the X-ray data. The *d* values from the sedimentation and dielectric dispersion data are somewhat larger than 1.7 nm, although the uncertainties of the derived values preclude a definite conclusion.

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

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ABSTRACT: The solution polycondensation of 4,6-diamino-1,3-benzenediol dihydrochloride with various para-aromatic dicarboxylic acids in poly(phosphoric acid) (PPA) or in PPA/sulfolane mixtures afforded soluble, thermally stable, rigid-rod polymers with 2,6-benzo[1,2-*d*:5,4-*d′*]bisoxazole units in the main chain. Three *p*-terphenylene dicarboxylic acids with varied phenyl substitution on the middle phenylene ring were prepared. The polymers had intrinsic viscosities in methanesulfonic acid at 30 °C in the range 2.5–9.3 dL/g. The polymers showed excellent thermal stability, as determined by thermogravimetric analysis (TGA) in nitrogen and by thermogravimetric–mass spectral analysis (TGMS) in vacuo, and excellent thermooxidative stability, as determined by TGA and isothermal aging at 316 and 371 °C in air. The rigid-rod polymers with phenyl substituents showed limited solubility in PPA/sulfolane and *m*-cresol/strong acid mixtures; these mixtures were nonsolvents for similar polymers without phenyl substituents.

A series of 12 papers appearing in this issue reports the results of a research program[2] sponsored by the U.S. Air Force and directed toward the development of new structural materials having low density, high strength, high modulus, and long-term retention of these properties at elevated temperatures. Research in the past 2 decades has led to numerous aromatic heterocyclic polymer systems having excellent thermal and thermooxidative stability. In general, however, suitable fabrication techniques were lacking to obtain the high degree of molecular order in a bulk form required for extremely high mechanical properties.

It is well-established from both the theoretical considerations of Flory[3] and the extensive research conducted on extended-chain polyamides[4] that liquid crystalline solution behavior results from a high degree of molecular shape anisotropy, which is dependent on molecular structure and molecular weight, if another important condition is met. The polymer must be soluble above the critical concentration, which is dependent on the degree of shape anisotropy, at which anisotropic phase separation occurs. The utilization of liquid crystalline solutions of poly(*p*-benzamide) has produced highly ordered fibers of extremely high tensile modulus and strength.[5] Modulus values of 1400 g/denier (>90% of the theoretical[6]) and tenacities as high as 28 g/denier have been reported.[7] The synthesis and fabrication of aromatic heterocyclic rodlike polymers that form liquid crystalline solutions hold promise of extending not only the mechanical but also the thermal capabilities of polymers closer to the theoretical limits of organic polymer crystals.

Our approach, therefore, has centered on the study of totally aromatic rigid-rod molecules, that is, polymers comprised exclusively of aromatic and aromatic heterocyclic units, each having two exocyclic, catenating bonds which are positionally and angularly well-defined, such that the backbone configuration is regular and rodlike. The goals of the synthesis effort were to determine the effects of various structural features, such as the type and position of the heteroatoms and phenyl substitution of the main chain and methods of synthesis on the attainable molecular weight and the solubility characteristics necessary for liquid crystalline solution fromation. This paper reports the synthesis and thermal properties of polymers containing the benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl unit combined with *p*-phenylene, *p*-biphenylene, or phenyl-substituted *p*-terphenylene units.

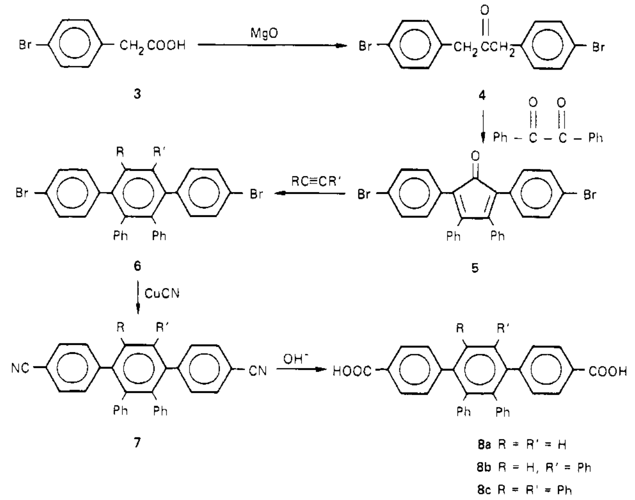
The condensation of *o*-aminophenols with aromatic carboxylic acid derivatives has been employed previously to prepare thermally stable polymers containing a variety of benzoxazole units in the main chain. Poly(2,6-benzoxazole) was prepared by both melt and poly(phosphoric acid) (PPA) solution techniques from 3-hydroxy-4-aminobenzoic acid.[8,9] The 2,2′-bibenzoxazole unit has been incorporated into the main chain by the reaction of either 3,3′-dihydroxybenzidine dihydrochloride or 3,3′-diamino-4,4′-dihydroxybiphenyl dihydrochloride with various dicarboxylic acids.[10] The benzo[1,2-*d*:5,4-*d*′]bisoxazole unit has been incorporated into polymers by two methods: (1) the condensation of 4,6-diamino-1,3-benzenediol dihydrochloride (1) with 4,4′-bis(carbomethoxy)diphenyl ether in PPA[11] and (2) the prior formation of the heterocycle from 1 and an amino acid followed by polyimide formation with various dianhydrides.[11,12] None of these polymers possessed the rodlike configuration required for our study, but all showed excellent thermooxidative stability.

Two classes of aromatic polymers, the poly(phenylquinoxalines)[13] and the phenylated polyphenylenes,[14] are completely soluble in common organic solvents, whereas the parent polymers void of phenyl substituents are soluble only in strong acid solvents. Since the parent polymer in this study, PBO, was found to be soluble only in strong acids and since it was desirable to fabricate from aprotic solvents, three new *p*-terphenylene dicarboxylic acids with two, three, and four phenyl substituents on the middle ring were synthesized.[15a] Their incorporation into the subject polymers[15b] allowed the determination of the effect of main-chain phenyl substituents on the solubility of these rigid-rod polymers.

Results and Discussion

Monomer Synthesis. The bis(*o*-aminohydroxy) monomer 4,6-diamino-1,3-benzenediol dihydrochloride (1) was prepared by a modification of the published procedure.[16] The desired dinitrated isomer, 4,6-dinitro-1,3-benzenediol (2), was obtained in 30% yield by the treatment of diacetyl-1,3-benzenediol with fuming nitric acid. Repeated recrystallizations from ethyl acetate gave 2 without the presence of 2,4,6-trinitro-1,3-benzenediol. The catalytic hydrogenation of 2 was performed in dilute hydrochloric acid. Filtration of the hydrogenation mixture directly into tetrahydrofuran that had been saturated with dry hydrogen chloride gave 1 as a light pink powder. Monomer 1 recrystallized from deoxygenated water containing stannous chloride as colorless needles upon the addition of concentrated hydrochloric acid.

Scheme I



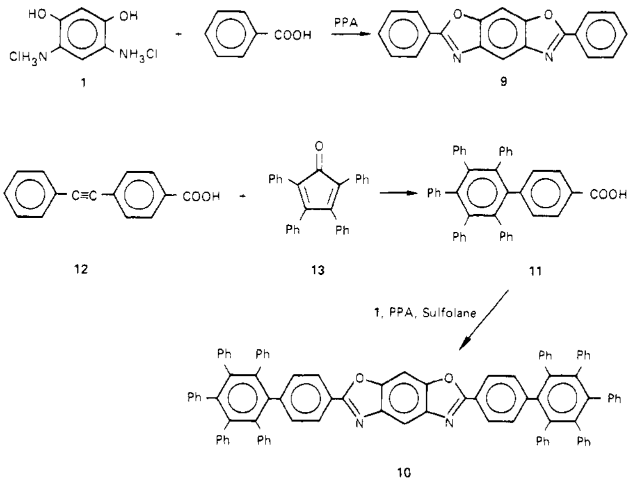
The phenyl-substituted *p*-terphenylene dicarboxylic acids used in this study were prepared as outlined in Scheme I. When an intimate mixture of (*p*-bromophenyl)acetic acid (3) and magnesium oxide was heated to 340 °C under reduced pressure, 1,3-bis(*p*-bromophenyl)-2-propanone (4) was collected by distillation in a 70% yield. Condensation of 4 with benzil in ethanolic potassium hydroxide gave 2,5-bis(*p*-bromophenyl)-3,4-diphenylcyclopentadienone (5) in 93% yield. The Diels–Alder reactions of 5 with norbornadiene at 110 °C, phenylacetylene at 139 °C, and diphenylacetylene at 305 °C gave the 4,4″-dibromophenyl-substituted *p*-terphenylene compounds 6a–c, respectively, in yields of >90%. These reactions were easily monitored visually because of the loss of the dark purple color of 5. The nucleophilic displacement of the bromo groups by cyanide ion in dry *N*-methyl-2-pyrrolidinone (NMP) gave the dicyano intermediates 7a–c in yields of 65–86%. The use of dry NMP decreased the amount of hydrolyzed cyano groups and thus facilitated purification of 7. Hydrolysis of 7a–c in alkaline ethylene glycol gave the dipotassium salt of monomers 8a–c, which crystallized directly from the hydrolysis mixture. Acidification of the purified salt gave monomers 8a–c in yields of 60–70%. The diacid monomers 8a–c were white solids that were thermally stable up to their melting points of 425, 425, and 450 °C, respectively, as shown by differential scanning calorimetry (DSC).

Model Compound Synthesis. The synthesis of the model compound 2,6-diphenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (9) was accomplished in essentially quantitative yield by the reaction of 20% excess benzoic acid with monomer 1 (Scheme II). Elemental and mass spectral analyses were consistent with the assigned structure. The crystal structure of 9 has been determined[17] and showed the desired linear structure. The model compound 2,6-bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazole (10) was prepared in 87% yield by the reaction of 1 with *p*-(pentaphenylphenyl)benzoic acid (11) in a mixture of PPA and sulfolane. The acid 11 was prepared by the

Table I
Synthesis of Poly(*p*-phenylenebenzobisoxazoles) (PBO and PBBO)

polymer	polymerization solvent	reaction temp, °C	$[\eta]$, dL/g	comments
PBO-9	PPA	130-200	3.7	
PBO-31	PPA	130-200	3.1	recrystallized diaminobenzenediol
PBO-41	PPA	100-200	2.9	slow heating rate
PBO-51	PPA	110-195		low molecular weight; tetratosylate monomer
PBO-84	PPA	100-200	2.80	purified terephthalic acid
PBO-115	PPA/sulfolane	100-175	oligomer	early precipitation of yellow oligomer
PBBO-81	PPA	100-185	2.45	dicarboxybiphenyl monomer

Scheme II



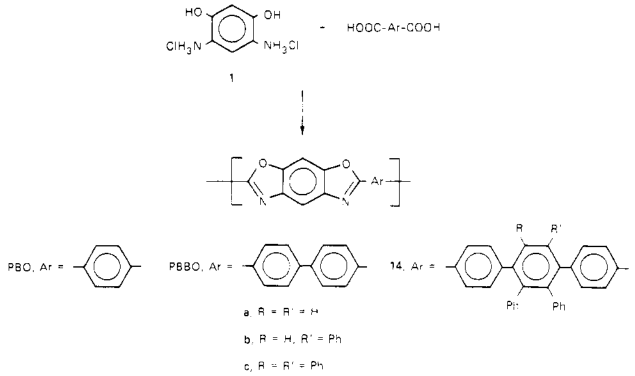
Diels–Alder reaction of *p*-(phenylethynyl)benzoic acid[18] (**12**) with tetraphenylcyclopentadienone (**13**). Compound **10** was initially soluble in hot methylene chloride but was no longer soluble after crystallization occurred upon cooling. Efforts are in progress to form single crystals of **10** for X-ray diffraction studies.

Polymer Synthesis. All polymerizations were conducted in freshly prepared poly(phosphoric acid) (PPA), either neat or with a cosolvent. PPA was prepared by adding a 1.52/1 weight ratio of phosphorus pentoxide to cold phosphoric acid and then heating at 150 °C under nitrogen for 6 h.

Poly[(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO) was synthesized by gently heating a stoichiometric mixture of **1** and terephthalic acid in PPA until hydrogen chloride ceased to be evolved and then slowly heating the mixture to a maximum temperature of 200 °C (Scheme III). The viscous polymerization mixture was then poured into water or methanol, washed thoroughly with water, and dried under reduced pressure. The polymer was then dissolved in methanesulfonic acid and reprecipitated into methanol. This procedure gave polymers with intrinsic viscosities in the range 2.8–3.7 dL/g, as measured in methanesulfonic acid (MSA) at 30.0 °C (Table I). Efforts to increase the molecular weight of PBO included rigorous purification of monomer **1** and terephthalic acid, preparation of the tetratosylate of **1**, and the study of various heating schedules. Polymerization of **1** with 4,4′-bibenzoic acid by the foregoing procedure gave the benzobisoxazole polymer with a 4,4′-biphenylene unit in the main chain. This polymer, PBBO, had an intrinsic viscosity in MSA of 2.45 dL/g.

Polymers with varied degrees of phenyl substitution (**14a–c**) were prepared as outlined in Scheme III. The foregoing procedure described for PBO was not applicable to the preparation of the phenyl-substituted analogues of PBO owing to the insolubility of monomers **8a–c** in PPA. Monomers **8a–c**, were, however, partially soluble in sulfolane at 120 °C. A modified procedure was therefore adopted to effect dehydrochlorination of **1** and then add a stoichiometric amount of finely powdered **8a–c** as a slurry in sulfolane.

Scheme III



The polymerization mixture became homogeneous at various temperatures depending on which diacid monomer **8** was used, on the monomer concentration, and on the PPA/sulfolane ratio. The solubility of **8** in a 1/1 mixture of PPA/sulfolane was **8a** > **8b** > **8c**. The monomer solubility increased with increasing sulfolane content in the PPA, but the polymer solubility decreased. Therefore, monomer concentration could be increased only by decreasing the PPA/sulfolane ratio, which lowered the polymer solubility. Monomer concentrations higher than 1.5% resulted in formation of insoluble polymer, owing to either incomplete solubility of monomers **8a–c** and the resultant decomposition of excess *o*-aminophenol functional groups or apparent irreversible aggregation of the polymer at high sulfolane content.

Copolymers with varied degrees of phenyl substitution along the backbone were prepared by the reaction of **1** with mixtures of the three diacids **8a–c** (Table II).

Polymer Solubilities. The dilute[19] and concentrated[19,20] solution properties of PBO are reported elsewhere. The solubility of the phenyl-substituted polymers **14a–c** showed marked differences from that of PBO. Whereas PBO precipitated from a 1/1 PPA/sulfolane polymerization mixture as a low-molecular-weight oligomer, polymers **14a–c** remained in solution to afford materials of high molecular weight. PBO was soluble only in strong acids, such as MSA and chlorosulfonic acid (CSA), whereas polymer **14b** was soluble in MSA, CSA, and benzenesulfonic acid and in mixtures of *m*-cresol/dichloroacetic acid (70/30) and of dichloroacetic acid/MSA (90/10). Sufficient concentration could not be achieved, however, to observe anisotropic phase separation with any of the polymers **14a–c**.

Table II
Synthesis of Phenyl-Substituted Poly(*p*-terphenylenebenzobisoxazoles) (14a-c)

polymer	monomers (mmol)[a]	[concn][b]	PPA/sulfolane by wt	reaction conditions[c]								[η],[d] dL/g
				t, h	*T*, °C	*t*, h	*T*, °C	*t*, h	*T*, °C	*t*, h	*T*, °C	
14a	**1** (2.816) + **8a** (2.816)	[0.83]	1.2/1	2	130	20	150	1	175			4.91
	1 (27.85) + **8a** (27.85)	[1.3]	1/1.74	3	120	1	140	1	150			4.0
14b	**1** (7.040) + **8b** (7.040)	[2.2]	1.6/1	20	135	24	155	24	175	12	195	insol[e]
	1 (2.347) + **8b** (2.347)	[0.85]	1/1	18	130	5	155	3	185			9.32
	1 (49.941) + **8b** (49.941)	[1.6]	1/1.3	5	135	16	165	6	190			5.70
14c	**1** (2.347) + **8c** (2.347)	[1.1]	1.1/1	1	120	12	145	2	175	1	210	2.48
Copolymers												
	1 (2.816) + **8a** (0.9387) + **8b** (0.9387) + **8c** (0.9386)	[0.91]	1.6/1	5	135	1	150	1	170	40	185	insol[e]
	1 (2.347) + **8a** (1.1734) + **8b** (1.1734)	[0.90]	1.2/1	1	135	1	150	1	170	20	185	2.50

[a] See Experimental Section. [b] (Weight of monomers)/(weight of mixed solvent) × 100. [c] Heating schedule after dehydrochlorination of **1** and addition of **8** in sulfolane. [d] In methanesulfonic acid at 30 °C. [e] Monomer **8** did not dissolve completely.

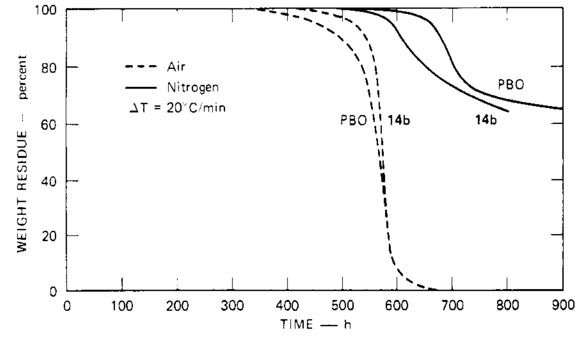


Figure 1. Thermogravimetric analysis of PBO and polymer **14b**.

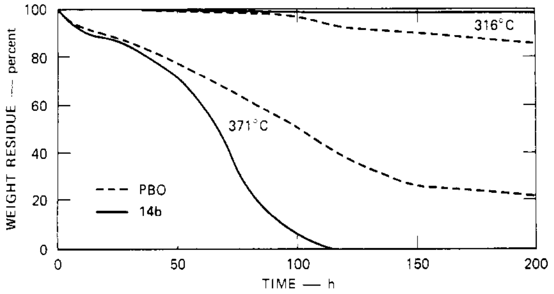


Figure 2. Isothermal aging at 316 and 371 °C of powder samples of PBO and **14b** in circulating air.

Thermal Evaluation. The thermal properties of the polymers were evaluated by thermogravimetric analysis (TGA), isothermal aging, and vacuum thermogravimetric–mass spectral analysis (TGMS). A typical TGA trace for the phenyl-substituted polymers is shown in Figure 1 for polymer **14b** and is compared with that for PBO. A comparison of the two polymers by isothermal aging at 316 and 371 °C is shown in Figure 2. Both polymers showed minimal weight loss at 316 °C. At the higher temperature (371 °C), PBO exhibited better thermooxidative stability than polymer **14b**, which can be attributed to the thermal loss of the phenyl substituents from the latter system.

TGMS studies were conducted under vacuum on PBO and the triphenyl-substituted polymer **14b**. The profiles of major volatiles as a function of temperature are shown in Figures 3 and 4. For PBO, the thermal decomposition of one of the heterocyclic rings begins at 600 °C and reaches a maximum at 660 °C, as indicated by the concurrent loss of CO_2, CO, and HCN. The lower temperature CO_2 evolution (543 °C maximum) is thought to be the result of interaction with trapped gases and/or residual acid solvent and therefore not a result of a primary thermal degradation mechanism. Water and ammonia were observed in small amounts, with benzene and benzonitrile only in trace amounts. These results were in striking contrast to those for **14b**, in which CO_2 evolution was small, water, benzonitrile, and ammonia evolution was moderate,

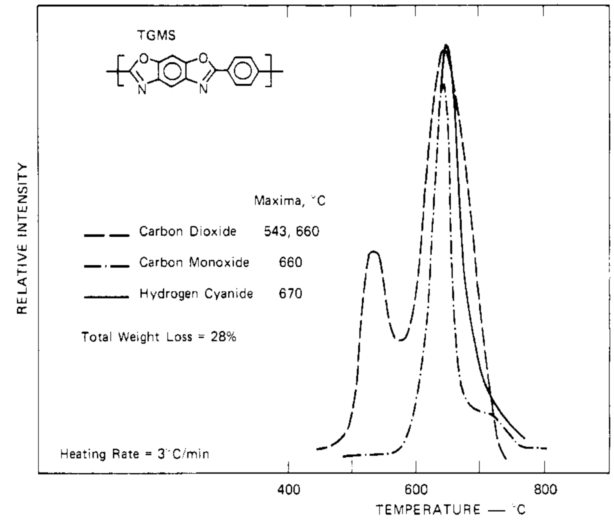


Figure 3. Thermogravimetric–mass spectral analysis of PBO.

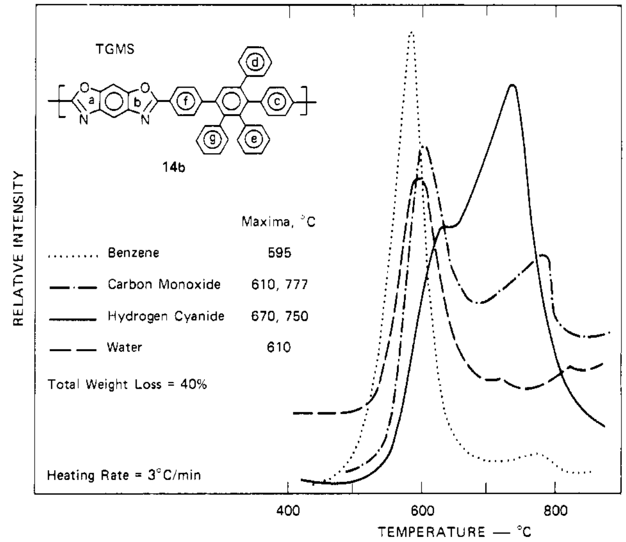


Figure 4. Thermogravimetric–mass spectral analysis of **14b**.

and benzene was the major product. The total weight loss at 1000 °C for PBO was 28%, which is consistent with 1 mol of CO, 1 mol of HCN, and 0.25 mol of CO_2 per repeat unit. The 40% weight loss of **14b** at 1000 °C seems to indicate a more extensive degradation of the benzobisoxazole unit than occurs in PBO. The observed weight loss is consistent with 1.8 mol of benzene, 0.2 mol of benzonitrile, 1.6 mol of HCN, 1 mol of CO, 1 mol of water, and 0.2 mol of ammonia; it is also consistent with incorporation of the benzo and triphenylbenzene moieties into the char. The weight loss data presented on the pyrolysis in nitrogen of polyphenylenes with triphenyl-substituted rings[14b] is also consistent with incorporation of triphenylbenzene into the char.

In addition to the differences in volatiles produced, another indication that the two polymers degraded by different mechanisms was that PBO showed essentially one maximum near 660 °C, whereas **14b** showed two maxima, one 60 °C lower and the other approximately 100 °C higher than the maximum of PBO. The first process will be discussed further below; the second, being broader and at higher temperature, is indicative of a process involving decomposition of secondary, more complex species. Since PBO did not produce volatiles appreciably between 750 and 1000 °C and **14b** showed a major evolution in that range, it is felt that the primary degradation residue of PBO (which contains heteroatomic species according to percent weight loss) is significantly different from and more thermally stable than the residue from **14b**. This could be a result of tighter chain packing expected for PBO, owing to the bulkier backbone of **14b**, which allows greater intermolecular interaction and results in a more tightly cross-linked structure.

The lower temperature degradation of one of the heterocyclic rings in **14b** can be explained by the differences in the neighboring groups attached to the heterocycles labeled a and b in Figure 4. The asymmetry of the triphenyl *p*-terphenylene moiety produces a heterocycle of type a on one side and one of type b on the other side as the monomer **8b** is incorporated into the polymer. Random incorporation of **8b** results in the benzobisoxazole moieties being of three types (a, a; a, b; b, b) in a ratio of 1:2:1. Heterocycle a is attached to a phenylene ring (c) that is sterically crowded by two adjacent phenyl rings (d and e). Heterocycle b is attached to a ring (f) that has only one adjacent phenyl ring (g). Elimination of ring c as benzene (595 °C maximum) or, to a lesser extent, as benzonitrile (620 °C maximum) initiated the decomposition of ring a at a lower temperature than for b or for the two heterocycles of PBO. The elimination of rings c and g relieves the steric crowding of the pentasubstituted ring and accounts for the 2 mol of aromatic species observed.

Conclusions. Aromatic heterocyclic polymers having rigid-rod configurations and excellent thermal and thermooxidative stability were prepared. PBO, however was the only polymer that had the solubility characteristics necessary to form liquid crystalline solutions. With respect to solubility, the effect of incorporating the phenyl-substituted *p*-terphenylene group was to allow the addition of certain organic solvents to an acid solution of the polymer and maintain polymer solubility; however, the necessity of the acid to protonate and thus disperse these rigid molecules was not eliminated. The fiber spinning of liquid crystalline solutions of PBO is described in another paper in this issue.[20]

Experimental Section

4,6-Diamino-1,3-benzenediol Dihydrochloride (1). A mixture of 4,6-dinitro-1,3-benzenediol[16] (10.0 g, 0.050 mol), 10% palladium-on-charcoal (1.0 g), and 10% hydrochloric acid (275 mL) was shaken under 50 psi of hydrogen at room temperature for 24 h. The mixture was then filtered through a Celite pad into 1 L of tetrahydrofuran that had been saturated with gaseous hydrogen chloride. The resulting pink crystals were recrystallized from deoxygenated water containing stannous chloride (3% by weight) by heating to 80 °C and then adding an equal volume of concentrated hydrochloric acid. The product was collected by filtration, washed with concentrated hydrochloric acid and ether, and then dried at 60 °C under reduced pressure for 6 h to give colorless needles: mp, decomposition without melting, ~200 °C; mass spectrum (70 eV), *m/e* 140 (M − 2HCl).

Anal. Calcd for $C_6H_{10}Cl_2N_2O_2$: C, 33.82; H, 4.73; N, 13.15; Cl, 33.28. Found: C, 33.64; H, 4.90; N, 13.20; Cl, 32.10.

1,3-Bis(*p*-bromophenyl)-2-propanone (4). An intimate mixture of (*p*-bromophenyl)acetic acid (323 g, 1.50 mol) and 94% magnesium oxide (66.5 g, 1.65 mol) was heated at 250 °C under reduced pressure to remove water of condensation. Raising the temperature to 340 °C at 1–3 torr caused distillation of **4** (225 g, 81.6%). Recrystallization from ethanol gave 192 g (70%) of **4** as colorless platelets; mp 120–122 °C (lit.[21] mp 121–122 °C).

2,5-Bis(*p*-bromophenyl)-3,4-diphenylcyclopentadienone (5). This intermediate was prepared by the condensation of benzil with **4**, as described in ref 21.

4,4″-Dibromo-2′,3′-diphenyl-*p*-terphenyl (6a). A mixture of **5** (190 g, 0.35 mol), bicyclo[2.2.1]hepta-2,5-diene (370 g, 4.0 mol), and toluene (1 L) was heated at reflux until the color faded to pink (3 h). The solution was cooled and the resultant pink crystals were collected, washed with methanol, and air-dried to give 150 g (80%) of **6a**: mp 275–278 °C.

Anal. Calcd for $C_{30}H_{20}Br_2$: C, 66.68; H, 3.73. Found: C, 65.95; H, 3.95.

4,4″-Dibromo-2′,3′,5′-triphenyl-*p*-terphenyl (6b). A mixture of **5** (120 g, 0.22 mol), phenylacetylene (56 g, 0.55 mol), and *o*-dichlorobenzene (925 mL) was heated at the reflux temperature for 2 h. The yellow solution was poured into methanol (3 L) to give 127 g (93%) of **6b**; mp 273–275 °C.

Anal. Calcd for $C_{36}H_{24}Br_2$: C, 70.15; H, 3.92; Br, 25.93. Found: C, 70.67; H, 4.08; Br, 25.52.

4,4″-Dibromo-2′,3′,5′,6′-tetraphenyl-*p*-terphenyl (6c). A mixture of **5** (14.2 g, 20.5 mmol), diphenylacetylene (10.7 g, 60.0 mmol), and benzophenone (50 g) was heated to a vigorous reflux with a flame. After 10 min, the color faded and heating was continued for an additional 10 min. Diphenyl ether (10 mL) was added to prevent the benzophenone from crystallizing. The reaction mixture was allowed to cool to room temperature. The resultant crystals were collected by filtration and washed with benzene to give 16 g (86%) of **6c**.

Compound **6c** was also prepared in 83% yield by heating the above reactants at reflux in *o*-dichlorobenzene for 3 days.

Phenyl-Substituted Dicyano-*p*-terphenylene Intermediates 7a–c. The following procedure was used to prepare compounds **7a–c**. To a mixture of **6b** (100 g, 0.16 mol) and cuprous cyanide (33 g, 0.37 mol) dry *N*-methyl-2-pyrrolidinone (800 mL) was added under a stream of dry nitrogen. After heating under reflux for 20 h, the hot, dark brown mixture was poured into 2 L of warm water containing 667 g of sodium cyanide. The resulting gray precipitate was washed twice with 10% aqueous sodium cyanide. The solid was air-dried at 100 °C and then continuously extracted with benzene overnight to give 61 g (74%) of 4,4″-dicyano-2′,3′,5′-triphenyl-*p*-terphenyl (**7b**): mp 305–307 °C; IR (KBr) 2200 (C≡N), 1670 cm^{-1} (weak, carboxyl C=O).

Anal. Calcd for $C_{32}H_{20}N_2$ (**7a**): C, 88.86; H, 4.66; N, 6.48. Found: C, 89.11; H, 4.75; N, 6.43.

Calcd for $C_{38}H_{24}N_2$ (**7b**): C, 89.72; H, 4.75. Found: C, 89.32; H, 4.81.

Calcd for $C_{44}H_{28}N_2$ (**7c**): C, 90.38; H, 4.83; N, 4.79. Found: C, 90.39; H, 4.83; N, 4.58.

4,4″-Dicarboxy-2′,3′-diphenyl-*p*-terphenyl (8a). A mixture of **7a** (4.6 g, 11 mmol), potassium hydroxide (20 g), and ethylene glycol (190 mL) was heated at reflux for 16 h. The light orange solution was cooled slightly and 150 mL of water added. After the solution cooled, the dipotassium salt of **8a** was collected by filtration and dissolved in hot water. The hot solution was then clarified with activated charcoal and filtered. After acidification, the diacid was further purified by dissolution in *N*,*N*-di-

Table III
Elemental Analysis of Polymers

	calcd, %			found, %		
	C	H	N	C	H	N
PBO	71.79	2.48	11.96	71.88	2.26	12.40
14a	84.74	4.12	5.20	83.95	4.01	
14b	85.97	4.26	4.56	85.12	3.59	3.81
14c	86.93	4.38	4.06	86.53	3.98	

methylacetamide, treatment with charcoal, and precipitation with dilute hydrochloric acid. The white powder was washed thoroughly with water and dried at 100 °C (0.1 torr) to give 4.70 g (94%) of **8a**: mp (DSC, ΔT = 20 °C/min) 425 °C; mass spectrum (70 eV), *m/e* 470 (M)$^+$, 453 (M + H − H_2O)$^+$, 427 (M + H − CO_2)$^+$; IR (KBr) 1670 cm^{-1} (C=O).

Anal. Calcd for $C_{32}H_{22}O_4$: C, 81.68; H, 4.72. Found: C, 81.50; H, 4.73.

4,4″-Dicarboxy-2′,3′,5′-triphenyl-*p*-terphenyl (8b). A mixture of **7b** (50 g, 98 mmol), potassium hydroxide (153 g), and ethylene glycol (1.3 L) was heated for 20 h. The diacid was isolated as described to give 39 g (72%) of **8b**: mp (DSC, ΔT = 20 °C/min) 425 °C; mass spectrum (70 eV), *m/e* 546 (M)$^+$, 529 (M + H − H_2O)$^+$, 503 (M + H − CO_2)$^+$.

Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.89. Found: C, 83.41; H, 4.65.

4,4″-Dicarboxy-2′,3′,5′,6′-tetraphenyl-*p*-terphenyl (8c). The monomer was prepared as described for **8b** to give a 60% yield of **8c**: mp, sublimation without melting at 450 °C (DSC, ΔT = 20 °C/min); mass spectrum (70 eV), *m/e* 622 (M)$^+$.

Anal. Calcd for $C_{44}H_{30}O_4$: C, 84.87; H, 4.86. Found: C, 84.64; H, 5.00.

2,6-Diphenylbenzo[1,2-*d*:5,4-*d*′]bisoxazole (9). A mixture of **1** (5.9 g, 28 mmol) and 350 g of freshly prepared poly(phosphoric acid) (PPA) was heated under a slow stream of nitrogen at 80 °C for 16 h and then at 110 °C until evolution of hydrogen chloride had ceased (8 h). Benzoic acid (4.1 g, 34 mmol) was then added and the mixture heated at 150 °C for 12 h and then at 175 °C for 4 h. The brown solution was then poured into water, washed with water, and dried. Recrystallization from toluene gave 8.2 g (95%) of **9** as colorless crystals: mass spectrum (70 eV), *m/e* 312 (M)$^+$.

Anal. Calcd for $C_{20}H_{12}N_2O_2$: C, 76.91; H, 3.87; N, 8.97. Found: C, 76.80; H, 3.95; N, 8.82.

4-(Pentaphenylphenyl)benzoic acid (11). A mixture of tetraphenylcyclopentadienone (5.0 g, 13 mmol), *p*-(phenylethynyl)benzoic acid[18] (5.5 g, 25 mmol), and benzophenone (25 g) was heated at reflux (305 °C) for 30 min. Diphenyl ether (7 mL) was added and the mixture allowed to cool. The resultant precipitate was collected by filtration and washed with benzene to give 7.4 g (98%) of **11**; mp >350 °C; IR (KBr) 1710 (C=O), 730 and 698 cm^{-1} (5 adjacent aromatic H).

2,6-Bis(2′,3′,5′,6′-tetraphenyl-*p*-terphenyl)benzo[1,2-*d*:5,4-*d*′]bisoxazole (10). A mixture of **1** (0.72 g, 3.4 mmol) and PPA (79 g) was dehydrochlorinated as described for **9**. A mixture of **11** (4.30 g, 7.48 mmol) and sulfolane (175 g) was heated to 140 °C and added to the solution of **1** in PPA. This mixture was heated at 130 °C for 16 h, at 155 °C for 5 h, at 185 °C for 2 h, and, finally, at 200–205 °C for 1.5 h. The mixture became homogeneous at 200 °C, and fine needles crystallized from solution. The mixture was cooled to 160 °C and the precipitate collected by filtration. The fine tan powder was washed with water and dried at 100 °C to give 1.8 g of **10**. An additional 1.8 g was obtained by adding water to the filtrate; yield, 3.6 g (87%). An analytical sample was obtained by recrystallization from dichloromethane: mp >350 °C; IR (KBr) 730 and 698 cm^{-1} (5 adjacent H).

Anal. Calcd for $C_{92}H_{60}N_2O_2$: C, 90.16; H, 4.93; N, 2.28. Found: C, 90.14; H, 4.90; N, 1.99.

Poly[(benzo[1,2-*d*:5,4-*d*′]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO). Poly(phosphoric acid) (PPA) was prepared immediately before each use by the following method. Phosphorus pentoxide (330 g) was added slowly to 85% phosphoric acid (217 g) while the mixture was stirred under nitrogen and cooled with an ice-water bath. The viscous slurry was then heated with stirring under nitrogen at 150 °C for 6 h to give colorless, homogeneous PPA.

4,6-Diamino-1,3-benzenediol dihydrochloride (**1**) (1.8806 g, 8.8268 mmol), terephthalic acid (1.4665 g, 8.8268 mmol), and 75 mL of PPA were added to a 100-mL resin flask. The viscous mixture was mixed with a high-shear stirrer and heated such that foaming did not raise the level of the medium more than 0.5 in. The temperature was raised to 55 °C after 2 h, 70 °C after 18 h, and 95 °C after 21 h. The yellow mixture was then heated as follows: 130 °C/3 h; 150 °C/3 h; 172 °C/3 h; 185 °C/3 h, 195–200 °C/16 h. The mixture was then dark brown and formed a ball on the stirring rod. The polymer was precipitated into methanol, washed with methanol, and then continuously extracted with methanol overnight. The polymer was allowed to air-dry and then dissolved in methanesulfonic acid, filtered, and precipitated by addition of methanol. The polymer was stirred with concentrated ammonium hydroxide (orange-red color), washed with water, with methanol, with methanol/benzene mixtures, and finally with benzene. The swollen polymer was then frozen and dried under reduced pressure to give 2.05 g (99%) of PBO: $[\eta]$ = 2.8–3.7 dL/g in methanesulfonic acid at 30 °C. Table III shows the elemental analysis.

Phenyl-Substituted Poly(*p*-terphenylenebenzobisoxazoles) 14. The polymers were prepared by adding a stoichiometric quantity of **8a**, **8b**, or **8c** in sulfolane to a dehydrochlorinated mixture of 4,6-diamino-1,3-benzenediol dihydrochloride and PPA. The experimental details and resultant viscosities are given in Table II. The polymers were isolated as described for PBO. Elemental analyses are given in Table III.

Methods. TGA's were conducted on powdered samples at 20 °C/min. See ref 22 for the TGA traces of 105 other polymers conducted under these conditions. Isothermal aging studies were conducted in air at a flow rate of 40 mL/min on powdered samples with comparable particle size. Intrinsic viscosities were determined on Cannon-Ubbelohde capillary viscometers by extrapolation of $\eta_{rel} - 1/c$ and $\ln \eta_{rel}/c$ to zero concentration, using freshly distilled MSA.

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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

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