

# Polybenzobisthiazoles with crosslinking sites for improved fibre axial compressive strength

T. D. Dang, C. S. Wang\* and W. E. Click

*University of Dayton Research Institute, Dayton, OH 45469, USA*

and H. H. Chuah

*Shell Development Co, Houston, TX 77001, USA*

and T. T. Tsai, D. M. Husband and F. E. Arnold

*Materials Directorate, Wright Laboratory, Wright-Patterson AFB, OH 45433, USA*

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A number of homo- and copolymer benzobisazole rigid-rod polymers have been synthesized, containing labile methyl pendants and benzocyclobutene groups for thermally induced crosslinking studies. Polycondensations of tetraamino, diaminodihydroxy and diaminodithio monomers with methyl, dimethyl and benzocyclobutene terephthalic acid derivatives in polyphosphoric acid (PPA) provided high molecular weight anisotropic liquid crystalline reaction mixtures. Selected benzobisthiazole polymers were dry-jet wet-spun into fibres from these PPA solutions. Depending on their thermal treatment conditions, the fibres showed Young's moduli from 18 to 43 Msi (124–296 GPa) and tensile strengths from 240 to 460 Ksi (1650–3170 MPa), comparable to those of unsubstituted benzobisazole rigid-rod polymer fibres. The highest axial compressive strength obtained from these fibres was 70 Ksi (480 MPa), a marginal improvement over that of unsubstituted rigid-rod polymer fibres. © 1997 Elsevier Science Ltd. All rights reserved.

**(Keywords: rigid-rod polymers; rigid-rod copolymers; polybenzobisthiazole)**

## INTRODUCTION

Research in our laboratory of lyotropic liquid crystalline polymers has provided a series of high modulus, high tensile strength materials based on the benzobisazole family of rigid-rod polymers. These polymers exhibit superior thermal and thermo-oxidative properties compared to other liquid crystalline organic materials, because of their heterocyclic aromatic structures. Unlike extended-chain polymers, such as polyaramides, which have both translational and rotational degrees of freedom owing to their bond angles, the all *para*-configured rigid-rod polymers have only rotational freedom around the chain axis. As a result, rigid-rod polymers can be readily processed, with uniaxial orientation and outstanding tensile mechanical properties. Modulus values of 30 to 50 Msi (210–340 GPa) accompanied by tensile strengths of 400 to 800 Ksi (2800–5500 MPa) have been obtained on wet-spun benzobisazole fibres after heat treatment<sup>1</sup>.

The high modulus and high tensile strength of rigid-rod polymer fibres offer potential advantages for applications such as advanced composites and light-weight structural materials. However, this class of fibres suffers from relatively low axial compressive strength

(about 50 Ksi (340 MPa)), which is critical for many structural applications that undergo considerable compressive loadings, such as aircraft wings. The poor axial compressive strength of these polymer fibres is believed to be due to insufficient lateral interactions between the highly oriented molecules or supramolecular structures, causing them to buckle under an axial compressive load. Although a number of approaches have been attempted, for example by the introduction of large pendants to disrupt the uniaxial molecular packing order<sup>2</sup>, by incorporation of thermally crosslinkable moieties into the polymers<sup>3</sup>, by infiltration of sol-gel glass or thermosetting resins<sup>4</sup>, and by forming pseudo-ladder structures through intramolecular hydrogen bonds<sup>5</sup>, only marginal success has been achieved in improving the fibre axial compressive strength of these systems.

This paper describes our efforts to incorporate chemical crosslinks into rigid-rod polymer fibres to provide permanent lateral support to the highly aligned molecules. Crosslinks were introduced by two different synthetic routes. In the first approach, labile methyl groups were attached to the polybenzobisthiazole (PBT) backbone as pendants via methyl and dimethyl terephthalic acids and derivatives. On thermal treatment the methyl pendants generate aromatic free radicals for a biradical coupling reaction, with the evolution of methane. This method is analogous to the recently published biradical coupling of thermally treated PBTs

\* To whom correspondence should be addressed

containing halo aromatics<sup>5</sup>. Crosslinking density can be controlled by preparing various copolymer compositions using terephthalic acid monomers. The second approach was to synthesize PBT polymer incorporating benzocyclobutene (BCB) moieties along the polymer backbone. BCBs have been utilized in a number of matrix resins<sup>6</sup> as addition crosslinked systems, as well as utilized in the crosslinking of extended-chain polyaramides<sup>7,8</sup>. Homopolymer and copolymer PBTs were prepared from the condensation of 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl chloride and 2,5-diaminobenzenedithiol dihydrochloride in polyphosphoric acid (PPA). In the following sections, the synthesis, fibre fabrication, post-treatment and mechanical evaluation of a series of homo- and copolymers, including monomethyl-PBT (MM-PBT), dimethyl-PBT (DM-PBT) and BCB-PBT, are reported and discussed.

## EXPERIMENTAL

### Monomers

Polymer-grade 2,5-diamino-1,4-benzenedithiol dihydrochloride and 1,2,4,5-tetraaminobenzene tetrahydrochloride were obtained from DayChem, Inc. (Dayton, Ohio) and recrystallized from concentrated hydrochloric acid containing stannous chloride. 4,6-Diamino-1,3-benzenediol dihydrochloride was prepared by the catalytic reduction of 4,6-dinitro-1,3-benzenediol using 10% palladium on charcoal<sup>9</sup>. Recrystallization from concentrated hydrochloric acid containing stannous chloride provided anhydrous polymer-grade monomer. 1,2-Dihydrocyclobutabenzene-3,6-dicarboxylate was obtained as a gracious gift from Prof. D. C. Martin (University of Michigan, Ann Arbor, Michigan). The diacidchloride was prepared according to a synthetic procedure described previously<sup>10</sup>.

**2-Methylterephthalic acid.** A solution of 14.22 g (0.1 mol) of 2,5-dicyanotoluene and 400 g of 100% phosphoric acid was heated under nitrogen atmosphere to 180°C for 18 h to prepare 2-methylterephthalic acid. The solution was cooled to 25°C and then poured into 1 litre of water to precipitate a white solid. The solid was collected by filtration, washed with water and dried. This crude product was recrystallized from anhydrous ethanol to give 11.4 g (63.3%) of white crystals, mp: 250–252°C.

Analysis calculated for C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>: C, 60.00; H, 4.47. Found: C, 59.86; H, 4.40.

**2-Methylterephthaloyl chloride.** A solution of 10.8 g (0.06 mol) of 2-methylterephthalic acid and 100 ml of thionyl chloride was refluxed under nitrogen atmosphere for 24 h. The excess thionyl chloride was removed by rotary evaporation. The crude product was recrystallized from heptane to give 8.5 g (65.3%) of white needles, mp: 39–40°C.

Analysis calculated for C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 49.8; H, 2.79; Cl, 32.7. Found: C, 49.95; H, 2.71; Cl, 32.43.

**2,5-Dicyanoxylene.** A mixture of 2,5-dibromoxylene (100 g, 0.38 mol), cuprous cyanide (77.92 g, 0.87 mol) and dry dimethylformamide (400 ml) was heated under nitrogen atmosphere to reflux for 3 h. The reaction mixture was cooled and then poured into 600 ml of water

containing 400 g of ferric chloride and 100 ml of hydrochloric acid. The resulting precipitate was filtered and dried. The crude product was dissolved in 150 ml of methylene chloride and passed through a quartz column containing about 1500 g of silica gel using a 50/50 mixture of chloroform and hexane as the eluting solvent. The collected light yellow solution deposited white crystals after standing at room temperature. The product was collected and recrystallized from anhydrous ethanol to give 34 g (58%) of white crystals, mp: 210–212°C.

Analysis calculated for C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>: C, 76.9; H, 5.16; N, 17.94. Found: C, 76.5; H, 5.34; N, 17.81.

**2,5-Dimethylterephthalic acid.** A solution of 45.3 g (0.29 mol) of 2,5-dicyanoxylene and 900 g of 100% phosphoric acid was heated under nitrogen atmosphere to 180°C for 18 h. The solution was cooled to 25°C and then poured into 2.5 l of water to precipitate a white solid. The solid was collected by filtration, washed with water and dried. The crude product was recrystallized from anhydrous ethanol to give 41.2 g (73%) of white crystals, mp: 198–199°C.

Analysis calculated for C<sub>10</sub>H<sub>10</sub>O<sub>4</sub>: C, 61.85; H, 5.19. Found: C, 61.69; H, 5.25.

**2,5-Dimethylterephthaloyl chloride.** A solution of 23.51 g (0.12 mol) of 2,5-dimethylterephthalic acid and 150 ml of thionyl chloride was refluxed under nitrogen atmosphere for 24 h. The excess thionyl chloride was removed by rotary evaporation. The crude product was recrystallized from heptane to give 16.74 g (60%) of white needles, mp: 120–121°C.

Analysis calculated for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 51.98; H, 3.49; Cl, 30.68. Found: C, 52.36; H, 3.48; Cl, 30.49.

### Polymers

Each of the following polymerizations was carried out in a mixing flask equipped with a high torque mechanical stirrer, nitrogen inlet and outlet, pressure regulator, and a side opening for additions. At the end of each polymerization, a larger portion of the polymer was reserved for fibre spinning. The remainder was precipitated into water, broken up with a blender, collected by suction filtration, washed with water and dried under reduced pressure (0.05 mm Hg) at 100°C. The intrinsic viscosity,  $[\eta]$ , of these polymers was measured in methanesulfonic acid (MSA) at 30°C.

**Poly[benzo[1,2-d:5,4-d']bisoxazole-2,6-diyl(2-methyl-p-phenylene)].** To the mixing flask as described above was added 3.4321 g (0.0158 mol) of 2-methylterephthaloyl chloride, 3.3691 g (0.0158 mol) of 1,3-dihydroxy-4,6-diaminobenzene dihydrochloride and 19.56 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 65°C for 24 h, 85°C for 4 h and 95°C for 2 h. Upon completion of the dehydrochlorination, as indicated by a visually clear solution, the solution was cooled to 50°C and 10.44 g of phosphorus pentoxide was added to it to maintain the phosphorus pentoxide content of PPA at about 83%. The solution mixture was stirred vigorously until a smooth paste was obtained. Then the polymerization was continued by heating and stirring the solution mixture under nitrogen atmosphere at 60°C for 2 h, 100°C for 2 h and 190°C for 24 h. Stir-palescence, an indication of liquid crystalline state,

was observed at approximately 160°C as the solution was heated from 100 to 190°C in 2 h. The polymer content of this solution was 14% and the polymer had an intrinsic viscosity of 23.5 dl g<sup>-1</sup>.

Analysis calculated for C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.58; H, 3.25; N, 11.28; O, 12.89. Found: C, 71.61; H, 3.30; N, 11.49; O, 13.60.

*Poly[1,7-dihydrobenzo[1,2-d:5,4-d']bisimidazole-2,6-diyl(2-methyl-p-phenylene)]*. To the mixing flask as described above was added 3.4321 g (0.015 mol) of 2-methylterephthaloyl chloride, 4.4911 g (0.015 mol) of 1,2,4,5-tetraaminobenzenetetrahydrochloride and 15.22 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 65°C for 24 h, 85°C for 8 h and 95°C for 4 h. Upon completion of the dehydrochlorination, the solution was cooled to 50°C and 8.13 g of phosphorus pentoxide was added and mixed. The polymerization was then continued by heating the solution mixture under nitrogen atmosphere at 60°C for 2 h, 100°C for 2 h and 190°C for 24 h. Stir-opalescence was observed at about 160°C as the solution was heated from 100 to 190°C. The polymer content of this solution was 14% and the polymer had an intrinsic viscosity of 14.7 dl g<sup>-1</sup>.

Analysis calculated for C<sub>15</sub>H<sub>10</sub>N<sub>4</sub>: C, 73.16; H, 4.09; N, 22.75. Found, C, 71.21; H, 4.41; N, 22.91.

*Poly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl-(7,8-dihydrocyclobutabenzene-2,5-diyl)]*. To the mixing flask as described above was added 3.4233 g (0.015 mol) of 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl dichloride, 3.6779 g (0.015 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride and 26.82 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 65°C for 24 h. Upon completion of the dehydrochlorination, the solution was cooled to 50°C and 12.10 g phosphorus pentoxide was added and mixed. The polymerization was then continued by heating the solution mixture under nitrogen atmosphere at 60°C for 2 h, 100°C for 2 h and 140°C for 24 h. Stir-opalescence was observed after the solution was heated at 140°C for 2 h. The polymer content of this solution was 10% and the polymer had an intrinsic viscosity of 35.0 dl g<sup>-1</sup>.

Analysis calculated for C<sub>16</sub>H<sub>2</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.73; H, 2.76; N, 9.58; S, 21.93. Found: C, 65.34; H, 2.92; N, 9.47; S, 21.8.

*Copoly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl]-(p-phenylene)75%/(7,8-dihydrocyclobutabenzene-2,5-diyl)25%*. To the mixing flask as described above was added 2.4363 g (0.012 mol) of terephthaloyl chloride, 0.9126 g (0.004 mol) of 1,2-dihydrocyclobutabenzene-3,6-dicarbonyl dichloride, 3.9231 g (0.016 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride and 27.9 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 65°C for 24 h. Upon completion of the dehydrochlorination, the solution was cooled to 50°C and 11.21 g phosphorus pentoxide was added and mixed. The polymerization was then continued by heating the solution mixture under nitrogen atmosphere at 60°C for 2 h, 100°C for 2 h and 140°C for 24 h. Stir-opalescence was observed after the solution was heated at

140°C for 2 h. The polymer content of this solution was 10% and the polymer had an intrinsic viscosity of 20.0 dl g<sup>-1</sup>.

Analysis calculated for C<sub>14.5</sub>H<sub>6.5</sub>N<sub>2</sub>S<sub>2</sub>: C, 63.83; H, 2.40; N, 10.27; S, 23.50. Found: C, 62.09; H, 2.51; N, 10.97; S, 22.65.

*Poly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl(2-methyl-p-phenylene)]*. To the mixing flask as described above was added 2.6793 g (0.0211 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride, 1.5533 g (0.011 mol) of 2,5-biscyanotoluene and 20.40 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 45°C for 18 h, 78°C for 8 h and 80°C for 16 h. Upon completion of the dehydrochlorination, the solution was cooled to 50°C and 5.34 g of phosphorus pentoxide was added and mixed. The polymerization was then continued by heating the solution mixture under nitrogen atmosphere at 90°C for 16 h, 170°C for 24 h and 190°C for 6 h. Stir-opalescence was observed at about 160°C when the solution was heated from 90 to 170°C in 2 h. The polymer content of this solution was 13% and the polymer had an intrinsic viscosity of 23.0 dl g<sup>-1</sup>.

Analysis calculated for C<sub>15</sub>H<sub>8</sub>N<sub>2</sub>S<sub>2</sub>: C, 64.26; H, 2.87; N, 9.99; S, 22.80. Found: C, 64.61; H, 3.06; N, 9.96; S, 20.08.

*Poly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl(2,5-dimethyl-p-phenylene)]*. To the mixing flask as described above was added 4.835 g (0.02 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride and 35.5 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 45°C for 18 h, 78°C for 8 h, 80°C for 16 h and 90°C for 4 h. Upon completion of dehydrochlorination, the solution was cooled to 50°C and 4.5604 g of 2,5-dimethyl-terephthaloyl chloride and 16.0 g of phosphorus pentoxide were added and mixed. The polymerization was then continued by heating the solution mixture under nitrogen atmosphere at 80°C for 16 h, 150°C for 16 h, 170°C for 20 h and 190°C for 4 h. The polymer content of this solution was 10% and the polymer had an intrinsic viscosity of 30.8 dl g<sup>-1</sup>.

Analysis calculated for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>S<sub>2</sub>: C, 65.28; H, 3.42; N, 9.51; S, 21.78. Found: C, 64.77; H, 3.41; N, 9.38; S, 20.37.

*Copoly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl]-(p-phenylene)50%/(2-methyl-p-phenylene)50%*. To the mixing flask as described above was added 3.382 g (0.014 mol) of 2,5-diamino-1,4-benzenedithiol dihydrochloride, 1.1460 g (0.007 mol) of terephthalic acid, 0.9806 g (0.007 mol) of 2,5-biscyanotoluene and 19.5 g of PPA (77% phosphorus pentoxide). While stirring, the resulting mixture was dehydrochlorinated under reduced pressure (176 mm Hg) at 45°C for 18 h, 78°C for 8 h, 80°C for 16 h and 90°C for 4 h. Upon completion of the dehydrochlorination, the reaction mixture was cooled to 50°C and 8.10 g of phosphorus pentoxide was added and mixed. The polymerization was then continued by heating the solution mixture under a positive nitrogen flow at 80°C for 16 h, 150°C for 16 h, 170°C

for 20 h and 190°C for 4 h. Stir-opalescence was observed at about 160°C as the solution temperature was increased from 150°C to 170°C. The polymer content of this solution was 12% and the polymer had an intrinsic viscosity of 31.0 dl g<sup>-1</sup>.

Analysis calculated for C<sub>14.5</sub>H<sub>7</sub>N<sub>5</sub>S<sub>2</sub>: C, 63.60; H, 2.57; N, 10.02; S, 23.44. Found: C, 61.35; H, 2.54; N, 10.31; S, 22.17.

#### Processing

Selected benzobisthiazole homo- and copolymers of various compositions were processed into high modulus fibres for evaluation. These polymers had intrinsic viscosities from 23 to 35 dl g<sup>-1</sup> in MSA at 30°C, indicative of very high molecular weights. The polymers were in a nematic liquid crystalline state at above 10 wt% concentrations in PPA. They were spun into single-filament fibres by a dry-jet wet-spin process at elevated temperatures and coagulated in distilled water. The spin draw ratio (SDR) varied from 8 to 51. The fibres were washed in distilled water for 7 days to remove residual solvent and then dried under tension with low heat or at ambient conditions. Such fibres are designated 'as-spun'. The as-spun fibres were heat-treated at elevated temperatures to induce crosslinking. Some fibres were heat-treated in air and others in nitrogen to investigate the effect of environment on the polymer crosslinking reactions. The temperature and time for crosslinking the polymers were determined on the basis of thermal properties obtained from differential scanning calorimetry (d.s.c) and thermogravimetric analysis coupled with mass spectroscopy (t.g.a./m.s). The criterion was to achieve effective polymer crosslinks without thermal degradation of the polymer. The effectiveness of the crosslinks was characterized by the solubility of the heat-treated fibres in MSA.

#### MECHANICAL CHARACTERIZATION

The tensile and compressive properties of the various M-PBT (including both mono- and dimethyl substituted PBTs) and BCB-PBT fibres were measured at ambient conditions with an Instron tensile tester. The fibres were glued with epoxy on paper tabs that provided gauge lengths of 1, 3 and 5 in. respectively. The test began by cutting off the arms of the paper tab after a fibre was mounted in the Instron machine. The tensile properties of each fibre were determined by six measurements at the three gauge lengths to correct for machine compliance. The axial compressive strength of the various fibres was determined by the tensile recoil method<sup>11</sup> using 1 in. gauge length fibres. Initially, a fibre was loaded in tension to a selected stress and was then cut at its midpoint with an electric spark to generate recoil. The recoil propagated to the base of the fibre and converted the tension into a compression of the fibre which might or might not cause the fibre to buckle, depending on the tensile load applied initially. In a series of tests at different tensile stress loading, a transition from very few fibre failures at low loads to 100% failures at high load was observed. In this paper, if the transition from non-failure to failure occurred over a wide range of initial tensile loads, then the transition range is reported as the compressive strength of the fibre; otherwise, the maximum stress for which there were no fibre failures is reported as the compressive strength.

## RESULTS AND DISCUSSION

#### Monomer synthesis

The required methyl and dimethyl terephthalic acids were prepared in a two-step reaction sequence starting from 2,5-dibromotoluene and 2,5-dibromoxylene (Figure 1). Reaction of cuprous cyanide with methyl aryl bromides provided dinitriles in 50–60% yields. The reaction proceeded rapidly and efficiently in refluxing dimethylformamide (DMF). The complex formed from the nitrile and cuprous halide was oxidatively destroyed with ferric chloride in hydrochloric acid. Hydrolysis of the dinitriles in phosphoric acid provided nearly quantitative yields of diacids. The diacids were converted to diacid chlorides with thionyl chloride. In contrast to the insolubility of terephthalic acid, the alkyl-substituted monomers could be extensively purified through sublimation or recrystallization in hydrocarbon solvents. The dinitriles, diacids and diacid chlorides were all utilized as monomers in this study.

#### Polymer synthesis

Polymerization of the methyl-substituted diacids and derivatives were carried out in polyphosphoric acid (PPA) at polymer concentration of 10–15% to promote anisotropic reaction mixtures. The amine monomers used were 2,5-diamino-1,4-benzenedithiol dihydrochloride, 4,6-diaminoresorcinol dihydrochloride and 1,2,4,5-tetraaminobenzene tetrahydrochloride to give the corresponding benzobisthiazole, benzobisoxazole and benzobisimidazole rigid-rod polymers (Figure 2). Stoichiometric amounts of both monomers were heated in the PPA of 77% P<sub>2</sub>O<sub>5</sub> content at 60–80°C to effect thermal dehydrochlorination of the amine monomer.

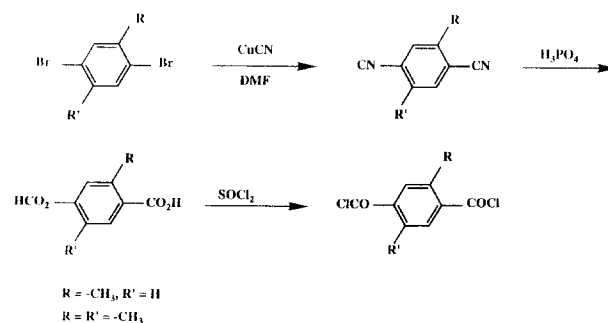


Figure 1 Preparation of monomethyl and dimethyl terephthalic acid monomers

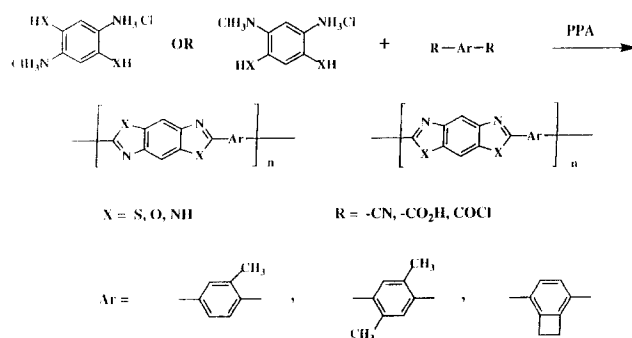
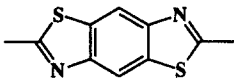
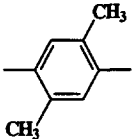
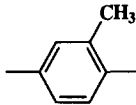
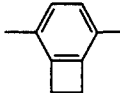
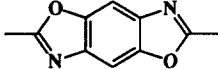
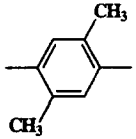
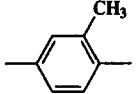
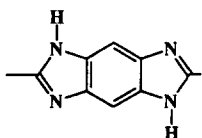
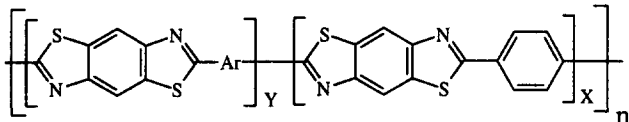
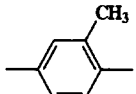
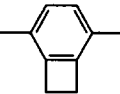


Figure 2 Preparation of benzobisazole rigid-rod homopolymer systems

**Table 1** Summary of homopolymerization conditions and intrinsic viscosity ( $[\eta]$ ) data

Polymer	Heterocycle	Aromatic (Ar)	Monomer	Concentration (wt%)	Temperature (°C)	$[\eta]$ (dl g <sup>-1</sup> )
A			-CN	10	190	5
B	—	—	-CO <sub>2</sub> H	10	190	13
C	—	—	COCl	10	190	31
D	—		-CO <sub>2</sub> H	15	190	23
E	—		-COCl	10	160	gels
F	—	—	-COCl	10	140	35
G			-COCl	10	190	10
H	—		-COCl	14	190	23.5
I		—	-COCl	14	190	14.7

**Table 2** Summary of copolymerization conditions and intrinsic viscosity ( $[\eta]$ ) data

Polymer	X (mol%)	Y (mol%)	Aromatic (Ar)	Concentration (wt%)	Temperature (°C)	$[\eta]$ dl g <sup>-1</sup>
						
J	98	2		12	190	32
K	90	10	—	12	190	29
L	50	50	—	12	190	31
M	50	50		10	160	gels
N	75	25	—	10	140	24

This step was carried out under reduced nitrogen pressure. After completion of the dehydrochlorination, the solution was cooled to 50°C and phosphorus pentoxide was added under nitrogen atmosphere to adjust the P<sub>2</sub>O<sub>5</sub> content of the PPA to 82–84%, as well as to compensate for the water generated during polycondensation. The reaction mixture was gradually

heated to 190°C under a positive nitrogen flow. Since the dinitrile and diacid chloride monomers tended to sublime at elevated temperatures, the reaction mixture was first kept at 90°C overnight to produce oligomers and then heated to a high temperature to generate high molecular weight polymers. The viscous, anisotropic polymerization mixtures were poured into water,

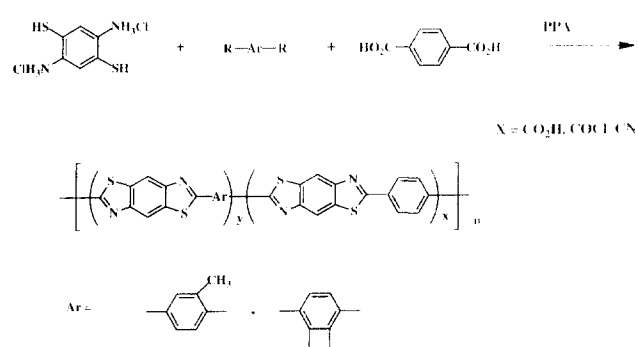
**Table 3** Spin draw ratio (SDR), heat treatment (HT), Young's modulus ( $E$ ), tensile strength (TS), elongation at break ( $\epsilon_b$ ) and compressive strength (CS) of various M-PBT fibres

Polymer	SDR	HT <sup>a</sup>	$E$ (Msi) <sup>b</sup>	TS (Ksi) <sup>c</sup>	$\epsilon_b$ (%)	CS (Ksi) <sup>c</sup>
C	19	350 C:30 s	17	306 ± 43	2.8 ± 0.3	—
D	8	500 C:30 s	32 ± 2	270 ± 26	1.7 ± 0.2	47–53
D	51	500 C:30 s	31 ± 2	344 ± 30	1.7 ± 0.2	20–30
J	20	500 C:30 s	31 ± 4	350 ± 43	1.5 ± 0.3	37–43
K	18	500 C:30 s	28	240 ± 32	1.8 ± 0.6	66–75
L	8	500 C:30 s	33	290 ± 12	1.0 ± 0.1	25–46
L	8	500 C:30 s air	38	341 ± 33	1.0 ± 0.1	12–25
L	30	500 C:30 s	41	465 ± 24	1.3 ± 0.1	19–30
L	30	500 C:30 s air	43	404 ± 30	1.2 ± 0.1	12–30

<sup>a</sup> In N<sub>2</sub> unless otherwise indicated

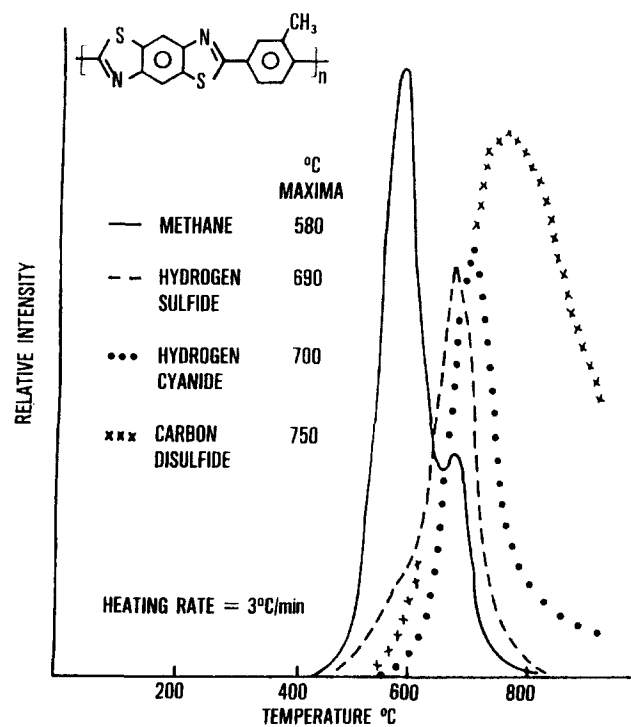
<sup>b</sup> 1 Msi = 6.895 GPa

<sup>c</sup> 1 Ksi = 6.895 MPa



**Figure 3** Preparation of benzobisthiazole copolymer systems

neutralized with ammonium hydroxide, washed extensively with water and methanol and then dried under reduced pressure. The various polymers prepared showed intrinsic viscosities ranging from 5 to 35 dl g<sup>-1</sup>



**Figure 4** T.g.a./m.s. thermogram of monomethyl-substituted PBT homopolymer

(Table 1). At the same polymer concentration, for example at 10 wt%, the monomer reactivity with 2,5-diamino-1,4-benzenedithiol dihydrochloride was in the order of diacid chloride > diacid > dinitrile. When 1,2-dihydrocyclobutabenzene-3,6-dicarboxylate was polymerized, the temperature had to be maintained at 140°C or below to prevent the ring-opening of BCB leading to a gel formation.

In an analogous fashion, a series of benzobisthiazole copolymers was prepared using terephthaloyl chloride as the comonomer (Figure 3). These copolymers contained 2–50 mol% of monomethyl- or benzocyclobutene-substituted PBT units in their backbone. Their intrinsic viscosities ranged from 24 to 32 dl g<sup>-1</sup> (Table 2). In all cases, anisotropic reaction mixtures were obtained and were used directly for dry-jet wet-spinning experiments.

#### Thermal properties of M-PBT

All the M-PBT polymers shown in Table 3 were processed into single-filament fibres for evaluation of mechanical properties. Some as-spun fibres were heat-treated in both air and N<sub>2</sub> to effect polymer crosslinking. The heat-treatment temperature was determined on the basis of results obtained from thermal analysis. The criterion was to effectively introduce sufficient polymer crosslinks at an elevated temperature without thermal degradation of the polymer. The t.g.a./m.s. thermogram of a homopolymer of monomethyl-substituted PBT (MM-PBT, Polymer D in Table 3) is shown in Figure 4. It shows that MM-PBT begins to evolve CH<sub>4</sub> at 420°C as a result of losing the labile methyl pendants. Once being heat-treated at above 400°C, the polymer is no longer soluble in MSA; this is indicative of polymer crosslinking. The slightly higher CH<sub>4</sub> liberation temperature may be due to the dynamic nature of t.g.a./m.s. and the time delay between the polymer degradation in thermogravimetric analysis (t.g.a.) and the identification of degradation species in mass spectroscopy (m.s.).

Dimethyl-substituted PBT homopolymer fibre (DM-PBT, Polymer C in Table 3) became insoluble in MSA once it was heat-treated at above 350°C. However, the fibre also showed blisters on its surface, apparently due to liberation of CH<sub>4</sub> gas. When the fibre was heat-treated at 275°C, there was no visual damage to the fibre but it was soluble in MSA, indicating that effective crosslinking had not occurred. Therefore, effort was concentrated on MM-PBT and its copolymer fibres, which

could be heat-treated at 500°C in N<sub>2</sub> to achieve effective polymer crosslinking as indicated by insolubility in MSA. The crosslinking reaction of MM-PBT copolymers in air was found to occur at a lower temperature, about 400°C.

#### Mechanical properties of M-PBT

The Young's modulus ( $E$ ), tensile strength (TS), elongation at break ( $\epsilon_b$ ) and compressive strength (CS) of the heat-treated M-PBT fibres are shown in Table 3. The homopolymer fibre of dimethyl-substituted PBT showed an unusually low modulus of 17 Msi (117 GPa) and a high elongation at break of 2.8%. This could be due to the low heat-treatment temperature (350°C) that was adequate for inducing polymer crosslinks but insufficient to perfect the structural order and molecular orientation in the fibre. For MM-PBT and its copolymer fibres, their modulus and tensile strength are in the range of 30–40 Msi (210–280 GPa) and 300–400 Ksi (2.10–2.80 MPa) respectively. These properties are comparable to those of unsubstituted PBT fibre processed under similar conditions. Thus, the addition of methyl pendants on the PBT backbone does not seem to affect the tensile properties of highly oriented PBT fibre. Furthermore, there is no direct correlation between the tensile properties of M-PBT fibres and the spin draw ratio achieved, which ranged from 8 to 51.

The primary objective in preparing the M-PBT polymers was to improve the axial compressive strength (CS) of rigid-rod polymer fibres via crosslinking. Most M-PBT polymers, except the copolymer of 10 mol% monomethyl-substituted PBT (Polymer K), showed comparable or lower compressive strength than unsubstituted PBT fibre, whose compressive strength is about 40–60 Ksi (280–410 MPa). The 10 mol% monomethyl-substituted PBT fibre had a marginally higher axial compressive strength of 66–75 Ksi (460–520 MPa). However, this fibre also had a slightly lower modulus and tensile strength than unsubstituted PBT fibre. Within the series of M-PBT fibres, the compressive strength appeared to decrease with increasing tensile modulus; this may be due to the tensile recoil technique that tends to penalize more rigid fibres. There was no systematic correlation between methyl pendant content and fibre compressive strength; the lowest compressive strength was exhibited by the polymer containing 50 mol% monomethyl-substituted PBT. The M-PBT fibres heat-treated in air showed a lower compressive strength than those heat-treated in nitrogen.

#### Thermal properties of BCB-PBT

The t.g.a. thermogram of BCB-PBT homopolymer in air showed a weight loss beginning at about 400°C and a major thermal breakdown at about 530°C (Figure 5). The weight loss of BCB-PBT in helium was significantly less. The d.s.c. thermogram of BCB-PBT homopolymer exhibited a small transition at about 180°C and a large exotherm that started at about 320°C and reached a maximum at 421°C (Figure 6). However, the small thermal transition disappeared in the d.s.c. rescan. The large exotherm in Figure 6 is expected to be a result of thermal crosslinking or other bond formation reactions of BCB moieties. The crosslinking reaction of flexible-chain polymers or oligomers containing BCB moieties normally occurs at about 250°C. Possible explanations for the higher reaction temperature of BCB-PBT are: (1) benzobisthiazole is a strong electron-withdrawing group

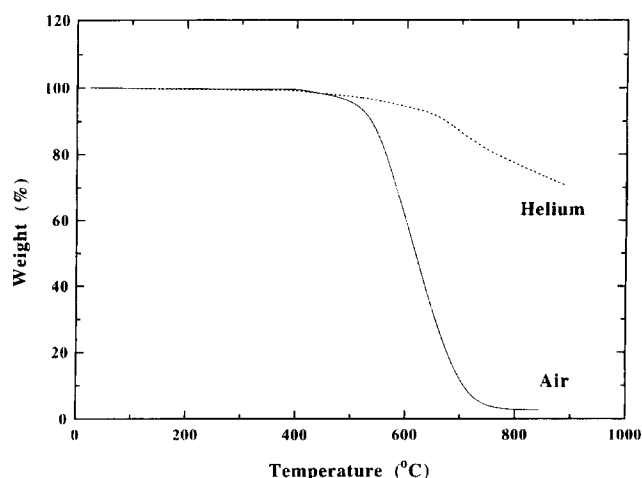


Figure 5 T.g.a. weight loss of BCB-PBT homopolymer

that stabilizes BCB reactivity to some degree; (2) the BCB moieties on rigid-rod polymers have limited mobility and therefore do not react at the normal BCB crosslinking temperature.

The t.g.a./m.s. thermogram of BCB-PBT homopolymer showed evolution of ethylene and methane at temperatures between 330 and 600°C and between 400 and 700°C, respectively (Figure 7). Evidently, the ethylene and the methane were degradation products from BCB moieties at elevated temperatures. This observation supports the BCB crosslinking mechanism that involves the formation of stilbenes and/or dibenzocyclooctadienes<sup>12</sup>. The peak evolution temperature of ethylene (420°C) coincided with the peak exothermic reaction temperature of BCB-PBT observed in the d.s.c. thermogram, suggesting that both bond degradation and bond-forming reactions proceeded at that temperature in BCB-PBT. However, the bond-forming reaction dominated because the overall reaction was exothermic and the total weight loss of BCB-PBT at 420°C was minimal. The peak temperature at which methane evolved in t.g.a./m.s. coincided with the temperature at which the entire BCB-PBT underwent a major thermal breakdown in t.g.a.

The d.s.c. exotherm (Figure 6) showed that the bond formation reaction of BCB-PBT was not complete at 450°C. However, the BCB-PBT fibre heat-treated at

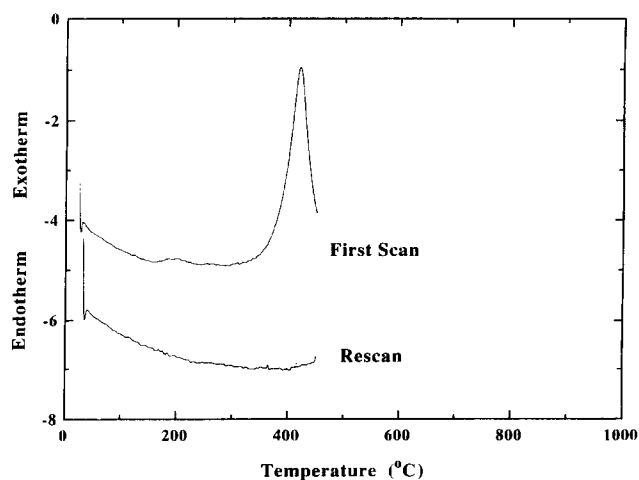
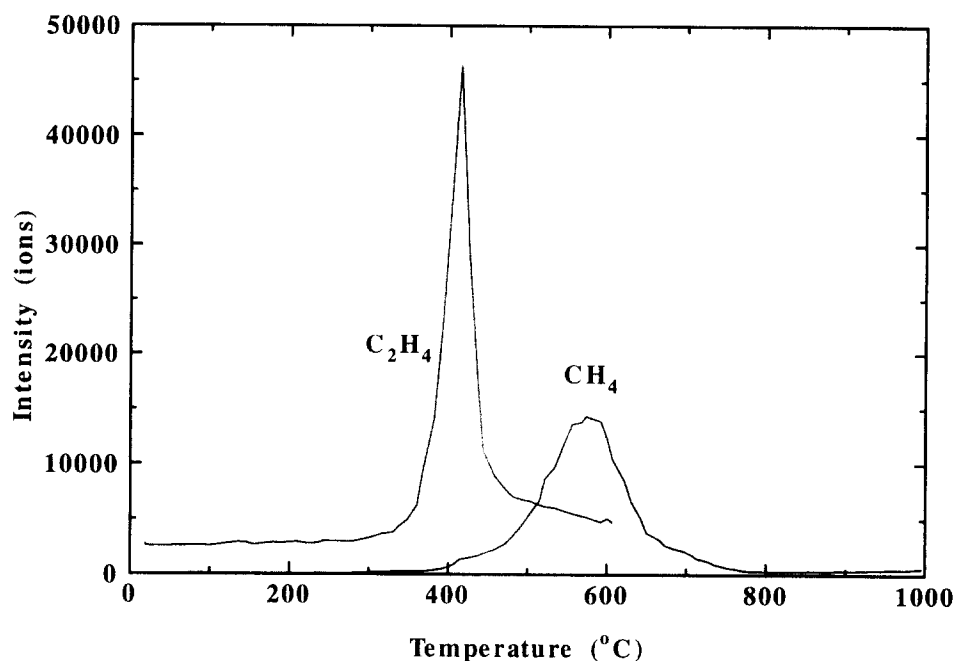


Figure 6 D.s.c. thermogram of BCB-PBT homopolymer

**Table 4** Spin draw ratio (SDR), heat treatment (HT), Young's modulus ( $E$ ), tensile strength (TS), elongation at break ( $\epsilon_b$ ) and compressive strength (CS) of BCB-PBT fibres

Polymer	SDR	HT	$E$ (Msi) <sup>a</sup>	TS (Ksi) <sup>b</sup>	$\epsilon_b$ (%)	CS (Ksi) <sup>b</sup>
F	8	450 C/30 s	18.3 ± 1.8	309 ± 14	1.14 ± 0.06	15
F	8	53308C/20 min	17.5 ± 0.9	375 ± 17	1.38 ± 0.08	70
N	10	330 C/10 min	21.2 ± 1.0	345 ± 20	1.03 ± 0.02	18
N	10	330 C/20 min	18.2 ± 1.5	348 ± 61	1.29 ± 0.27	16

<sup>a</sup> Msi = 6.895 GPa<sup>b</sup> Ksi = 6.895 MPa**Figure 7** T.g.s./m.s. analysis of BCB-PBT homopolymer showing release of ethylene and methane

450°C in nitrogen for 30 s had a very dark colour and was very brittle. It was almost black in MSA and was insoluble. This fibre also showed a skin and core morphology. The bonding between the skin and core seemed weak because they could easily be separated. Therefore, subsequent heat treatments for these fibres were carried out at 330°C, a temperature near the onset of the d.s.c. exotherm. The heat treatment time, however, was prolonged to 10–20 min to achieve a high crosslink density. These fibres had a red colour and swelled in MSA.

#### Mechanical properties of BCB-PBT

The tensile compressive properties of heat-treated BCB-PBT fibres are listed in *Table 4*. The tensile strength of 330°C heat-treated BCB-PBT fibres is comparable to that of unsubstituted PBT fibre. Their tensile modulus, however, is lower than that normally reported for unsubstituted PBT fibre, probably as a result of the lower heat treatment temperature (330°C vs 500°C and above). The BCB-PBT homopolymer fibre heat-treated at 450°C showed a very low axial compressive strength (only 15 Ksi) (103 MPa), while the fibre heat-treated at 330°C had an axial compressive strength of 70 Ksi (480 MPa). The heat-treated BCB-PBT fibres were insoluble in methanesulfonic acid, indicative of chemical crosslinks. The improvement in the axial compressive strength of the BCB-PBT homopolymer fibre heat-treated at 330°C,

compared to unsubstituted PBT fibre, may be attributed to the formation of chemical crosslinks. The low axial compressive strength of the heat-treated BCB-PBT copolymer fibres cannot be explained by the same reason, because their compressive strength is even lower than that of unsubstituted PBT fibre. This low compressive strength may be due to the undesired effects of side reactions which occurred during heat treatment for which limited polymer crosslinks could not compensate.

The crosslinking reaction of BCB-PBT is not a clean addition reaction since ethylene volatilizes at the same temperature as crosslinking occurs. Optical micrographs (not shown) of heat-treated BCB-PBT fibres show humps on the fibre surface. These humps are not likely to be composed of PBT molecules, because rigid-rod molecules are not expected to have such a large degree of mobility at the crosslinking temperature and because unsubstituted PBT fibres heat-treated at even higher temperatures do not show humps. The humps are believed to result from further reactions of the leaving groups, such as the ethylene from BCB moieties, by thermal polymerization or crosslinking during heat treatment.

#### CONCLUSION

In an effort to improve the compressive strength of the benzobisazole family of rigid-rod polymers, crosslinks



were introduced in poly(p-phenylene benzobisthiazole) (PBT) through the interactions between free radicals generated from the thermal degradation of methyl and dimethyl pendants along the PBT backbone. The compressive strength of these materials showed, however, no significant improvement over unsubstituted polymer. Further work was conducted to induce crosslinking via 'clean' addition reaction that does not produce volatiles. Benzocyclobutene (BCB) crosslinking moieties were incorporated into the polymer backbone to produce BCB-substituted PBT as well as random copolymers of PBT and BCB-PBT. While the compressive properties of the copolymer were poorer than those of unsubstituted PBT, the homo-BCB-PBT exhibited modestly improved compressive strength, indicating that crosslinking may have favourably enhanced lateral interactions between the molecules. However, the compressive strength improvement achieved in this work (up to 70 Ksi (480 MPa)) is not yet sufficient to enable these materials to meet the requirements of advanced structural composites.

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