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# Rigid-Rod Polymers. 2. Synthesis and Thermal Properties of Para-Aromatic Polymers with 2,6-Benzobisthiazole Units in the Main Chain[1]

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ABSTRACT: Poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4-phenylene] (PBT) was prepared by the polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthalic acid in poly(phosphoric acid) (PPA). Polymerization mixtures with polymer concentrations between 5 and 10 wt % were liquid crystalline at early stages of conversion and were suitable for dry-jet wet spinning into high-modulus/high-strength fibers either directly from PPA or after isolation and redissolution in strong acids. Polymerization in the liquid crystalline state by using concentrations >5% gave lower viscosity solutions than polymerizations that remained isotropic, owing to the use of polymer concentrations of <3%. The lower bulk viscosity for a given molecular weight facilitated the attainment of higher molecular weight samples. Intrinsic viscosities of isolated PBT measured in methanesulfonic acid were as high as 30.3 dL/g. PBT showed excellent thermal and oxidative stability as determined by vacuum thermogravimetric–mass spectral analysis and isothermal aging at 316 and 371 °C. Rigid-rod poly(benzobisthiazoles) with various degrees of phenyl substitution were prepared but were soluble only at low concentrations in certain mixed solvents.

The attainment of a new ultrahigh-modulus, ultrahigh-strength, thermally stable organic fiber has been realized with the synthesis and spinning of nematic solutions of poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4-phenylene], referred to as PBT. This paper describes the synthesis and thermal properties of PBT and related poly(benzobisthiazoles) with phenyl substituents on the rigid-rod chain. Another paper in this series[2] describes the preparation of PBT fibers that have tensile moduli greater than 2000 g/denier and tenacities greater than 20 g/denier.

The realization of ultrahigh mechanical properties from an organic polymer depends on the cooperation of numerous factors that concern chemical structure, molecular weight, method of synthesis, and characteristics of processing and solubility. Less than optimal performance in any one of these areas without compensation from another can be the polymer's "fatal flaw". When the attainable molecular weight of poly[(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO)[3] appeared to be too low to give spinning dopes of sufficient integrity to apply dry-jet wet-spinning methods,[4] we directed our efforts toward the synthesis of other heterocyclic systems of the desired configuration (see Figure 1). The synthesis of a rodlike positional isomer of PBO, poly[(benzo[1,2-*d*:4,5-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene] (1), was attempted[5] by heating 2,5-diamino-1,4-benzenediol dihydrochloride[6] with terephthalic acid in PPA, but polycondensation did not proceed below temperatures at which monomer decomposition occurred. Poly(*p*-phenylenebenzobisimidazole) (2) had been prepared[7] in relatively high molecular weight but was eliminated from further development as a structural material, owing to its high level of moisture absorption. The preparation and thermal evaluation of totally aromatic polymers containing the 2,6-benzothiazole[8,9] and the 2,2′-(6,6′-bibenzothiazole) units[10,11] indicated that the benzothiazole moiety possessed excellent thermooxidative stability. The two possible rigid-rod benzobisthiazole polymers, 3 and PBT, required the preparation of the dihydrochloride salts of 4,6-diamino-1,3-benzenedithiol (4) and 2,5-diamino-1,4-benzenedithiol (5), respectively. Monomer 4 had been reported previously[12] and was incorporated into thiazine-containing polymers by the reaction of 4 with tetrachloro aromatic compounds. The low molecular weight of these polymers was attributed to inherent instability of 4 toward oxidation and difficulties in its purification. We attempted the synthesis of 4 by the published procedure and by methods analogous to those presented in this paper but were unable to obtain 4 of sufficient purity and stability to give 3 of high molecular weight.[5]

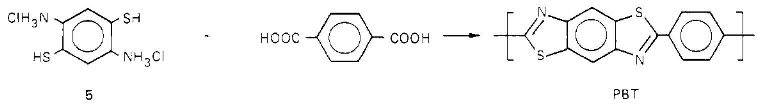
Monomer 5, although never prepared heretofore to our knowledge, has been erroneously cited in the literature.[13] The synthesis as presented would actually yield a positional isomer of 5, namely, 3,6-diamino-1,2-benzenedithiol. The synthesis was based on the reduction of a diaminobenzenedithiosulfonic acid prepared by the method of Perkin and Green.[14] The structural assignment of a 1,2,4,5 configuration to this intermediate has been shown to be erroneous.[15,16] In this paper, we report the first successful synthesis of monomer 5 in a form suitable for the preparation of a high-molecular-weight polymer.

Although the preparation of benzobisoxazole polymers with various degrees of phenyl substitution did not lead to solubility in aprotic solvents,[3] the phenyl-substituted benzobisthiazole polymers were prepared to determine the effect of phenyl substituents on the solubility characteristics of the new polymer.

## Results and Discussion

**Monomer Synthesis.** The synthesis of the monomer, 2,5-diamino-1,4-benzenedithiol dihydrochloride (5), was performed as shown in Scheme I. The synthesis of 2,6-diaminobenzo[1,2-*d*:4,5-*d*′]bisthiazole (6) via the *p*-phenylenebis(thiourea) (7) has been reported.[15,16] We

Table I
Typical Polymerizations of 5 and Terephthalic Acid in Poly(phosphoric acid)



| PBT run no. | monomer 5 concn,[a] % | dehydrochlorination time, h | PBT concn,[b] % | reaction time, h at T °C | | | [η],[c] dL/g | notes |
|---|---|---|---|---|---|---|---|---|
| | | | | 100–150 °C | 150–160 °C | 160–200 °C | | |
| 1-20 | 3.9 | 40[e] | 3.1 | 2 | 4.5 | 1.5 | 6.2 | *d, g, i* |
| 1-43 | 2.0 | 30[e] | 1.4 | 5.5 | 9 | 8 | 9.0 | *d, g, i* |
| 1-57 | 3.0 | 52[e] | 2.2 | 8 | 4 | 22 | 18.0 | *d, g, i* |
| 1-62 | 6.5 | 28[e] | 5.1 | 6.5 | 8 | 26 | 26.5 | *f, g, i* |
| 1-72 | 7.0 | 60[e] | 5.0 | 8 | 8 | 30 | 18.0 | *f, g, j* |
| 2-9 | 11.4 | 58[e] | 5.6 | 5 | 12 | 24 | 30.3 | *f, g, j* |
| 2-15 | 11.9 | 48[k] | 9.7 | 1 | 2 | 26 | 26.0 | *f, h, i* |
| 2-17 | 14.1 | 48[k] | 7.8 | 5 | 8 | 15 | 27.8 | *f, h, i* |
| 3-26 | 11.2 | 52[k] | 5.6 | 1 | 4 | 47 | 18.3 | *f, g, j* |
| 3-32 | 13.9 | 48[k] | 9.2 | 5 | 15 | 24 | 14.0 | *f, h, j* |

[a] Weight percent of 5 in PPA during dehydrochlorination. [b] [Weight of PBT (based on 100% yield)]/[weight of solution] × 100. [c] In methanesulfonic acid at 30.0 °C. [d] Isotropic; too viscous to stir. [e] Reduced pressure not applied during dehydrochlorination. [f] Stir opalescent. [g] Freshly prepared PPA (see reference 3). [h] 115% PPA (FMC). [i] Small scale (yield <100 g). [j] Large scale (yield >500 g). [k] Reduced pressure applied at later stages.

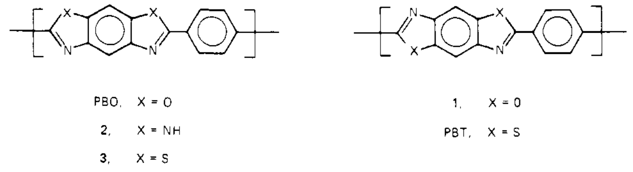
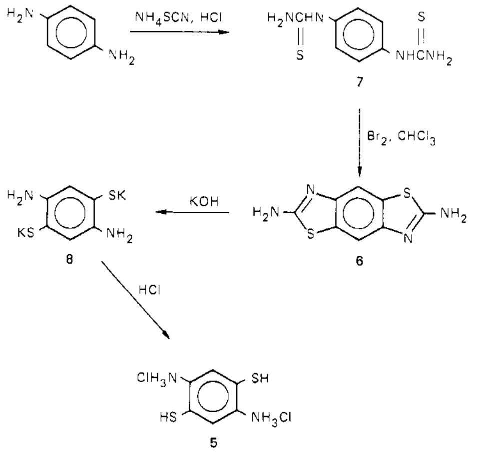


**Figure 1.** Rigid-rod polymer structures.

found that 2.2–2.3 mol of molecular bromine for each mole of 7 was required to obtain optimal yields. The crude product of this cyclization, obtained in 90–95% yield, was contaminated with an isomer of 6, 2,7-diaminobenzo[1,2-*d*:6,5-*d*′]bisthiazole. Two recrystallizations from glacial acetic acid were necessary to obtain pure 6 in a yield of 40–55%. Failure to remove the isomer would lead to contamination of 5 with 1,4-diamino-2,3-benzenedithiol and subsequent incorporation of angular linkages in the otherwise rodlike PBT. Removal of the isomer was indicated by complete loss of absorptions at 970, 935, and 810 cm$^{-1}$ in the infrared spectrum. The $^{1}$H and $^{13}$C NMR spectra gave one and four sharp resonances, respectively, as expected for pure 6.

Compound 6 was hydrolyzed by heating to 160 °C under a blanket of argon with concentrated aqueous potassium hydroxide. The dipotassium salt of 2,5-diamino-1,4-benzenedithiol (8) crystallized from the reaction mixture upon cooling. The air-sensitive crystals of 8 were collected by filtration in an argon-filled glovebox, pressed as dry as possible, and then isolated as the dihydrochloride salt 5 by two methods. In the first method, 8 was dissolved in carefully deaerated water and then passed through a filter into a large volume of 6 N hydrochloric acid. The resulting colorless crystals were collected, washed with methanol, and dried at room temperature under reduced pressure. Monomer 5 prepared in this manner gave PBT with intrinsic viscosities as high as 27.8 dL/g on a small scale (~40 g per run), but on a large scale (>4.0 kg per run) the highest intrinsic viscosity obtained was 14.9 dL/g. The difficulty with this method was twofold: (1) 8 was extremely sensitive to oxidation by even traces of residual oxygen while in the solution used for transfer and (2) the average crystal size of 5 was very small, which caused difficulty in controlling dehydrochlorination on a large scale. In the second method, 8 was transferred under argon as a solid into a large volume of 6 N HCl. The resulting solid was collected by filtration and transferred immediately into a large volume of dilute HCl. Concentrated HCl was then added slowly to give large hexagonal prisms of 5. Monomer prepared in this manner gave PBT prepared on a large scale with intrinsic viscosities between 18 and 30 dL/g.

Scheme I



**Model Compound Synthesis.** The reaction of 5 with benzoic acid in poly(phosphoric acid) (PPA) afforded the model compound 2,6-diphenylbenzo[1,2-*d*:4,5-*d*′]bisthiazole (9), in 98.9% yield. Mass spectral, elemental, and $^{13}$C NMR analysis are consistent with the assigned structure. The crystal structure of 9 has been determined[17] and shows the two exocyclic bonds to be parallel but not collinear. They are offset by 0.6 Å.

The model compound 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]-bisthiazole (10) was prepared in only 79% yield. The crystal structure[17] indicated that polymer 3 from monomer 4 would be less rodlike than PBT, owing to both a curvature and a bowing of the heterocyclic unit.

The two model compounds, 9 and 10, had identical mass spectra, including all fragments.

**Polymer Synthesis.** The polycondensation of 5 with terephthalic acid in PPA afforded poly[(benzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl)-1,4-phenylene], referred to as PBT (see Table I). A precise quantity of 5 (2–15% by weight) in degassed PPA was stirred for 24 h at room temperature under a stream of argon. At higher monomer concentra-

**Figure 2.** Fractured PBT film. Film was prepared from a 5% PBT/PPA solution by pulling through rollers and then precipitating the solution by dipping in water.

tions, periodic cooling to 15 °C or application of argon pressure was necessary to control the level of foaming. The temperature was slowly raised to a maximum of 100 °C. Reduced pressure was then applied until the mixture became clear. The complete loss of hydrogen chloride is essential to obtain the monomer in a reactive form. Deleterious side reactions, as evidenced by the evolution of hydrogen sulfide, occur if the dehydrochlorination is not conducted below 100 °C.

A stoichiometric amount of terephthalic acid (based on 5) that had been reduced to a particle size of 95% <10 μm by an air impact method was then added. Additional PPA was added to adjust the polymer concentration to the desired value. The yellow mixture was then heated under argon to 160 °C within 5 h. Reduced pressure was applied again, evolution of volatiles (water of condensation and trapped gas added with the terephthalic acid) became vigorous, the last trace of terephthalic acid dissolved, and the bulk viscosity increased noticeably. Initial polymerizations in this study were conducted at concentrations [(theoretical weight of polymer)/(weight solution) × 100] of <3%. The runs remained isotropic throughout the polymerization and became a rubbery mass that was too viscous to stir in the later stages of heating. Later runs with polymer concentrations between 5 and 10% formed bright, yellow-green, stir-opalescent solutions within 30 min of complete dissolution of the terephthalic acid. These solutions remained stirrable throughout the polymerization, despite the higher concentration and the attainment of higher intrinsic viscosity, in most cases, than earlier runs. This observation is another indication (in addition to stir opalescence) of the liquid crystalline nature of the polymerization medium. After final heating at 190–200 °C for 12 h, the opalescent reaction mixture was cooled and either bottled for subsequent processing or pressed into films to attain a high surface area and then precipitated into water.

When shear was applied to a 5.5% solution of PBT in PPA by calendering between two Teflon-clad rollers followed by precipitation, opaque films with a copper color and a unidirectional fibrillar structure were obtained (see Figure 2). Even though this procedure was designed only to obtain polymer in a form suitable for washing, tensile measurements of 12 samples of this film gave an average strength of 33 000 psi with one sample as high as 44 000 psi. X-ray diffraction showed the film to be highly ordered. When a sample of the polymerization mixture was elongated by simple pulling to a thin strand and then precipitated into water, it could be separated into smaller diameter, ribbon-like fibers that ran the entire length of the strand (see Figure 3). These observations provide additional evidence for the ordered nature of the polymerization medium.

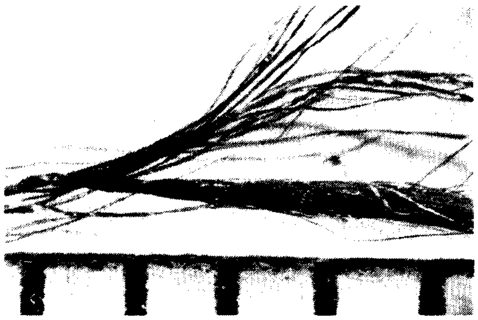


**Figure 3.** PBT strand, prepared by stretching a 5% PBT/PPA solution, showing ribbon-like structure of fibrils. Each division equals 1 mm.

During the course of this study, intrinsic viscosities as high as 30.3 dL/g were measured, using dilute methanesulfonic acid (MSA) solutions of washed and dried PBT obtained from various polymerizations (see Table I). Conditions that were determined to be necessary to afford PBT with high intrinsic viscosity were (1) the use of monomer 5 of high purity, (2) the use of terephthalic acid of small particle size, (3) complete dehydrochlorination of the PPA/5 mixture below 100 °C, and (4) sufficient reaction time at elevated temperature (160–200 °C). The polymerization proceeded slowly at temperatures between 100 and 150 °C and showed rapid color change, dissolution of terephthalic acid, and viscosity increase only after a temperature of 155–160 °C was reached. Heating to 160 °C within 3–5 h after terephthalic acid addition was found to be optimal, the time allowing for removal of last traces of hydrogen chloride, for wetting of the terephthalic acid, and for loss of trapped gases added with the terephthalic acid. Either freshly prepared PPA[3] or commercial grade 115% PPA were used without noticeable effect on the resultant intrinsic viscosity, provided the PPA was thoroughly degassed prior to use.

Small aliquots of one polymerization were removed at various stages, precipitated into methanol, and dried, and the intrinsic viscosity was determined from dilute MSA solutions. The values obtained are plotted vs. time elapsed from the terephthalic acid addition in Figure 4. Samples 1–7 were reprecipitated from 0.2–0.5% solutions of MSA into methanol and then dried in addition to the foregoing precipitation before the viscosity was determined. The substantially lower values for samples 5, 6, and 7 when compared with samples 8 and 9 indicate that intrinsic viscosity is highly dependent on solution history and that irreversible molecular aggregation had occurred upon precipitation from MSA for the samples of higher molecular weight.

Initial studies of PBT fiber formation were performed at Carnegie-Mellon University and at Celanese Research Co.,[18] using nematic solutions prepared from MSA and PBT that had been precipitated and dried. The structure and mechanical behavior of these early as-spun fibers have

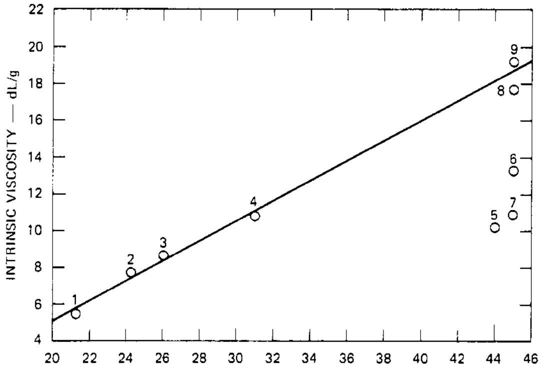
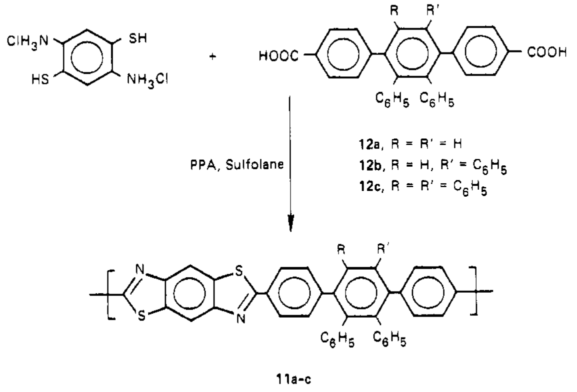


**Figure 4.** Intrinsic viscosity vs. reaction time for a typical PBT polymerization.

Scheme II



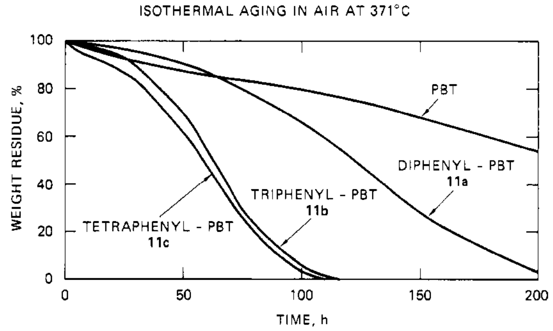


**Figure 5.** Isothermal aging in air at 371 °C for PBT and polymers **11a–c**.

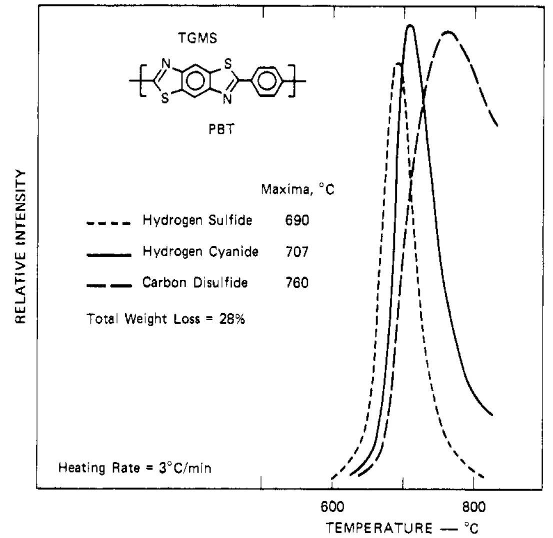


**Figure 6.** Thermogravimetric–mass spectral analysis for PBT.

been reported.[19] Subsequent studies showed that heat treatment under tension of fibers prepared from both MSA and PPA solutions resulted in fiber with extremely high orientation and outstanding mechanical properties.[2]

Phenyl-substituted poly(benzobisthiazoles) **11a–c** with two, three, and four pendant phenyl groups on the middle ring of a *p*-terphenylene unit were prepared from **5** and the three diacids **12a–c**[3] by methods described in the previous paper[3] (see Scheme II). The three polymers were light tan, as opposed to the copper color of PBT. Extending the reaction time beyond that given in the Experimental Section afforded insoluble polymers. Intrinsic viscosities obtained for the diphenyl-substituted polymer **11a** were as high as 6.5 dL/g and, for the triphenyl-substituted polymer **11b**, as high as 4.0 dL/g in MSA at 30.0 °C. The tetraphenyl-substituted polymer **11c** precipitated from the reaction mixture and was obtained as a tan powder insoluble in all solvents attempted.

**Thermal Evaluation.** A preliminary evaluation of the thermooxidative stability of PBT and the phenyl-substituted polymers **11a–c** was performed by isothermal aging studies at 316 and 371 °C in air. The samples were prepared by precipitation from dilute MSA solution and thus were not highly ordered. At 316 °C, PBT, **11a**, **11b**, and **11c** retained 98, 96, 96, and 93% of their weight after 200 h of testing. At 371 °C, PBT retained 53% of its weight after 200 h (see Figure 5). The better weight retention of **11a**, compared with **11b** and **11c**, can be explained by either the lower degree of steric strain in **11a** or that the groups eliminated to relieve the strain are different. In **11a**, the most sterically crowded groups are pendant to the main chain. In **11b** and **11c**, they are in and pendant to the main chain. Elimination of the phenylene group in the backbone, which we believe occurs to a greater extent in **11b** and **11c**, leads to decomposition of the adjacent heterocycle.[3] Infrared and elemental analyses of other benzothiazole-containing polymers before and after thermogravimetric analysis in air provided evidence that the excellent weight retention was owing to high intrinsic thermooxidative stability rather than a compensating weight gain by pickup of oxygen.[10]

Thermogravimetric–mass spectral analysis was performed in vacuo on PBT and **11b** at a heating rate of 3 °C/min. The ion intensity as a function of temperature for PBT is shown in Figure 6. The evolution of hydrogen sulfide, followed closely with hydrogen cyanide, indicates that the thermal decomposition of one of the heterocyclic rings begins near 600 °C, with a maximum rate near 700 °C. The total weight loss of 28% at 1000 °C is consistent with the loss of 1 mol of hydrogen sulfide, 1 mol of hydrogen cyanide, and 0.25 mol of carbon disulfide per mole of repeat units. The carbon disulfide is presumably released from the char and evolution is not complete even at 1000 °C. The thermal decomposition of the triphenyl-substituted polymer **11b** is shown in Figure 7 to be similar to the benzobisoxazole polymer in the previous paper.[3] The decomposition of one of the heterocycles occurs 70–80 °C lower than in PBT with the other heterocycle undergoing decomposition at temperatures comparable to PBT. The total weight loss at 1000 °C of 41% is consistent with the incorporation of the benzo moiety and triphenylbenzene into the char.

## Experimental Section

***p*-Phenylenebis(thiourea) (7).** To a 22-L flask were added 1.7 kg (15.7 mol) of *p*-phenylenediamine (Mallinckrodt, reagent grade), 14 L of deaerated water, 3.07 L of concentrated hydrochloric acid, and 110 g of activated charcoal. The mixture was warmed to 50 °C and transferred with filtration into another 22-L flask. Ammonium thiocyanate (4.84 kg, 63.6 mol, Mallinckrodt

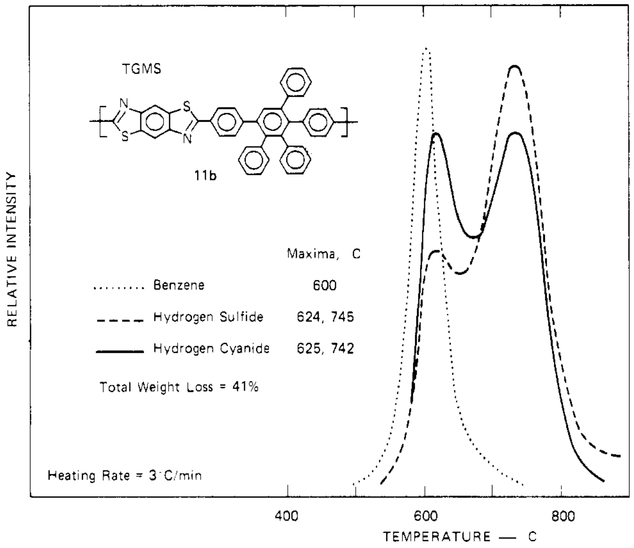


**Figure 7.** Thermogravimetric–mass spectral analysis for polymer **11b**.

reagent) was added and the mixture was stirred at a pot temperature of 90–100 °C for 20–24 h. The yellow, granular product began to precipitate after 2 h of reaction. The mixture was allowed to cool, and the product was collected by filtration. The product was washed with 8 L of hot water and then dried at 100 °C under reduced pressure. The yield was 3.4 kg (95.6%) of a light yellow, granular solid of purity suitable for the next step: IR (KBr) 3330, 3260, and 3170 (NH and $NH_2$), 1070 $cm^{-1}$ (C=S).

Anal. Calcd for $C_8H_{10}N_4S_2$: C, 42.46; H, 4.45; N, 24.76. Found: C, 42.76; H, 4.39; N, 24.80.

**2,6-Diaminobenzo[1,2-*d*:4,5-*d'*]bisthiazole (6).** To a stirred suspension of 3.0 kg (13.25 mol) of **7** in 14 L of dry chloroform was added a solution of 4.9 kg (30.7 mol of $Br_2$) of bromine in 2 L of chloroform such that the pot temperature did not rise above 50 °C. The orange slurry was stirred at room temperature overnight and then heated at reflux for 24 h. The mixture was allowed to cool under a slow stream of argon. The granular orange solid was then collected by filtration. The crude product was washed with 6 L of chloroform, dried in air, and stirred with aqueous sodium bisulfite (2 kg of $NaHSO_3$/15 L of water). The yellow solid was collected by filtration, washed with 5 L of concentrated ammonium hydroxide, and then washed with 10 L of water. The crude **6** was recrystallized twice from 140 L of glacial acetic acid. After drying to constant weight at 85 °C under reduced pressure, 1.6 kg (54.3%) of **6** was obtained as feathery needles: mp >350 °C; IR (KBr) 3400, 3280 ($NH_2$), 1640 $cm^{-1}$ (C=N); $^{13}C$ NMR 164.4, 147.5, 129.1, 109.3 ppm; $^1H$ NMR $\delta$ 7.8.

Anal. Calcd for $C_8H_6N_4S_2$: C, 43.13; H, 2.71. Found: C, 42.95; H, 2.45.

**2,5-Diamino-1,4-benzenedithiol Dihydrochloride (5).** To a 22-L flask, equipped with a stopcock at the bottom and containing 11.5 L of deaerated water, was added 10.9 kg (167 mol) of 85.9% potassium hydroxide. The solution was allowed to cool slightly and then 2.70 kg (12.14 mol) of **6** was added while the flask was swept with a stream of argon. The mixture was heated to the reflux temperature under an argon blanket and maintained at that temperature for 5 h. The resulting yellow solution was allowed to cool with stirring overnight. After the solution cooled to 15 °C the resultant yellow needles of **8** were transferred via a closed system to an argon-filled glovebox, collected by filtration, and pressed as dry as possible. The extremely air-sensitive potassium salt was dissolved in 6 L of deaerated water and filtered directly into an evacuated, stirred flask that contained 20 L of deaerated water and 20 L of concentrated hydrochloric acid. Fine, colorless crystals of **5** formed rapidly. The monomer was collected by filtration under an argon blanket, washed with methanol (10 L), and dried to constant weight at room temperature under reduced pressure. The yield was 2.53 kg (85%): mp, decomposition at 200–210 °C without melting; IR (KBr) 3000–2700 (br) and 2580 ($NH_3Cl$), 2460 $cm^{-1}$ (SH); mol wt (aqueous titration with 0.1 N NaOH of HCl and SH) 244–246 (theoretical = 245.19).

Anal. Calcd for $C_6H_{10}N_2S_2Cl_2$: C, 29.39; H, 4.11; N, 11.43. Found: C, 29.17; H, 4.08; N, 11.60.

Monomer **5** was also prepared as above except that the dipotassium salt crystals were transferred as a solid directly to a flask containing 40 L of 6 N hydrochloric acid. The resulting solid was recrystallized, without drying, from dilute hydrochloric acid (30 L of deaerated water/1.8 L of concentrated HCl gave 0.7 kg of **5**) by slowly adding concentrated hydrochloric acid (10-L total) at room temperature. Monomer **5**, prepared by this slow recrystallization, eliminated HCl in a more controlled fashion when mixed with PPA on a large scale.

**2,6-Diphenylbenzo[1,2-*d*:4,5-*d'*]bisthiazole (9).** 2,5-Diamino-1,4-benzenedithiol dihydrochloride (3.35 g, 13.7 mmol) was stirred at room temperature with 56 g of PPA and 20 g of sulfolane until the dehydrochlorination was complete (24 h). The mixture was then heated to 90 °C, and 4.00 g (32.7 mmol) of benzoic acid was added. The mixture was then heated as follows: 90 °C for 5 h, 145 °C for 13 h, 170 °C for 4 h, and 200 °C for 1 h. The dark solution was poured into methanol to give a colorless precipitate. The product was washed with water and dilute ammonium hydroxide, dried in air, and recrystallized from toluene as colorless platelets to afford 4.66 g (98.9%) of **9**: mp 303–304 °C; IR (KBr) 1515, 1480, 1305, 1235, 950 $cm^{-1}$; mass spectrum (70 eV), *m/e* 344 $(M)^+$, 241 (M − $C_6H_5CN$); $^{13}C$ NMR ($ClSO_3H$-$DHSO_4$) 177.3 (s), 136.7 (s), 136.1 (d), 129.4 (s), 128.8 (d), 126.8 (d), 121.9 (s), 111.1 (d) ppm.

Anal. Calcd for $C_{20}H_{12}N_2S_2$: C, 69.74; H, 3.51; N, 8.13. Found: C, 70:55; H, 3.37; N, 8.34.

**2,6-Diphenylbenzo[1,2-*d*:5,4-*d'*]bisthiazole (10).** To a flask containing 11 g of freshly prepared PPA were added 0.54 g (2.2 mmol) of 4,6-diamino-1,3-benzenedithiol dihydrochloride[10] and 0.56 g (5% excess) of benzoic acid. The mixture was heated slowly to 100 °C to effect dehydrochlorination and then treated as described for compound **9**. The model compound **10** was recrystallized from toluene to give 0.60 g (79%) of yellow crystals; IR (KBr), identical with IR spectrum of **9**; mass spectrum (70 eV), *m/e* 344 $(M)^+$, 241 (M − $C_6H_5CN$), all fragments identical with those of **9**.

Anal. Calcd for $C_{20}H_{12}N_2S_2$: C, 69.74; H, 3.51; N, 8.13. Found: C, 70.84; H, 3.36; N, 8.17.

**Poly[(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)-1,4-phenylene] (PBT).**[20] In a 6-L resin flask were placed 386.76 g (1.5774 mol) of **5** and 2.98 kg of freshly prepared PPA. The mixture was stirred at room temperature under a stream of argon for 24 h and then at 60–70 °C for 34 h. The resulting solution was clear with no evidence of bubbles. Terephthalic acid (262.35 g, 1.5792 mol) was then added and incorporated into the solution by rapid stirring at 110 °C. Additional PPA (4.1 kg) was then added. The yellow mixture was heated as follows: 110–165 °C in 5 h, 165 °C for 12 h, 180 °C for 12 h, and 195 °C for 12 h. The mixture became stir opalescent after 6 h into the polymerization. Reduced pressure was applied during the first 6 h of reaction but was alternated with an argon stream such that the mixture did not foam above a predetermined position. The hazy green solution with yellow-green opalescence was removed from the flask, pulled between two sets of rollers on a carrier film into a large volume of water. The copper-colored polymer was washed until the water was no longer acidic and then was dried at 80–100 °C under reduced pressure for 48 h. A portion of the reaction solution was bottled for use in fiber-spinning studies: intrinsic viscosity $[\eta]$ = 30.3 dL/g (MSA); $^{13}C$ NMR ($ClSO_3H$–15% $HDSO_4$), broad band with intensity and chemical shifts similar to those of **9**.

Anal. Calcd for $C_{14}H_6N_2S_2$: C, 63.13; H, 2.27; N, 10.51; S, 24.08. Found: C, 61.75; H, 2.46; N, 10.24; S, 23.22.

The foregoing procedure affords a 5.6 wt % solution of PBT in PPA. Polymerization mixtures of higher concentration (up to 10%) were prepared. These runs required higher monomer **5** concentration during dehydrochlorination. Intermittent cooling was cycled with argon pressure as required to control foaming at the desired level in the reaction vessel. Similarly, PBT/PPA solutions of lower concentration were prepared and these required less time for complete dehydrochlorination than that described.

**Phenyl-Substituted Poly(*p*-terphenylenebenzobisthiazoles) 11a–c.** The following procedure is typical for the preparation of **11a–c**: Dehydrochlorination was performed as described for PBT, using 2.14804 g (8.7606 mmol) of **5** in 210 g of freshly prepared[3] PPA. The clear solution was then heated to 125 °C. A slurry of **12a**[3] (4.1221 g, 8.7606 mmol) and sulfolane (154 g) was heated to 120 °C and added quantitatively to the PPA/**5** solution. The mixture was then heated under nitrogen as follows: 125 °C, 1 h; 140 °C, 0.5 h; 160 °C, 5 h; 175 °C, 1 h; 195 °C, 1.5 h. The polymerization mixture was then precipitated in methanol, washed with methanol, and dried. After reprecipitation from dilute methanesulfonic acid (MSA) solution, a tan polymer with an intrinsic viscosity of 6.5 dL/g (MSA, 30.0 °C) was obtained.

**Methods.** Intrinsic viscosities were obtained from solutions in freshly distilled methanesulfonic acid (MSA) by extrapolation of $\eta_{rel} - 1/c$ and $\ln \eta_{rel}/c$ to zero concentration. Polymer concentrations were chosen such that the relative viscosity ($\eta_{rel}$) was between 1.5 and 1.1. Monomer grade terephthalic acid was obtained from Amoco Chemicals Corp. with an average particle size of 54 μm. The monomer was reduced to a particle size of 95% <10 μm by an air impact method.

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# Synthesis, Spinning, and Fiber Mechanical Properties of Poly(*p*-phenylenebenzobisoxazole)

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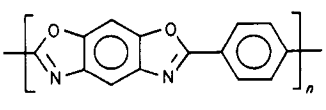
ABSTRACT: The synthesis and the processing of poly(*p*-phenylenebenzobisoxazole) (PBO) into high-modulus organic fibers and films are described. The monomer 4,6-diaminoresorcinol was polymerized with terephthaloyl dichloride in poly(phosphoric acid) at 90–210 °C to attain fibrillar poly(*p*-phenylenebenzobisoxazole). PBO in methanesulfonic acid with a small amount of chlorosulfonic acid was spun into high-modulus fibers and films. The mechanical properties and flammability of the fiber and film are described.

This report covers a part of the work carried out in support of the Air Force effort on the synthesis and solution processing of the high molecular weight rodlike polymers poly(*p*-phenylenebenzobisoxazole) (PBO) and poly(*p*-phenylenebenzobisthiazole) (PBT). These polymers are characterized by a high degree of molecular order, their thermal stability, and fabricated shaped items of high strength and modulus.[1]



PBO

PBO can be prepared by polycondensation of 4,6-diaminoresorcinol and terephthalic acid in poly(phosphoric acid).[2,3] However, the polymer which is produced exhibits an undesirably low molecular weight and, when spun, yields fibers having undesirably low strength properties, especially modulus. Therefore, it is desirable to provide a process for the production of high molecular weight para-ordered aromatic heterocyclic polymer.

An improvement in the polymerization of linear high molecular weight PBO, the preparation of spinning solution, and the wet-spun fiber properties of PBO are described in this paper. These high molecular weight PBO polymers were prepared by polymerization of 4,6-diaminoresorcinol with an intermediate derived from the reaction of poly(phosphoric acid) and terephthaloyl dichloride, presumably a dipoly(phosphoric) terephthalic anhydride.

**Polymerization.** The general procedure is to charge the desired quantities of terephthaloyl dichloride and poly(phosphoric acid) into a reaction vessel and dehydrochlorinate by heating at 30–95 °C for 3–24 h in order to form the poly(phosphoric terephthalic anhydride). 4,6-Diaminoresorcinol dihydrochloride is then added and the resulting mixture is again dehydrochlorinated prior to polymerization.

It is also possible to mix 4,6-diaminoresorcinol dihydrochloride, terephthaloyl dichloride, and poly(phosphoric acid) and dehydrochlorinate the entire mixture. Following dehydrochlorination, the polymerization is begun with stepwise heating. Stepwise heating is preferred

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