of the mechanical properties of fibers produced from anisotropic solutions of poly(*p*-phenylenebenzobisthiazole) (PBT) by dry-jet wet spinning. PBT, with repeat unit



is characteristically a rigid-rod polymer (details of the synthesis, preparation, and chemical structure of PBT can be found in other articles in this issue). PBT was prepared as part of the Air Force Ordered Polymers Research Program,[1] which is aimed at the attainment of high strength, high temperature resistance, and environmental stability in a material of an organic base for use as a structural material. Of the polymers investigated in this program PBT has shown the most promise. The PBT fibers, as spun and heat treated, exhibit both a high specific modulus and a high strength, and their environmental stability in all but strong acid environments is excellent.

Experimental Details. The PBT fibers investigated in this work were produced by a dry-jet, wet-spinning process at Celanese Research Co. and at Carnegie-Mellon University. A schematic of the spinning apparatus is given in Figure 1. Fibers designated as PBT/PPA were spun from solutions of 5–6% polymer in poly(phosphoric acid) (PPA), while those designated as PBT/MSA were spun from solutions of roughly 10% polymer in a dissolvent of 97.5% methanesulfonic acid/2.5% chlorosulfonic acid. Coagulation baths of water or water/methanesulfonic acid were used. Heat treating of the fibers was accomplished by drawing them through a tubular oven under a nitrogen atmosphere.

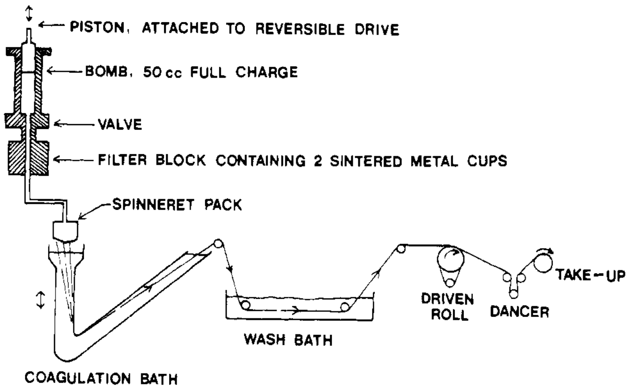


Figure 1. Schematic diagram of PBT spinning apparatus.

The tensile mechanical properties of the as-spun and heat-treated PBT fibers reported here were determined in compliance with ASTM D3379-75e. A Toyo Tensilon Model UTM-II and an Instron universal testing machine were used for the tensile tests to determine axial mechanical properties. A strain rate of 1%/min was commonly used. Fiber deniers were determined by the vibroscope technique (ASTM D1-577-73).

Fiber Properties. PBT fibers as spun and after heat treating have demonstrated both high modulus and high strength. Moduli of 800 g/denier are typical for as-spun fibers with strengths around 8 g/denier. Heat treatment yields fibers with moduli as high as 2100 g/denier and strengths of 20 g/denier. Table I summarizes typical strength and modulus values for both as-spun and heat-treated fibers produced from PBT/MSA and PBT/PPA

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Table I
Modulus and Strength of PBT Fibers

spinning dope	fiber condition	modulus, g/denier	strength, g/denier
PBT/MSA	as spun	350-1200	3-12
	heat set	1000-2100	11-18
PBT/PPA	as spun	400-600	4-18
	heat set	600-2100	6-20

Table II
Typical Mechanical Properties

	modulus		strength			density,
fiber	g/denier	GPa	g/denier	GPa	elongation, %	g/cm^3
PET[8]	50-110	5-12	6-9	1	10-16	1.38
nylon[9]	55	5	10	1	18	1.14
glass[9]	260	55	9	2	4	2.55
steel[9]	280-300	180-200	3-5	2-3	2-3	7.9
Kevlar 29[9,10]	480	60	29	3.7	3-4	1.44
Kevlar 49[10,11]	980	120	32	4.1	2.5	1.44
graphite[8,12]	600-4000	100-700	6-25	1-4	0.6-1.6	1.8-2.1
PBT	2100	250	20	2.4	1.5	1.5

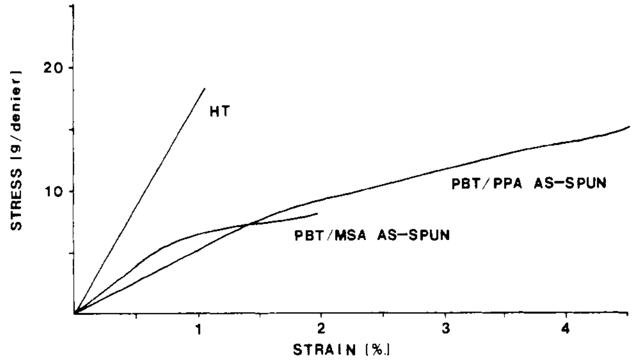

Figure 2. Stress–strain behavior of as-spun and heat-treated (HT) PBT fibers.

dopes. The stress–strain behavior of both as-spun and heat-treated PBT fibers is illustrated in Figure 2. The nonlinear character of the stress–strain behavior of the as-spun fibers has been discussed elsewhere[2,3] in terms of residual stresses arising during coagulation. These stresses can be relieved by heat treating to give an essentially linear-elastic behavior (Figure 2).

The high-modulus, high-strength properties derive from the high degree of molecular orientation along the fiber axis and a well-developed two-dimensional order, which have been revealed by electron and X-ray diffraction studies.[4]

The mechanical properties of heat-treated PBT fibers are compared to those of other materials in Table II. It is seen that PBT fiber has superior modulus and strength over common polymeric fibers and over both steel and glass. The modulus obtainable for PBT is higher than for commercial Kevlar [poly(*p*-phenyleneterephthalamide) (PPTA)] and similar to that of certain graphite fibers. PBT fiber strength at present is comparable to that of PPTA fibers, which far exceeds the strength of the other materials given in Table II. However, as reported previously,[2,3] PBT fiber strength has been limited due to the presence of large voids in the fibers. Considering the presence of large voids in the PBT fibers and the possible variations of both spinning and heat-treating conditions that are yet to be employed, it is not unreasonable to expect the attainment of higher values for the strength of PBT fibers as further improvements in processing occur.

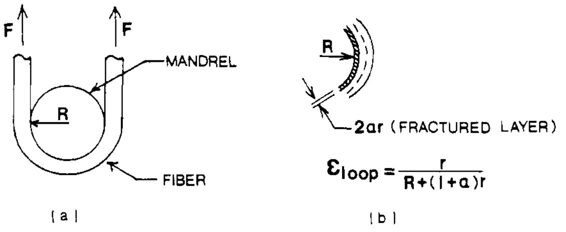

Figure 3. (a) Loop test geometry. (b) Schematic showing redistribution of strain field due to compressive failure.

Influence of Spinning Conditions. While it has been noted that the mechanical properties of fibers produced from PBT/MSA dopes have been restricted by the presence of large voids,[2] some variability in these properties has been achieved by adjustment of the spinning conditions. Generally, higher values of as-spun fiber modulus are obtained with higher spin/draw ratios, and slightly higher values of fiber strength have been found with higher extrusion velocities. Slower coagulation rates, obtained by using coagulation baths with high MSA/H_2O ratios and/or low bath temperatures, have, in general, produced fibers with higher modulus and strength. These conditions have produced fibers of lower denier and lower void content than the fibers produced under faster coagulation conditions (low MSA/H_2O ratios, higher bath temperatures), although spinnability has only been marginal for processing conditions using slow coagulation rates. In spite of these processing difficulties and the fiber void content, fibers produced from PBT/MSA dopes exhibit both high modulus and high strength in comparison with common polymeric and nonpolymeric materials (Table II).

The processing of PBT fibers from PBT/PPA dopes represents two advantages over spinning from PBT/MSA dopes. The spinnability of PBT/PPA dopes has been found to be better than for PBT/MSA dopes and the spinning of fibers from PBT/PPA dopes represents fiber production directly from the PBT polymerization medium. The isolation of the polymer after polymerization and redissolving in a suitable solvent, which is a necessary step for other aromatic fibers,[5] is thus eliminated. The dependence of fiber properties on specific PPA spinning conditions is currently being evaluated, although in terms of fiber mechanical properties no significant difference exists between PBT/MSA and PBT/PPA fibers.

Anisotropic Behavior. Mechanical anisotropy of PBT fibers was demonstrated in fiber loop tests similar to those used by Schoppee and Shelton[6] (see Figure 3). Fiber loop strength is analyzed by consideration of both the strain imposed by bending and the applied axial strain. Assuming for simplicity that the tensile and compressive properties of the fiber are the same, that the material is linear elastic, and that plane sections remain plane during bending, the expected strength at failure is given by eq 1,

$$\sigma^* = E[\epsilon_b - r/(R + r)] \qquad (1)$$

where ϵ_b is the strain at break in a simple tensile test, r is the fiber radius, R is the mandrel radius, and E is the fiber modulus. In this equation the fiber strength σ^* is determined by the maximum tensile stress in the cross section. The theoretical loop strength is thus equal to the tensile strength if $R \gg r$, decreases with increasing values of $r/(R + r)$, and becomes equal to zero for $\epsilon_b = r/(R + r)$.

The behavior predicted by eq 1 was not found for the loop strengths of PBT fibers. Figure 4 summarizes the

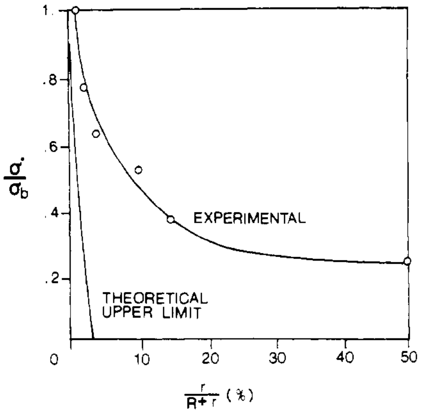

Figure 4. Fiber loop efficiency as a function of loop radius.

results as the ratio of loop strength to tensile strength as a function of $r/(R + r)$. The loop strength is found to be higher than predicted by eq 1 and is even finite down to a value of $r/(R + r) = 0.5$. Similar results have been found for Kevlar fibers tested in loop tests.[6]

The discrepancy between the behavior of PBT fibers in the loop test and that predicted by eq 1 is the result of fiber tensile and compressive properties being different, the strength in compression being much lower than in tension. Figure 5 illustrates compressive failure of a PBT fiber subjected to bending. (In another study,[4] emphasizing the microstructural aspects of PBT fibers, we employed ultrasound to disperse fine fiber fragments. This treatment produces a large number of kinks in the fiber due to the susceptibility to compressive buckling and interlaminar shear failure.) This compressive failure gives rise to a redistribution of the strain field in the fiber cross section in the loop (see Figure 3b). The effective fiber diameter is reduced, giving a lower maximum bending strain, and allows for much higher loop strengths than expected by eq 1.

Retention of Properties in Harsh Environments. The retention of mechanical properties of as-spun PBT fibers has been found to be extremely good after exposure to a variety of chemical environments. The environments investigated include Skelly F, chloroform, dimethylacetamide, acetone, water, nitric acid (69%), and sulfuric acid (95%). After 200 h of exposure to all but the two acid environments, essentially 100% retention of both modulus and strength was observed. The same modulus retention was also observed after 2700 h of exposure for the Skelly F, dimethylacetamide, and water environments, with a 67% retention of strength.

The strong acid environments (nitric and sulfuric acids), however, showed immediate effects of deterioration on fiber mechanical properties. Reductions of up to 50% in both the modulus and strength were observed after a few exposure hours. After 200 h of exposure, the nitric acid environment yielded a 50% reduction in both fiber strength and modulus while 80–85% reductions were caused by the sulfuric acid environment.

Isothermal aging of a powder sample of PBT gave a weight retention of 50% after 200 h at 371 °C,[7] indicating good thermal stability. When tested at 200 °C, the heat-treated PBT fibers exhibited an 82% retention of modulus and a 73% retention of strength, quite similar to Kevlar 49 fibers tested at 200 °C, which show 70% modulus retention and 66% strength retention. At −200 °C a 40% higher PBT fiber strength was measured, with a 100% retention of modulus.

Summary. The molecular design of poly(*p*-phenylenebenzobisthiazole) has resulted in a material possessing both thermal and environmental stability. Essentially 100% retention of PBT fiber mechanical properties was found in a variety of harsh chemical environments after 200 h of exposure. PBT has demonstrated good thermal stability as well as retention of mechanical properties at elevated tempertures. While PBT fibers, at present, are characterized by a large number of macrovoids, these fibers still possess a high specific modulus and strength. A specific modulus 5 times that of glass or steel and comparable to that of graphite fibers has been obtained. The specific strength of these fibers is up to 5 times that of steel and equal to that of the poly(*p*-phenyleneterephthalamide)-type high-strength fibers.

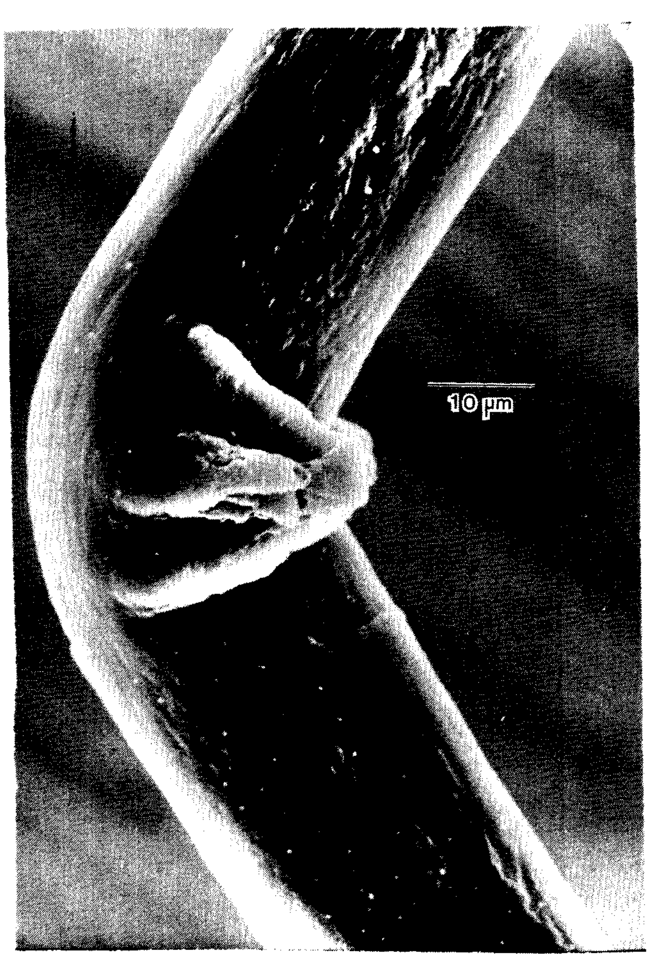

Figure 5. SEM micrograph of compressive failure of a PBT fiber.

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Observation of Triad Stereosequences in a Polystyrene Derivative

Although the stereochemical structures of most vinyl polymers can be measured relatively easily by ^{1}H NMR and/or ^{13}C NMR spectroscopy,[1-3] this has not been the case with polystyrene or with many of its analogues.[4] The ortho-aromatic proton resonances of polystyrene contain stereosequence information but these are not adequately understood at present.[5-7] The methine proton resonance of polystyrene (e.g., Figure 1A, $\delta = 1.6$–2.3) occurs in two general areas, and recent studies on partially epimerized isotactic polystyrene samples have shown that the lower field methine proton resonance area is due to mm stereosequences.[8] Fine structure due to pentad or higher stereosequences is observed in the methine proton resonances of poly(β,β-dideuteriostyrene),[9,10] but it is not well defined and the (mr + rm)- and rr-methine proton resonances are not separated in the spectrum of this polymer, even when deuterium–proton decoupling is employed. The methylene[3,11] and quaternary aromatic carbon[3,12] resonances of polystyrene are sensitive to hexad and heptad stereosequence effects. The abundant information available in the ^{13}C NMR spectra of polystyrene cannot be extracted precisely, because the individual resonances cannot be resolved and because of the difficulty of making unequivocal assignments for the various resonances.

In contrast to polystyrene, the resonances of methine protons in poly(β,β-dideuterio-2-vinylpyridine)[13] and in poly(β,β-dideuterio-4-vinylpyridine)[14] are resolved into signals representing mm, (mr + rm), and rr triads when the polymers are dissolved in D_2SO_4 at 60 °C, although the methine proton resonance patterns of these polymers are similar to those of polystyrene when the polymers are dissolved in *o*-dichlorobenzene at 160 °C. This result suggested to us that the methine proton resonances might be resolved in the spectra of polystyrenes substituted with sufficiently electronegative groups, due either to a decreased "ring current" effect or to a change in the conformation of the polymer imposed by the electronegative groups. We therefore investigated the 300-MHz ^{1}H NMR spectra of various para-substituted polystyrenes (substituent: F, Br, Cl, NH_2, CH_3CO, CN) prepared by AIBN-initiated polymerization at 65 °C for evidence of enhanced separation of the methine proton resonances. In most cases the methine proton resonances of the polymers were very similar to those of polystyrene. However, in the case of poly(*p*-acetylstyrene) (Figure 1B), the resonances of methine protons centered in (mr + rm) and rr triads occurred about 0.3 ppm upfield from that of the corresponding resonances in polystyrene. This enabled the mm-resonance area to be completely resolved from the (mr + rm) and rr resonances, but, unfortunately, these latter resonances were shifted into the methylene proton resonance region. Cheng and Pearce[15] reported 220-MHz spectra of poly[*p*-(trifluoroacetyl)styrene] and poly[*p*-(difluoroacetyl)styrene] in nitrobenzene solution at 91 °C and a similar phenomenon is evident in these spectra.

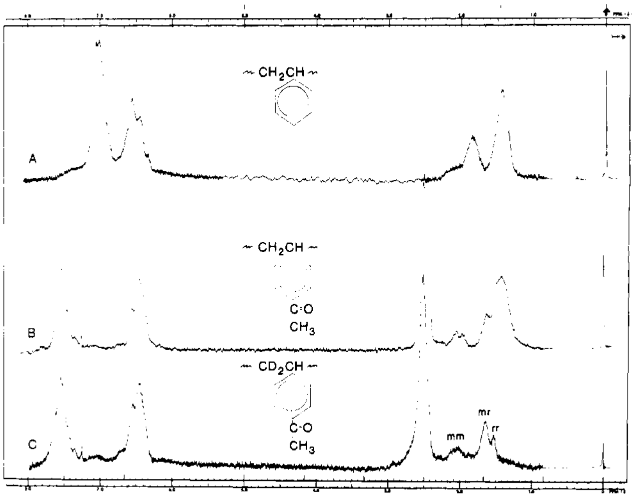

Figure 1. 300-MHz ^{1}H NMR spectra of (A) polystyrene, (B) acetylated polystyrene, and (C) acetylated poly(β,β-dideuteriostyrene) in $CDCl_3$ solution at room temperature.

To observe the (mr + rm)- and rr-methine proton resonances of poly(*p*-acetylstyrene) independently of methylene proton resonances, a sample of poly(β,β-dideuteriostyrene) prepared by AIBN-initiated polymerization at 65 °C was acetylated according to the procedure of Kenyon and Waugh.[16] The 300-MHz ^{1}H NMR spectrum of the product, poly(*p*-acetyl-β,β-dideuteriostyrene), is shown in Figure 1C. Resonances assignable to (mr + rm) and rr stereosequences are partially resolved in this spectrum and the mm-, (mr + rm)-, and rr-resonance areas are approximately in a 1:2:1 ratio, as would be expected for an essentially atactic polymer. The presence of a small amount of resonances due to residual methylene protons precludes an exact analysis from being made, but the mm area can be measured from spectrum 1B and it is 0.25 ± 0.02 of the total methine proton resonance area expected, indicating a σ value of $\sim$0.50 ± 02.

As a control experiment, to determine whether the stereochemical structure of polystyrene is altered by the acetylation conditions, a sample of partially epimerized isotactic polystyrene[11] known to have an mm content of 0.70 was acetylated according to the procedure of Kenyon and Waugh.[16] The mm content of the resulting polymer was 0.72, based on the intensity of the lowest field methine proton resonance area, indicating that the polymer configuration does not change under the acetylation conditions employed and that the resonance assignments provided in Figure 1C are probably valid. It is possible, as a reviewer has pointed out, that the mr + rm + rr pattern may not be separated clearly into triad resonances, but that it may be the result of overlapped pentad resonances. Extensive

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