Synthesis and Characterization of a Poly(benzobisthiazole) with a Substituted Biphenyl Moiety in the Main Chain

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ABSTRACT: Poly(benzobisthiazole)s containing an ortho-tetrasubstituted biphenyl moiety were synthesized via the polymerization of 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid. Sulfolane was used as a cosolvent with poly(phosphoric acid) (PPA), owing to the insolubility of the ortho-tetrasubstituted biphenyl monomer in PPA. The intrinsic viscosities of the poly(benzobisthiazole)s in methanesulfonic acid at 30 °C were in the range of 0.5−2.3 dL/g. Copolymerizations of 2,5-diamino-1,4-benzenedithiol dihydrochloride with terephthalic acid and 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid were carried out as well by varying the ratio of the two dicarboxylic acid monomers in the reaction mixture. Intrinsic viscosities of up to 9.93 dL/g were achieved for the copolymers. Thermal stability of the copolymers was evaluated by thermogravimetric analysis (TGA). The stability for the copolymers was found to decrease with increased amount of the substituted biphenyl structure in the polymer backbone.

Introduction

There has been a consistent interest in rodlike aromatic heterocyclic polymers for the last 2 decades. The class of rigid-rod ordered polymers, such as poly[(benzo[1,2-*d*:5,4-d′]bisoxazole-2,6-diyl)-1,4-phenylene] (PBO),[1] poly[(benzo[1,2-*d*:4,5-d′]bisthiazole-2,6-diyl)-1,4-phenylene] (PBZT),[2] and poly[(benzo[1,2-*d*:4,5-d′]bisimidazole-2,6-diyl)-1,4-phenylene] (PBI),[3] exhibit excellent physicochemical and thermal properties.[4] These polymers can therefore be fabricated into fibers or films with extremely high tensile strengths and moduli.[5] The inherent desirable mechanical and thermal properties of this group of rodlike polymers stimulated research activity on other aspects of the properties such as solution behavior,[6,7] electronic structure,[8,9] and potential nonlinear optical properties.[10,11]

However, PBZTs and PBOs suffer certain drawbacks such as relatively low compressive strength and limited solubility, as do most high-performance polymeric fibers. The compressive strengths of the PBO and PBZT fibers are approximately 10−15% of their tensile strengths.[4] The characteristically low compressive properties of these polymeric fibers are less than desired for certain structural composites. On the other hand, PBOs and PBZTs dissolve only in a few strong acids such as concentrated sulfuric acid and methanesulfonic acid (MSA). Thus, fibers or films with ultrahigh axial strengths and moduli are fabricated via coagulation of acid solutions of polymers with nonsolvents. Harsh processing conditions have greatly restricted their potential commercial applications as well.

Recently, a considerable amount of research effort has been directed toward the chemical modification of PBO and PBZT in an attempt to enhance the compressive strengths of polymeric fibers[12−14] or the solubility of these polymers in organic solvents.[15−17] It was demonstrated that the substitution at the 2 and 2′ positions of 4,4′-biphenyldiamine produced polyamides with enhanced solubility.[18] The substitution at the 2 and 2′ positions of the biphenyl moiety forces the phenyl rings to adopt a noncoplanar conformation, which disrupts the crystal packing and thus provides enhanced solubility.[19] This noncoplanar biphenyl moiety has been introduced into the backbones of polyamides,[18,19] polyesters,[20,21] and polyimides.[22] The structural feature of noncoplanar molecular units in the backbone not only enhances the solubility of the polymers but gives rise to specific optical properties such as high birefringence[18] and promising nonlinear optical behavior.[23]

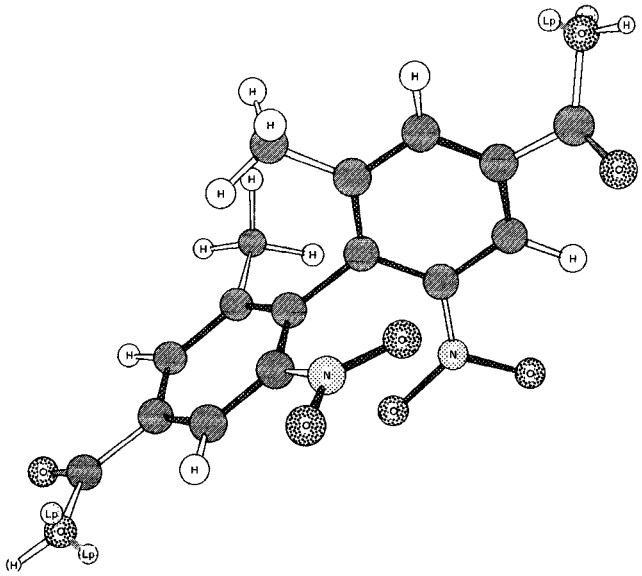

Figure 1. Three-dimensional presentation of 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′- dicarboxylic acid.

The objective of this work is to synthesize a poly(benzobisthiazole) with a 2,2′- and 6,6′-tetrasubstituted biphenyl moiety in the polymer backbone. It was hoped that this modified PBZT would incorporate certain pendant groups, such as methyl, which would result in cross-linking between the polymer chains under thermal treatment or irradiation conditions in postprocessing.[12,24] The introduction of four pendant groups in the ortho positions of the biphenyl ring is designed to make the noncoplanar molecular conformation more prominent (Figure 1). The torsional angle between the two noncoplanar phenyl rings shown in Figure 1 was calculated to be 81° (Chem 3D software from Cambridge

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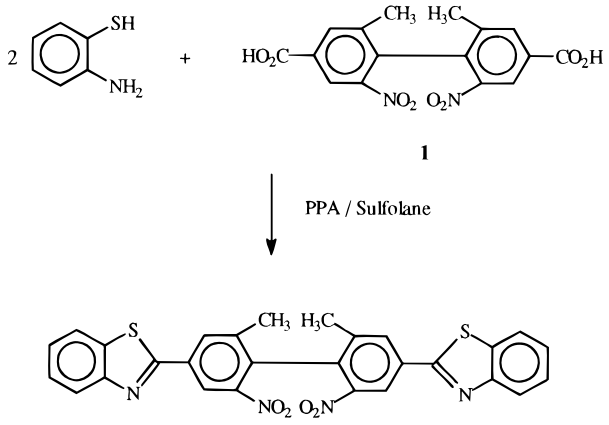
Scheme 1. Synthesis of the Model Compound



Scientific Computing). The pendant groups in this conformation point along different directions in the three-dimensional projection, which would cause the presumed cross-linking reaction induced by thermal treatment or irradiation to occur in the different directions. Then, this kind of chemical modification at the molecular level will be examined to determine if it is helpful in enhancing the compressive properties of the polymer fibers. As the first part of the work, the synthesis and characterization of the PBZTs with the substituted biphenyl moiety in the main chain are reported.

Results and Discussion

Model Compound Synthesis. The model compound, 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dibenzthiazole, was synthesized by the reaction of 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid (**1**) with 2-aminothiophenol as shown in Scheme 1. The reaction in PPA for the preparation of the model compound resulted in decomposed product due to the insolubility of monomer **1** in PPA. When sulfolane, as a cosolvent with PPA, was added to the reaction mixture, the synthesis of the model compound was quantitatively accomplished (96% yield) in an actual solution by the reaction of 20% excess 2-aminothiophenol with monomer **1**. The mass spectrum showed a base peak that corresponded to the molecular ion and no peaks higher than the molecular ion appeared, which was consistent with the assigned structure.

The addition of sulfolane as a cosolvent facilitated the formation of a solution which was essential for the reaction process. However, introduction of this second solvent reduced the concentration of phosphorus pentoxide (P_2O_5) in the whole solution. PPA acts not only as a solvent but also as a catalyst or dehydrating agent in the formation of the benzothiazole ring.[25] The decrease in the concentration of P_2O_5 in the solution weakens the capacity of PPA as a dehydrating agent, which is a driving force for intramolecular cyclization with removal of water. Thus, a low content of P_2O_5 in the solution would result in incomplete formation of the benzothiazole structure. A residual carbonyl absorption was observed in the infrared spectrum, which was an indication of the incompletely ring-closed structure. In addition, it is possible that some hydrolysis may have occurred during model compound workup because some benzazoles are susceptible to acid hydrolysis. Elemental analyses also suggested that the ring closure was not completed under certain reaction conditions. When the model compound isolated from the reaction solution was heat treated at 250 °C under vacuum for 5 h, however, the elemental analyses were consistent with the calculated values. The absorption band corresponding to the carbonyl group disappeared in the infrared spectrum after heat treatment.

Polymer Synthesis. Initial polymer synthesis efforts were directed toward the polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (**2**) with monomer **1** by varying the polymerization conditions such as the concentration of the monomers, the ratio of PPA to sulfolane, and the heating schedules. The results are shown in Table 1. Fresh PPA was prepared before each use. Polycondensation reactions were conducted in the PPA/sulfolane mixture at a monomer content of 1.5−2.5% by weight. Sulfolane as a cosolvent was found to be a requisite for the formation of an actual solution. Without sulfolane, suspended and undissolved **1** had less opportunity to react with dehydrochlorinated **2** in the PPA solution, and this probably led to monomer decomposition at higher temperatures.[2] After the dehydrochlorination of **2** at room temperature to 70 °C over 2 days, the solution of **1** in sulfolane was introduced to the reaction flask. Then, the reaction temperature was gradually raised over several days to 190 °C. Increases in the ratio of PPA/sulfolane did lead to an increase in the intrinsic viscosity of the polymer (trials 3 and 4). A further increase in the PPA component (trial 5) caused the formation of an insoluble product instead, probably owing to limited solubility of monomer **1** in the solvent mixture.

In general, the solution polymerization of rigid-rod polymers is preferably carried out in the nematic phase for the enhancement of the reaction rate and final attainable molecular weight. When the polymerization of PBZT is conducted at greater than 5 wt % monomer concentration, a stir-opalescent liquid-crystalline solution is observed and high molecular weight polymer (intrinsic viscosity = 30.3 dL/g) is obtained.[2,25] At monomer concentrations below 3 wt %, the reaction mixture remains isotropic throughout the polymerization and the maximum attainable molecular weight is low.[2] In polymerizations of monomers **1** and **2**, a relatively low monomer content (below 2.5 wt %) and the existence of a cosolvent inevitably resulted in an isotropic solution and therefore low molecular weight polymers.

Preparation of the copolymers was carried out by polycondensation in PPA of **2** with terephthalic acid and monomer **1**, as shown in Scheme 2. The results are given in Table 2. After dehydrochlorination of **2** was completed in PPA with 85% P_2O_5 over 2 days, terephthalic acid was added to the solution and dissolved in it as the temperature was raised to 130 °C. The yellow solution was maintained at that temperature for a few hours. Then, addition of monomer **1** was followed by keeping the temperature of the mixture at 130 °C overnight, which yielded a slightly red solution. A gradual increase in the reaction temperature over 1 day to 190 °C yielded a brown fibrillar polymer. The copolymers exhibited higher intrinsic viscosities than the homopolymers described in Table 1.

The copolycondensation reactions were generally run at a solids content of approximately 5% by weight. In consideration of the insolubility of **1** in PPA, a low solids concentration of nearly 2 wt % was used because of the large mole fraction ($y = 0.3$) of this monomer. In a control experiment, the mixed solvent of PPA/sufolane (weight ratio: 5/1) resulted in a significant decrease in

Table 1. Synthesis of Substituted Biphenyl PBZT

trial	monomer,[a] g (mmol) M1	M2	PPA/ sulfolane, g	$[\eta]$,[b] dL/g	concn,[c] wt %	reaction conditions h	*T*, °C	h	*T*, °C	h	*T*, °C	h	*T*, °C	h	*T*, °C
1	1.492 (4.142)	1.016 (4.142)	80/68	1.51[d]	1.69	22	130	6	130	3	190				
2	1.469 (4.078)	1.000 (4.078)	80/70	0.57	1.65	3	130	3	150	3	170	5	190		
3	1.549 (4.299)	1.054 (4.299)	80/80	1.03	1.63	4	130	4	150	2	170	2	190	2	220
4	1.504 (4.174)	1.023 (4.174)	80/40	2.30	2.11	1	110	5	130	18	165	5	190		
5	1.475 (4.095)	1.004 (4.095)	82/24	insul[e]	2.34	2	130	18	165	6	190	1	205		
6	1.471 (4.082)	1.001 (4.082)	135/35	0.51	1.46	9	130	15	165	17	190	3	210		

[a] M1 is 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid; M2 is 2,5-diamino-1,4-benzenedithiol dichloride. [b] Intrinsic viscosity was measured in CH_3SO_3H at 30 °C. [c] (Weight of monomers)/(weight of mixed solvents) × 100. [d] Inherent viscosity measured at a concentration of 0.10 g/dL in CH_3SO_3H at 30 °C. [e] Polymer did not dissolve completely; solvents tested are CH_3SO_3H, H_2SO_4, and $ClSO_3H$.

Scheme 2. Synthesis of Copolymers with Substituted Biphenyl Structure. *n* = Mole Fraction

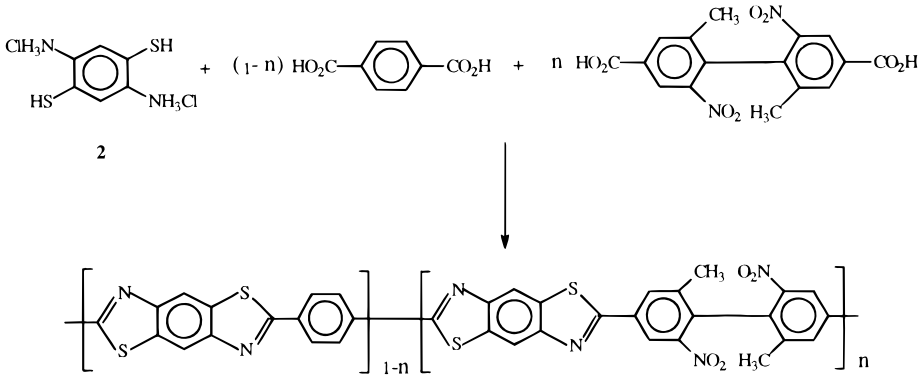


Table 2. Copolycondensation of 2,5-Diamino-1,4-benzenedithiol Dichloride with Terephthalic Acid and 2,2′-Dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic Acid Monomer

trial	copolymzn solvent[a] (g)	*n*[e]	$[\eta]$,[d] dL/g	reaction conditions h	*T*, °C	h	*T*, °C	h	*T*, °C
1	PPA (36)	0.00	9.98	4	130	16	160	20	190
2	PPA/sulfolane (30/6)	0.00	5.34	4	130	16	160	20	190
3	PPA (36)	0.03	9.93	10	130	20	160	18	190
4	PPA (36)	0.10	8.85	15	130	15	160	18	190
5	PPA[b] (100)	0.30	6.75	6	130	24	160	18	190
6	PPA/sulfolane[c] (80/40)	1.00	2.0	5	130	18	160	5	195

[a] Solid content 4.9−5.4% (w/w) unless specified. [b] Solid content 1.93% (w/w). [c] Same reaction conditions as trial 4 in Table 1. [d] In CH_3SO_3H at 30 °C. [e] Mole proportion.

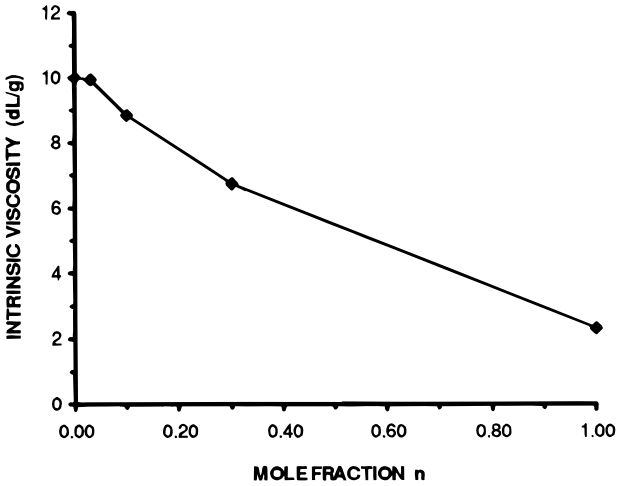


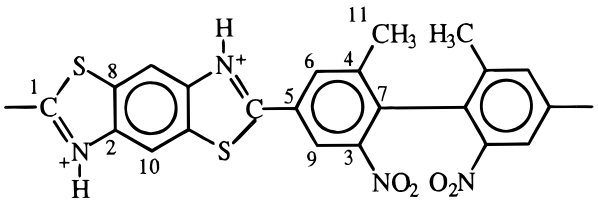
Figure 2. Intrinsic viscosity of copolymers vs mole proportion of substituted biphenyl unit.

the molecular weight of the parent PBZT, as seen from Table 2 (trials 1 and 2). It has also been reported[2] that rigid-rod PBZTs with various degrees of phenyl substitution had to be polymerized in the PPA/sulfolane mixed solvent due to the limited solubility of phenyl-substituted PBZT in pure PPA. The use of mixed solvent resulted in lower molecular weight phenyl substituted PBZTs compared to the nonsubstituted parent PBZT in pure PPA. Use of sulfolane as a cosolvent in the polymerization of PBZT probably affects the formation of the nematic phase or the alignment of rigid rods in the ordered phase, which causes reaction rate changes and therefore low molecular weights.[26]

Polymer Characterization. The homopolymers and most of the copolymers with the substituted biphenyl moiety in the backbone were soluble in MSA and chlorosulfonic acid. They were insoluble in common organic solvents such as dimethyl sulfoxide, dimethylformamide, chloroform, and *N*-methyl-2-pyrrolidinone, etc. The intrinsic viscosity measurements were carried out at 30 °C in MSA. The intrinsic viscosities decrease with an increase in mole proportion of the substituted biphenyl structure in the polymer chains, as shown in Figure 2. The deleterious effect of **1** on the attainment of high molecular weight probably resulted from its limited solubility in pure PPA solvent. The solubility behavior of the copolymers was quite different than that of homopolymers. For example, the parent PBZT (trial 1 in Table 2) formed a clear solution in 2 days at a concentration of 0.15 g/dL. Nevertheless, a copolymer with 0.03 mole proportion of the substituted biphenyl moiety (trial 3 in Table 2) required 5 days to form a transparent solution even under magnetic stirring in spite of the fact that the intrinsic viscosities of these two polymers are nearly equal. For copolymers with higher mole fractions of the substituted biphenyl structure (trials 4 and 5 in Table 2), complete dissolution took as long as 1−2 weeks under magnetic stirring even though their intrinsic viscosities were lower than that of the parent PBZT.

The ^{13}C NMR spectrum of the substituted biphenyl PBZT homopolymer was obtained in MSA solution. The

Table 3. Assignment of Chemical Shifts of Substituted Biphenyl PBZT in ^{13}C NMR Spectrum[a]



	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
actual shift, ppm	176	148	142	140	138	137	133	126	124	114	20
calcd, ppm	171	149	147	138	137	136	135	125	122	116	20

[a] Measured in the CH_3SO_3H solution of sample trial 5 in Table 1.

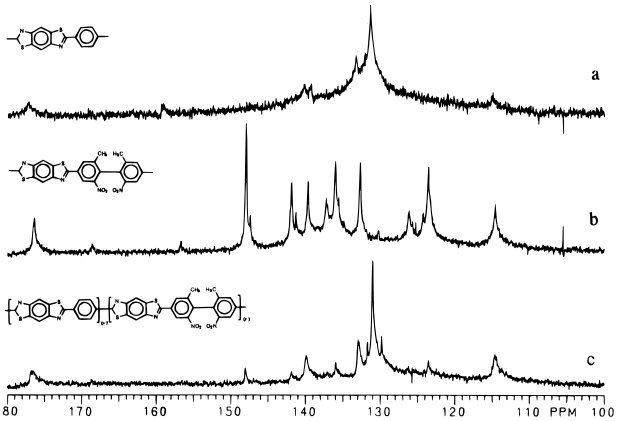


Figure 3. ^{13}C NMR spectra of (a) 2.5 wt % parent PBZT ([η] = 9.98 dL/g) in MSA, (b) 2.5 wt % substituted biphenyl PBZT homopolymer ([η] = 2.30 dL/g) in MSA, and (c) 2.3 wt % copolymer ([η] = 6.75 dL/g) in MSA. A total of 130 000 scans for data collecting.

assignment of the peaks to corresponding carbons in the protonated polymer chain was made by use of "^{13}C NMR Module" software (SoftShell International). That two nitrogen sites per repeat unit are protonated is based on the investigation[27] of protonation of *cis*-PBO in MSA solution and the calculation[28] of the order of protonation in the heterocycle. The observed chemical shifts in the ^{13}C NMR spectrum are reasonably consistent with the calculated values (Table 3).

The high molecular weight PBZT polymer exhibited a poor signal−noise ratio in the ^{13}C NMR spectrum, as shown in Figure 3a. At a concentration of 2.5 wt % in MSA, substituted biphenyl PBZT homopolymer with low molecular weight (Figure 3b) gave a better signal−noise ratio than the moderate molecular weight copolymer of PBZT (Figure 3c) after 130 000 scans and a much better signal−noise ratio than the high molecular weight parent PBZT. The spectrum of the copolymer resembles a combination of the spectra of the two homopolymers, and the copolymer chemical shifts are a combination of the chemical shifts of the two homopolymers, which is consistent with the expected structure of the copolymer.

The presence of the substituted biphenyl structure in the polymer backbone resulted in a lower degradation temperature compared to the parent polymer (no. 1 in Figure 4). This decrease in degradation temperature could be readily demonstrated by TGA studies in air. As seen from Figure 4, the polymers exhibited two degradation onset temperatures as the substituted biphenyl unit content increased, one at 345 °C and the other between 570 and 605 °C, depending on the amount

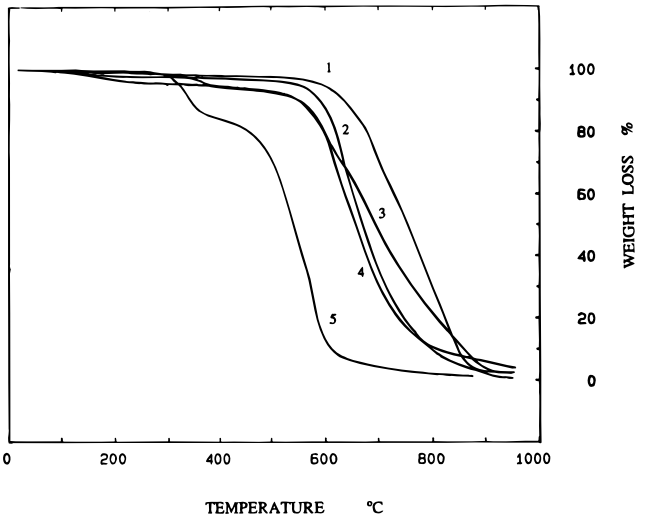


Figure 4. TGA scan of PBZTs with varied mole fractions of substituted biphenyl moiety in air. (1) $n = 0.0$; (2) $n = 0.03$; (3) $n = 0.10$; (4) $n = 0.30$; (5) $n = 1.0$.

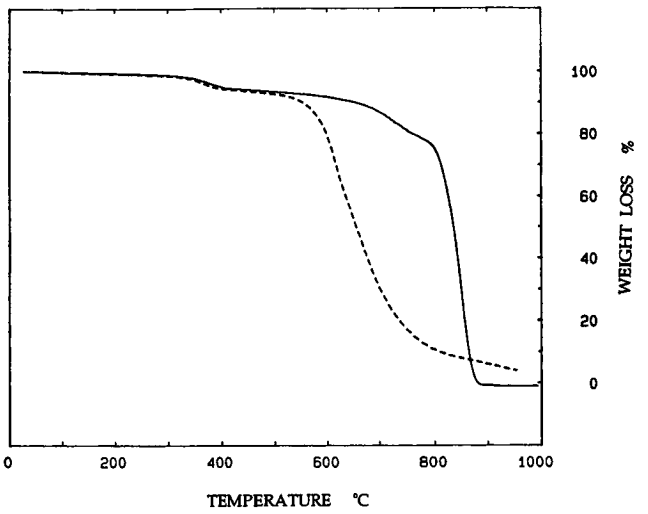


Figure 5. TGA scan of PBZTs with 0.30 mole proportion of substituted biphenyl unit. Solid line, in nitrogen; dashed line, in air.

of the substituted biphenyl component. The substituted biphenyl structure in the copolymer underwent degradation at the lower temperature (345 °C) compared to the parent polymer. The onset of this low degradation temperature became more prominent as the substituted biphenyl unit content increased.

As seen in Figure 5, the onset of the lower degradation temperature around 345 °C is independent of the atmosphere used (air or nitrogen). The weight loss of 7.1% between 345 and 570 °C is consistent with the weight percentage of nitro and methyl groups in the corresponding copolymer. However, the polymer backbone began to decompose at 570 °C in air. Thus, if cross-linking is desirable in postprocessing for the improvement of compressive properties, this copolymer may be considered as a desirable candidate. The polymer would initially be processed into fibers or films, which then would be treated at a temperature above 350 °C to induce the intermolecular cross-linking reaction[12,14,23] for the measurement of compressive strength and other mechanical properties.

Polymer Postheat Treatment. In consideration of the possibility of incomplete cyclization in polymers due to the introduction of sulfolane as a cosolvent, the

Table 4. Elemental Analysis of Substituted Biphenyl PBZT

	pristine-substituted biphenyl PBZT				heat-treated substituted biphenyl PBZT				heating conditions[b]	
trial[a]	C	H	N	S	C	H	N	S	time, h	*T*, °C
1	55.18	3.55	10.87		57.12	2.84	10.90		5	200
2	56.13	3.07	11.38	13.32	57.60	2.69	11.89	13.75	24	220
3	56.42	3.11	10.59	12.03	57.04	2.91	11.01	12.70	24	220
4	56.30	2.79	11.86	13.57	57.10	2.75	11.88	13.64	5[c]	250
5	55.74	2.93	11.25							
calcd					57.38	2.60	12.17	13.92		

[a] Same trials as in Table 1. [b] In an nitrogen stream unless specified. [c] Vacuum was used.

homopolymers with the substituted biphenyl moiety were heat treated at 200−250 °C in order to complete the ring-closure reaction. The presence of an absorption peak at 1720 cm^{-1}, which is characteristic of thioester or amide groups, indicates that ring closure was not complete. As a result of heat treatment, the intensity of the peak at 1720 cm^{-1} decreased. The results of elemental analysis are shown in Table 4. Postheat treatment should lead to the formation of the ring-closed polymer. However, all the heat-treated polymers were partially soluble in MSA, while untreated samples were soluble.

Conclusions

PBZT analogues with the substituted biphenyl structure in the backbone can be synthesized in low-to-moderate molecular weight. Incorporation of the dinitro−dimethyl-substituted biphenyl structure into the polymers did not lead to improved solubility in aprotic solvents. Thermal stability of the PBZT copolymers decreases with an increase in the content of the substituted biphenyl unit. These polymers, if their intrinsic viscosity is greater than 15 dL/g, are desirable candidates as precursors for postprocessing owing to the low degradation temperature of pendant groups in the substituted biphenyl structure.

Experimental Section

Monomer Synthesis. Compound **2** was prepared as described by Wolfe et al.[2]

The synthesis of **1** was adapted from the literature[29,30] with a modification of the Ullman coupling step. The original melt reaction process was replaced by coupling under solution conditions. The modified procedure is described as follows: A solution of 60 g of methyl 3-methyl-4-bromo-5-nitrobenzoate (mp 81.8 °C) in 180 mL of anhydrous dimethylformamide (Aldrich Chemical Co.) was heated to reflux. Activated copper bronze (40 g) was added to the solution cautiously. After heating the solution under reflux for 4 h, another 40-g portion of activated copper powder was added and reflux was continued for a second 4-h period. Allowed to cool, the reaction mixture was poured into 3.5 L of water. The precipitate was filtered, dried, and extracted with 400 mL of acetone in a Soxhlet apparatus. The extract was evaporated to dryness, and the residue was dissolved in methanol, treated with Norit, and filtered. The filtrate was allowed to recrystallize in methanol; yield 25.5 g (60%), mp 108 °C [lit.[31] mp 108−108.5 °C]. IR showed loss of the absorption at 555 cm^{-1} (C − Br) and appearance of absorption at 1618 cm^{-1} (biphenyl ring).

The substituted biphenyl dicarboxylate obtained was hydrolyzed to form compound **1** as described in the literature:[29] mp 363 °C [lit.[29,31] mp >340 °C]; IR 3092 (OH), 1708 (carbonyl), 1534 and 1298 cm^{-1} (NO_2); mass spectrum, *m/e* 360 $(M)^+$, 343 $(M - OH)^+$, 330 $(M - NO)^+$, 314 $(M - NO_2)^+$ (base peak).

Anal. Calcd for $C_{16}H_{12}N_2O_8$: C, 53.32; H, 3.36; N, 7.75. Found: C, 53.36; H, 3.43; N, 7.65.

Model Compound Synthesis. The PPA was prepared immediately before each use by the following method. Phosphorus pentoxide (10 g) was added to 115% PPA (90 g, Aldrich Chemical Co.). The viscous slurry was then heated to 150 °C under a nitrogen steam for 2 h to give colorless, homogeneous PPA with 85% content of P_2O_5.

A mixture of 0.7664 g (2.1273 mmol) of **1** and 75.6 g of sulfolane (Aldrich Chemical Co.) was heated to 100 °C until a clear yellow solution formed. To this solution, 75 g of freshly prepared PPA was added and the yellow solution changed to a brown color. 2-Aminothiophenol (0.585 g, 4.68 mmol, excess of 10 mol %) was added to the solution. The mixture was heated as follows: 100 °C for 1 h, 130 °C for 19 h, 160 °C for 4 h, 190 °C for 2 h, and 200 °C for 2 h. The dark brown solution was poured into hot water to give a yellow precipitate. The product was washed vigorously with hot water 3 times and dried in vacuo. The yield was 1.10 g (96%); mass spectrum, 538 $(M)^+$ (base peak), 523 $(M - CH_3)^+$, 508 $(M - NO)^+$, 492 $(M - NO_2)^+$, 269 $(M/2)^+$.

Anal. Calcd for $C_{28}H_{18}N_4O_4S_2$: C, 62.44; H, 3.37; N, 10.40. Found: C, 60.42; H, 3.78; N, 9.22. Found for heat-treated model compound: C, 62.62; H, 3.56; N, 10.12.

Homopolymer Synthesis (Trial 4). Table 1 shows detailed conditions for the PBZT homopolymer syntheses. In a 250-mL flask were placed 1.0234 g (4.1739 mmol) of **2** and 80 g of freshly prepared PPA. The mixture was stirred at room temperature under a stream of argon for 24 h and then at 70 °C for another 24 h. To the resulting clear solution was added a cooled solution of **1** (1.5038 g, 4.1739 mmol) in 40 g of sulfolane. The temperature was raised to 90 °C for 3 h, 110 °C for 1 h, 130 °C for 5 h, 165 °C for 18 h, and 190 °C for 5 h. The viscous solution was poured into water. The precipitated polymer was collected by filtration, washed thoroughly with hot water, and finally dried at 80 °C under reduced pressure for 48 h. The polymer was a dark brown color and was soluble in methanesulfonic acid. The yield was 1.90 g (99%). The intrinsic viscosity was 2.3 dL/g in methanesulfonic acid at 30 °C.

Copolymer Synthesis (Trial 5). Table 2 shows detailed data for the copolymer syntheses. A mixture of **2** (1.0079 g, 4.1105 mmol) and freshly prepared PPA (100 g) was dehydrochlorinated as described for the homopolymer. Then 0.4780g (2.8774 mmol) of terephthalic acid (Aldrich Chemical Co.) was added to the solution containing dehydrochlorinated **2** in PPA. This yellow mixture was heated to 130 °C for 4 h. Then compound **1** (0.4443 g, 1.2332 mmol) was added to the flask and the color of the mixture gradually changed to red. The temperature was maintained at 130 °C for 2 h and then raised to 160 °C for 24 h and 190 °C for 18 h. The dark brown mixture formed a ball on the stirring rod. The polymerization solution was treated, as described for the homopolymer, finally to give 1.25 g (94% yield) of PBZT copolymer. The intrinsic viscosity was 6.75 dL/g in methanesulfonic acid at 30 °C.

Anal. Calcd for $(C_{14}H_6N_2S_2)_{0.7}(C_{22}H_{12}N_4O_2S_2)_{0.3}$: C, 60.70; H, 2.41; N, 11.22; S, 19.74. Found: C, 59.57; H, 2.73; N, 10.81; S, 18.91.

Characterization. Infrared spectra were obtained on a Perkin-Elmer 1600 FTIR spectrometer. Thermal analyses were conducted on powder samples at 10 °C/min by a Seiko 220/320 thermogravimetric analyzer/differential scanning calorimeter (TGA/DSC). C^{13} NMR spectra were obtained on a Varian XL400 NMR spectrometer. Elemental analysis was done by Atlantic Microlab in Norcross, GA. Intrinsic viscosities were determined in MSA at 30 °C on a Cannon-Ubbelohde capillary viscometer by extrapolation of $(\eta_{rel} - 1)/c$.

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