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A Tetramethylbiphenyl Poly(benzobisthiazole): Synthesis, Chracterization, Fiber Spinning, and Properties

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ABSTRACT: Poly(benzobisthiazole)s containing an *o*-tetramethyl substituted biphenyl moiety were synthesized based on 2,5-diamino-1,4-benzenedithiol dihydrochloride and 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarbonyl chloride. Homopolymerization of the two monomers and copolycondensation of the two monomers with terephthaloyl chloride were carried out in poly(phosphoric acid) (PPA). The *interfacial polymerization* technique was used to enhance the formation of a homogeneous liquid crystalline polymer solution suitable for fiber spinning. Copolymers of tetramethylbiphenyl PBZT/PBZT (25/75) were successfully spun into fibers from liquid crystalline solutions in PPA. Fibers were thermally cross-linked between 500 and 550 °C. The thermal cross-linking reaction was studied by thermogravimeteric analysis and by ^{13}C solid-state NMR spectroscopy. Fiber morphology and properties are also reported and discussed.

Introduction

The rigid-rod polymer PBZT has outstanding tensile and thermal properties.[1,2] However, as compared to carbon and inorganic fibers, PBZT fibers have a relatively low axial compressive strength.[3] Molecular cross-linking has been attempted to enhance the compressive properties of PBZT fibers. Several cross-linkable PBZT systems,[3] such as methyl-pendent PBZT,[4−6] halogenated PBZT,[7] and benzocyclobutene PBZT,[8] have been designed to enhance the fiber compressive properties. Improvements in fiber compressive properties are apparent in certain systems as the degree of cross-linking increases.[6−8]

Another approach to provide a mechanism for lateral interchain buttressing has been to introduce hydrogen bonds into the PBZT polymer. A dihydroxy−PBZT was therefore synthesized, but its fiber compressive strength was reported to be lower than that of PBZT.[9] This was attributed to the formation of a pseudo-ladder structure corresponding to intramolecular hydrogen bonds, rather than the desirable intermolecular hydrogen bonds. Recently, the dihydroxy moiety was incorporated in polypyridobisimidazole,[10] a member of the rigid-rod polymer family. High compressive strength[10,11] in this polymer was attributed to the presence of two-dimensional intermolecular hydrogen bonding.

This work is a continuation of our research effort on substituted biphenyl type PBZTs.[12−14] The tetramethylbiphenyl structure is purposely incorporated into the PBZT backbone as a potential cross-linking unit. The dihedral angle between the two phenyl rings in the 2,2′,6,6′-tetramethylbiphenyl moiety is 87°.[15] Due to this prominent noncoplanar conformation, the PBZT analogue with such a fully ortho-substituted biphenyl moiety in the main chain is expected to induce multidimensional cross-linking. In previous papers, we reported the synthesis of substituted biphenyl type PBZTs prepared from 2,5-diamino-1,4-benzenedithiol dihydrochloride with 2,2′-dinitro-6,6′-dimethylbiphenyl-4,4′-dicarboxylic acid[12] or with 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarboxylic acid.[13] However, the molecular weights of these polymers were not sufficiently high for fiber spinning. This article describes the synthesis of a high molecular weight tetramethylbiphenyl PBZT and its copolymers with PBZT. Fiber spinning, properties, and the effect of thermal cross-linking on the fiber properties are also presented.

Results and Discussion

Polymer Synthesis. Polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (**1**) with 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarbonyl chloride (**2**) is carried out in poly(phosphoric acid) (PPA) under an inert atmosphere, as shown in Scheme 1. Dehydrochlorination is necessary for removal of HCl from monomer **1** prior to polymerization. The general procedure[1,16] is to mix the desired quantity of **1** and PPA in a reaction flask followed by heating of the mixture at 70 °C for 1 day. Then, monomer **2** alone or together with terephthaloyl chloride is added into the mixture and the polymerization begins with stepwise heating. Polymers and copolymers prepared by this method are summarized in Table 1 (trial numbers 1 and 2). To enhance the dispersion of **2** in PPA, monomer **2** alone or together with terephthaloyl chloride was mixed with **1** in PPA at the beginning of the process. This allowed the diacid chloride monomers to have a longer period for exposure to PPA for solubilization. In this way, the entire mixture is dehydrochlorinated. The diacid chloride groups can react with PPA to form an anhydride with evolution of hydrochloric acid. Polymers and copolymers prepared by this method are also summarized in Table 1 (trial numbers 3−6).

The dispersion of monomer **2** in PPA is of concern. Terephthaloyl chloride (melting point 78 °C) is in the liquid state at the reaction temperature, and can effectively be dispersed in PPA under vigorous stirring. In contrast, monomer **2** melts at 210 °C, and any trapped or unreacted residue of **2** in the reaction mixture may remain in the solid state throughout the polymerization process. With increasing molecular weight, the viscosity of the reaction mixture increases, making the diffusion of any trapped and unreacted monomer **2** particles in such an extremely viscous

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Scheme 1. Synthesis of Tetramethylbiphenyl PBZT Polymers, *n* = Mole Ratio

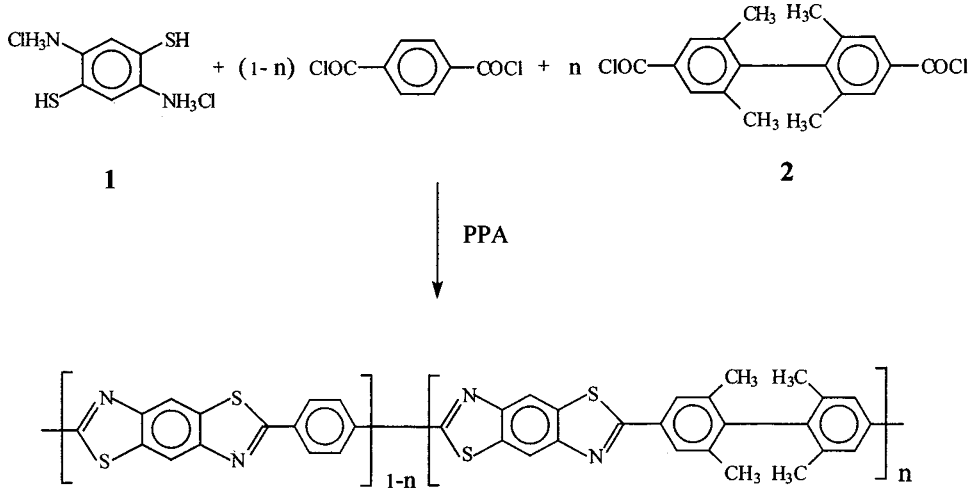


Table 1. Synthesis of Tetramethylbiphenyl PBZT

	monomer,[a] g (mmol)					reaction conditions							
trial no.	M1	M2	M3	concn[b], wt %	$[\eta]^c$, dL/g	*t*, h	*T*, °C	*t*, h	*T*, °C	*t*, h	*T*, °C	t, h	*T*, °C
1	0.800 (3.263)	1.094 (3.263)	0	18.9	19.5	1	120	3	140	12	160	24	180
2	1.000 (4.079)	0.684 (2.040)	0.414 (2.039)	21.0	16.3	2	110	5	140	2	160	5	180
3	5.076 (20.70)	6.939 (20.70)	0	25.7	14.5	1	110	5	140	24	160		
4	5.031 (20.52)	5.160 (15.39)	1.041 (5.130)	26.1	12.7	5	110	20	140	9	165		
5	6.083 (24.81)	4.158 (12.40)	2.519 (12.41)	27.3	15.8	1	110	5	140	24	160	4	180
6	6.142 (25.05)	2.099 (6.260)	3.814 (18.79)	28.4	14.1	20	110	24	140	14	165		
7	3.077 (12.55)	4.207 (12.55)	0	16.19	7.4	24	110	40	120	40	130	24	140
8	3.687 (15.04)	2.521 (7.520)	1.526 (7.520)	17.19	5.5	48	110	44	120	24	130	24	140
9	4.095 (16.70)	1.398 (4.170)	2.543 (12.53)	17.86	8.7	24	110	24	120	24	130	24	140
10[d]	4.095 (16.70)	1.398 (4.170)	2.543 (12.53)	17.86	16.7	2	110	24	140	24	165	12	190
11[d]	4.095 (16.70)	1.398 (4.170)	2.543 (12.53)	17.86	14.0	12	110	24	140	10	165		

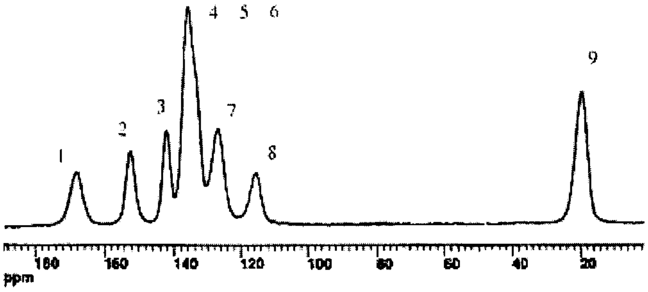
[a] M1 is 2,5-diamino-1,4-benzenedithiol dihydrochloride; M2 is 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarbonyl chloride; M3 is terephthaloyl chloride. [b] (Weight of monomers)/(weight of PPA) *x* 100, and unless otherwise noted, PPA with 85% of P_2O_5 is used. [c] All were measured in methanesulfonic acid at 30 °C. [d] Interfacial polymerization and PPA with 83% P_2O_5 is used.

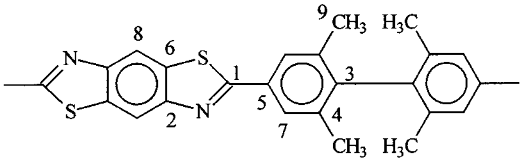
solution even more difficult.

Alternatively, monomer **2** was dissolved in anhydrous benzene, and the resulting benzene solution was poured into the flask after the dehydrochlorination of **1** in PPA. The reaction of acid chloride groups with *o*-aminothiophenol functional groups occurs *interfacially*. The slightly yellowish benzene layer gradually becomes colorless within 1 or 2 h, which is an indication of all reactive species entering into the bottom PPA phase. Benzene is then removed under vacuum. This procedure ensures dispersion of monomer **2** in PPA and results in a homogeneous solution. The polymers and copolymers prepared by this *interfacial polymerization* method are also summarized in Table 1 (trial numbers 7−11). The subsequent fiber-spinning studies indicate that a homogeneous polymer solution suitable for solution spinning can be obtained with this *interfacial polymerization* technique.

Polymer Characterization. The tetramethylbiphenyl PBZT and its copolymers with PBZT are soluble in methanesulfonic acid (MSA) and chlorosulfonic acid. They are insoluble in common organic solvents such as chloroform, dimethyl sulfoxide, and *N*-methyl-2-pyrrolidinone, etc. Table 2 includes the ^{13}C solid-state NMR spectrum of the tetramethylbiphenyl PBZT homopolymer. The assignment of the peaks to the corresponding carbons in the polymer repeat unit is made by use of "^{13}C NMR Module" software (SoftShell International). The observed chemical shifts in the ^{13}C solid-state NMR spectrum are in agreement with the calculated values.

Table 2. Assignment of Chemical Shifts of Tetramethylbiphenyl PBZT in ^{13}C Solid-State NMR Spectrum





	C1	C2	C3	C4	C5	C6	C7	C8	C9
actual, ppm	168.2	152.4	142.3	136	136	136	126.9	115	20
calcd, ppm	171	152	140	136	136	131	127	116	19

As seen from Figure 1, all tetramethylbiphenyl PBZT/PBZT copolymers (numbers 2−5 in Figure 1) exhibit two degradation temperatures in a nitrogen atmosphere. The lower degradation temperature at 505 °C can be attributed to the thermal degradation of the methyl-pendent groups, and the higher degradation tempera-

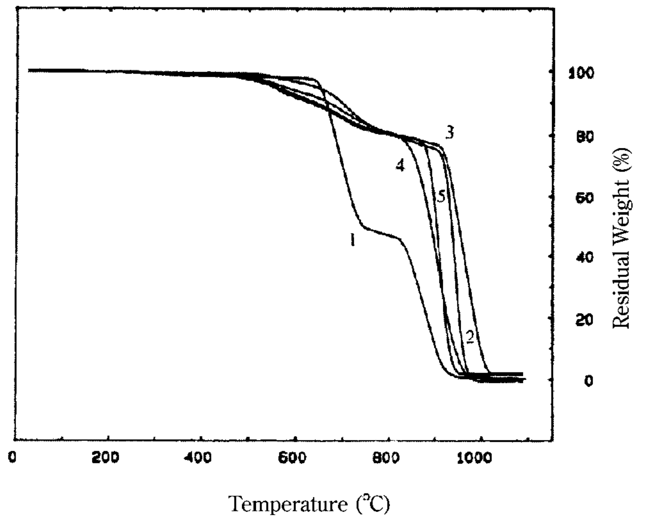


Figure 1. TGA scans (in nitrogen) tetramethylbiphenyl PBZT/PBZT copolymers with varying mole fraction (n) of tetramethylbiphenyl moiety: (1) $n = 0.0$; (2) $n = 0.25$; (3) $n = 0.50$; (4) $n = 0.75$; (5) $n = 1.0$.

Table 3. Elemental Analysis of Tetramethylbiphenyl PBZTs

	% calcd				% found			
trial[a]	C	H	N	S	C	H	N	S
1 (100/0)	72.33	4.55	7.03	16.09	72.07	4.69	7.03	15.92
3 (100/0)					70.92	4.71	6.90	15.84
7 (100/0)					70.93	4.72	6.92	15.55
4 (75/25)	70.65	4.14	7.67	17.54	68.98	4.29	7.44	17.24
2 (50/50)	68.65	3.64	8.43	19.29	68.21	3.92	8.44	19.26
5 (50/50)					67.00	3.81	8.22	18.72
8 (50/50)					66.81	3.86	8.18	18.56
9 (25/75)	66.19	3.03	9.36	21.42	65.95	3.16	9.15	21.14
11 (25/75)					65.73	3.13	8.96	20.22

[a] Trial 1, 3, and 7 are homopolymers, and the rest are copolymers. The trial numbers correspond to the trial numbers in Table 1. The ratios in parentheses indicate the mole ratios of the two acid chloride monomers, i.e., the ratio of 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarbonyl chloride to terephthaloyl chloride.

ture (840–920 °C) to the polymer backbone degradation. By comparison, the degradation of the parent PBZT (no. 1 in Figure 1) occurs at 640 °C. The cross-linked structure formed by degradation of the methyl groups has higher thermal stability than the parent PBZT.

The elemental analysis data are listed in Table 3. The observed values are generally consistent with calculated results for both homo- and copolymers.

Fiber Spinning. The tetramethylbiphenyl PBZT solutions obtained from the polymerization in PPA, as shown in Table 1, exhibit liquid crystalline behavior. The polymer concentrations are designed to be 15% (trials 3–6) and 10 wt % (trials 7–11), respectively. Fibers are spun using the dry-jet wet spinning technique. Polymer solutions prepared in trials 1–6 could only be drawn to a low spin–draw ratio of 2–3. At a spin–draw ratio of 4, frequent breakage occurred in the threadline before coagulation. This was attributed to high polymer concentration and inhomogeneous solution. Continuous fiber, with a spin–draw ratio in the range 8–12, was obtained from the 10 wt % polymer solution prepared from *interfacial polymerization* reported in trials 10 and 11 in Table 1.

The maximum achievable spin–draw ratio also decreased with increasing tetramethylbiphenyl content in the polymer chain. Interfacially polymerized 10 wt % tetramethylbiphenyl PBZT homopolymer in PPA could not be spun into a continuous fiber due to the drawing limitation. While the cause of this drawing limitation is not fully understood, this may be a result of the steric effect between the methyl groups in the tetramethylbiphenyl structure, which may make the polymer flow, even in the highly oriented state, difficult. The fiber-spinning effort was therefore focused on the 10 wt % solutions of the copolymer prepared by a 25/75 molar ratio of monomer **2** to terephthaloyl chloride as indicated by trials 9–11 in Table 1. Because of low molecular weight, the fibers prepared from the solution of trial 9, were rather weak. All the cross-linking and property studies are therefore limited to fibers spun from 25/75 tetramethylbiphenyl PBZT/PBZT copolymer solutions of trials 10 and 11 in Table 1.

Cross-Linking Evidence. It has previously been established that the thermal cross-linking reaction in methyl-pendent PBZT fiber occurs between 450 and 550 °C.[5] Evidence of cross-linking has been reported in the free-annealed methyl-pendent PBZT fiber using ^{13}C solid-state NMR. The free-annealed methyl-pendent PBZT fiber loses its fibrillar character on heat treatment at 550 °C. A tension-annealed sample retains its fibrillar character; however, it does become insoluble in methanesulfonic acid. The cross-linking reaction in the methyl-pendent PBZT and in the tetramethylbiphenyl PBZT results in the evolution of methane.[5,13] In both systems, the evolution of methane starts above 400 °C and peaks at about 550 °C.

On the basis of the methyl-pendent PBZT cross-linking conditions, tetramethylbiphenyl PBZT/PBZT copolymer fiber was free annealed in nitrogen at 450, 500, 520, and 550 °C for 10 min. Fiber free annealed at 450 °C partially dissolves in MSA after 2 days, while the fiber free annealed at 550 °C is only swollen by the solvent. The fiber heat-treated at 500 °C for 10 min under a 25 MPa tension also exhibits noticeable swelling when immersed in MSA for 2 days. By comparison, the as-spun fiber readily dissolves in MSA. However, it has been previously demonstrated that the lack of dissolution cannot be taken as sufficient evidence for cross-linking in methyl-pendent PBZT fiber.[5]

Figure 2 gives the ^{13}C solid-state NMR spectra of the as-spun and free-annealed tetramethylbiphenyl PBZT/PBZT copolymer fibers. Figure 2a represents the normal cross-polarization (CP) ^{13}C NMR spectrum of the copolymer fiber with a 25/75 molar ratio of the tetramethylbiphenyl PBZT unit to the parent PBZT unit. The percentage integral of the methyl carbons is 6.3, which is close to the theoretical value (6.06) for the copolymer. In the free-annealed fibers (parts b and c of Figure 2), a small peak at 39 ppm appears in the CP spectrum, which does not survive the 40 μs Opella sequence, which suggests that it is associated with either methylene or methine carbons.[17] Methylene and methine carbons do not survive the Opella sequence, as their intensities fall to less than 10% of the normal CP values.[17] Cross-linking in these methyl-pendent systems via a methine bridge does not appear to be a possibility. Cross-linking, however, can occur via methylene or ethylene bridge. Figure 2c also shows a shoulder at 28 ppm. On the basis of the band integrals, about 15% of the methyl carbons are eliminated in the fibers free annealed at 500 °C. Approximately 61% of this intensity is converted to methylene carbons at 39 ppm. The ^{13}C NMR spectrum of fiber free annealed at 550 °C indicates that about 30%

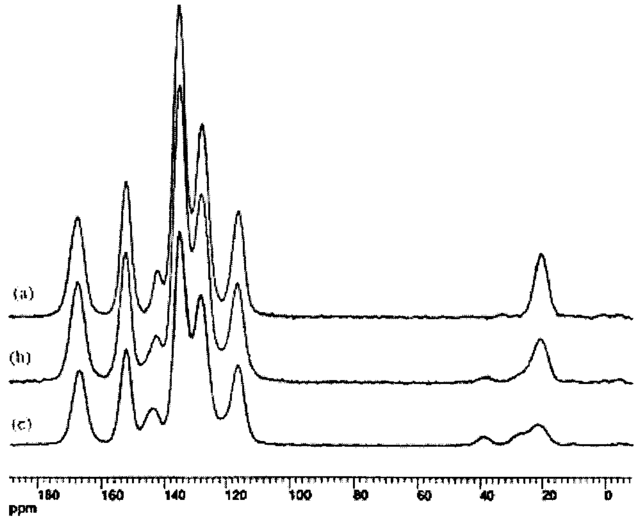


Figure 2. ^{13}C solid-state NMR spectra of tetramethylbiphenyl PBZT/PBZT copolymer fibers (25/75 in monomer mole ratio): (a) as-spun fiber, (b) free-annealed fiber at 500 °C for 10 min under nitrogen, and (c) free-annealed fiber at 550 °C for 10 min under nitrogen.

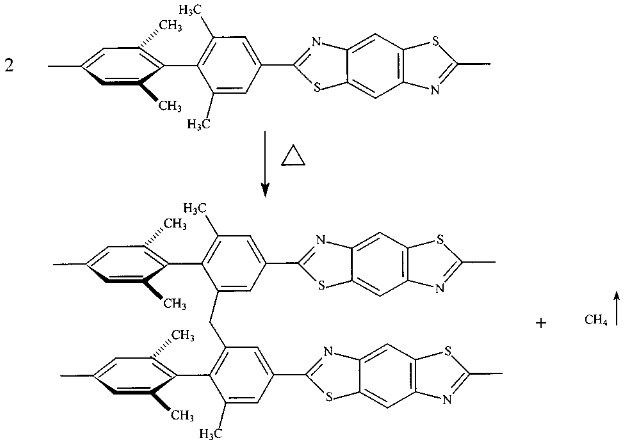


Figure 3. Cross-linking reactions in tetramethylbiphenyl PBZT.

of the methyl carbons are eliminated, of which approximately 62% are converted to methylene carbons. The intensity of the shoulder at 28 ppm was not separated from the main peak at 20 ppm. Because of sample limitations, ^{13}C solid-state NMR studies (for the evidence of cross-linking or lack thereof) have not been carried out on the tension-annealed samples.

The thermogravimetric mass spectrum of the tetramethylbiphenyl PBZT reveals that when the polymer is exposed to temperatures in the range of 450−550 °C, methane is a major degradation byproduct.[13] Also, ^{13}C solid-state NMR spectra explicitly demonstrate the conversion of methyl groups into methylene or methine groups. On the basis of these experimental results, a possible cross-linking reaction process associated with methyl elimination and methylene formation is suggested (Figure 3). The thermal elimination of the methyl groups from the polymer chain initially generates aryl and methyl free radicals. Then, methyl radicals extract hydrogen atoms from methyl groups in the polymer. As a result, methylene radicals form and methane evolves as a byproduct. The combination of reactions between the radicals may also result in direct phenyl to phenyl cross-linking or cross-linking via an ethylene bridge. In addition to the intermolecular cross-linking, intramolecular cross-linking may also result from coupling between two radicals in the neighboring benzene rings. Various possible intermolecular cross-links are shown in parts a−c of Figure 4. The possible intramolecular cross-links are shown in parts d and e of Figure 4.

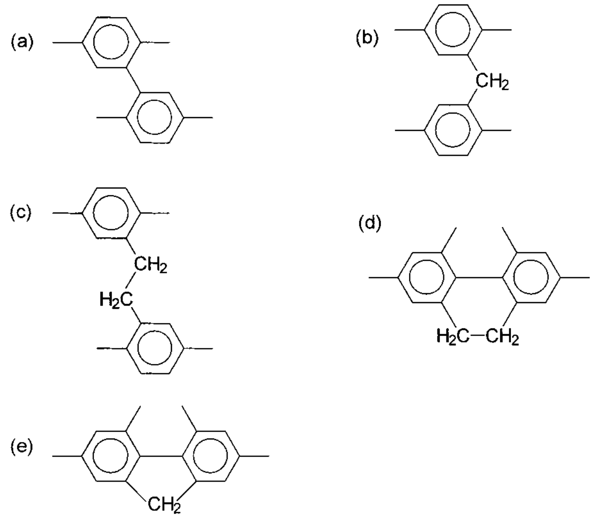


Figure 4. Various cross-linked structures in tetramethylbiphenyl PBZT/PBZT copolymer.

The ^{13}C chemical shift corresponding to CH_2 in 1,2-diphenylethane (bibenzyl) is reported[18a] at 37.89 ppm (calculated[20] 38.20 ppm), and in diphenylmethane it is reported[19] at 41.91 ppm (calculated 42.12 ppm). Corresponding chemical shifts in fluorene[18b] and in 9,10-dihydrophenanthrene[18c] are reported at 36.82 ppm (calculated 36.80 ppm) and 29.01 ppm (calculated 29.20 ppm), respectively. The observed shoulder at 28 ppm in Figure 2 is attributed to the intramolecular cross-link shown in Figure 4d. The structure in Figure 4e incorporating the fluorene moiety is a high energy structure. A high percentage of methyl groups remain even in the sample free annealed at 550 °C (Figure 2c). A proposed cross-link structure should be able to account for the presence of these unreacted methyl groups. MM2 (ChemOffice CS Chem 3D, Cambridge Soft Corporation 1999) molecular mechanics calculations for 1,8-dimethylfluorene suggest that some angle strains are too large for this molecule to exist. A search of the Beilstein database for 1,8-dimethylfluorene produced no citation. By comparison, 4,5-dimethyl-9,10-dihydrophenanthrene (structure corresponding to the cross-link in Figure 4d) is a lower energy structure, and a citation for this compound was found in the Beilstein database. On the basis of these considerations, the probability of the existence of the structure shown in Figure 4e was considered extremely low, if not nonexistent. Because of the instability of the fluorene moiety at high temperature, it has actually been introduced in PBZT to achieve intermolecular cross-links.[21] While the structures in parts b and c of Figure 4 can account for the observed chemical shift at 39 ppm, the structure in Figure 4b also accounts for the evolution of methane. On the basis of this discussion, we conclude that the intermolecular cross-link in Figure 4b and the intramolecular cross-link in Figure 4d are both present in the free-annealed fiber. Evidence for direct phenyl−phenyl coupling (Figure 4a) could not be obtained, as a small trace of this type of cross-link would be dwarfed by other, much stronger chemical shifts in the aromatic region.

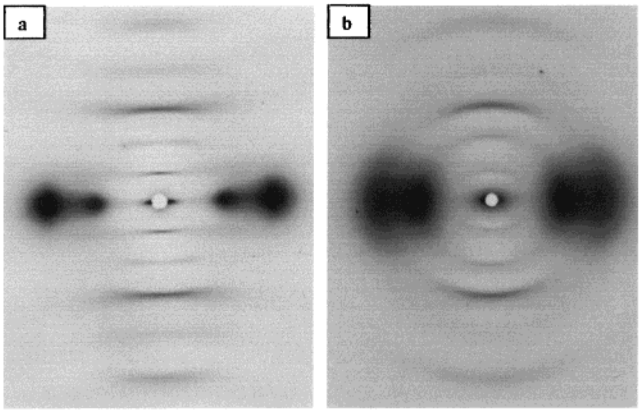


Figure 5. Wide-angle X-ray diffraction-flat plate photographs of (a) as-spun parent PBZT fiber and (b) as-spun tetramethylbiphenyl PBZT/PBZT (25/75) copolymer fiber.

Table 4. *d*-Spacings of Tetramethylbiphenyl PBZT Copolymer and Parent PBZT Fibers

	tetraMe PBZT copolymer[a]		as-spun PBZT	
	2θ, °	d, nm	2θ, °	d, nm
equatorial	15.64	0.565	15.37	0.576
	17.44	0.499	∼	∼
	25.17	0.353	25.64	0.345
meridional	7.12	0.124	7.12	0.1.4
	15.11	0.586	14.30	0.618
	21.80	0.407	21.81	0.407
	∼	∼	29.03	0.307
	36.87	0.243	36.95	0.243

[a] Tetramethylbiphenyl PBZT/PBZT (25/75) copolymer.

TGA data presented in Figure 1 also provides some insight into the cross-linking mechanism. The thermal stability of the tetramethylbiphenyl PBZT/PBZT copolymers is mostly unaffected by the PBZT content. The fact that the thermal decomposition of tetramethylbiphenyl PBZT/PBZT copolymer does not correspondingly yield a decomposition profile that is characteristic of the two individual repeat units means that the decomposition mechanisms for PBZT and tetramethylbiphenyl PBZT are not independent. Methyl radicals generated from the tetramethylbiphenyl PBZT repeat unit, may in turn initiate the formation of radicals in the phenyl group on the PBZT repeat unit. In this manner, not only will the tetramethylbiphenyl unit participate in the cross-linking reaction but the PBZT unit will participate as well. Cross-linked structures are more thermally stable than the un-cross-linked PBZT.

Structure and Mechanical Properties. The flat plate wide-angle X-ray diffraction (WAXD) photographs of the as-spun parent PBZT and the as-spun tetramethylbiphenyl PBZT/PBZT (25/75) copolymer fibers are shown in Figure 5. The *d* spacings for both fibers are listed in Table 4. In addition to the PBZT spacings, a new plane at 0.499 nm was observed in the tetramethylbiphenyl PBZT/PBZT copolymer fiber. Compared to the parent PBZT, the molecular orientation in the as-spun tetramethylbiphenyl PBZT copolymer fiber is rather poor. The molecular orientation in the fiber is improved by tension annealing, which results in improved tensile modulus (Table 5). The relatively low tensile strength of the tetramethylbiphenyl PBZT/PBZT copolymer (1.22 GPa for the as-spun fiber) at least in part may be attributed to the large fiber diameter (75 μm). This is due to the higher probability of defects in the larger diameter fibers. It is possible to enhance the tensile strength and modulus of this fiber through optimization of the polymerization and solution spinning conditions to achieve a substantially higher spin−draw ratio, which would result in a fine diameter fiber and also in high molecular orientation. Higher molecular weight is also expected to result in higher tensile strength fibers.

Table 5. Tensile Properties of Tetramethylbiphenyl PBZT/PBZT Copolymer Fiber[a]

fiber[c]	tensile str, GPa	modulus, GPa	RCS,[b] GPa
as-spun	1.22	20	0.57
500t	1.35	55	0.45
500f	0.64	21	>0.64
520f	0.73	24	∼0.73
550f	0.65	26	>0.65

[a] Fiber spun from the polymer obtained in trial no. 10 and trial no. 11 in Table 1. [b] RCS is recoil compressive strength. [c] Number indicates heat treatment temperature in °C. f and t mean free and tension annealing, respectively.

The degree of cross-linking increases with the free annealing temperature. Free annealing also results in a decrease in tensile strength. A similar decrease in tensile strength was also reported for the methyl-pendent PBZT, in which case transverse cracks were observed in the free-annealed fiber.[6] The cracks were thought to have been developed due to stresses resulting from cross-linking. The types of cracks observed in free-annealed methyl-pendent PBZT fiber, were not observed in the comparably heat-treated tetramethylbiphenyl PBZT/PBZT copolymer fiber. However, the stresses generated on intermolecular cross-linking are still a likely source for the drop in fiber tensile strength in the free-annealed fibers.[25] It can be argued that the tensile strength reduction in the free-annealed samples may be a result of degradation. However the degradation in the free- and tension-annealed samples should be comparable. Considering that the tension annealing results in increased fiber tensile strength, the tensile strength decrease on free annealing does not appear to be a result of degradation.

The compressive strength data is also given in Table 5. On the basis of the stress−strain behavior, the recoil compressive strength of the as-spun tetramethylbiphenyl PBZT/PBZT copolymer fiber represents an overestimation due to nonlinear and viscoelastic effects in the stress−strain curve. Somewhat lower compressive strength was measured for the tension heat-treated sample. Similar stress−strain and compressive strength behavior was reported for the as-spun and tension heat-treated methyl-pendent PBZT fiber.[6] The recoil compressive strength of the free-annealed fibers is comparable to or higher than their tensile strength, which is in the 0.64 to 0.73 GPa range. Both the as-spun and the tension-annealed fibers exhibit fibrillar morphology, while the fiber free annealed at 550 °C is nonfibrillar (parts a and b of Figure 6). This is also consistent with the observations made on the free and tension-annealed methyl-pendent PBZT fibers.[6] Similar to methyl-pendent PBZT, the skin of the tension-annealed tetramethylbihenyl PBZT/PBZT (25/75) copolymer fiber also dissolved in methanesulfonic acid, and the fibrillar core remained undissolved. The kink indicating the compression failure during the recoil test in the as-spun fiber is shown in Figure 6c. In contrast, the lack of kink formation in the free-annealed fiber (at 500 °C) at the same recoil stress as seen by the fiber in Figure 6c is shown in Figure 6d. Figure 6e shows that the fiber free-

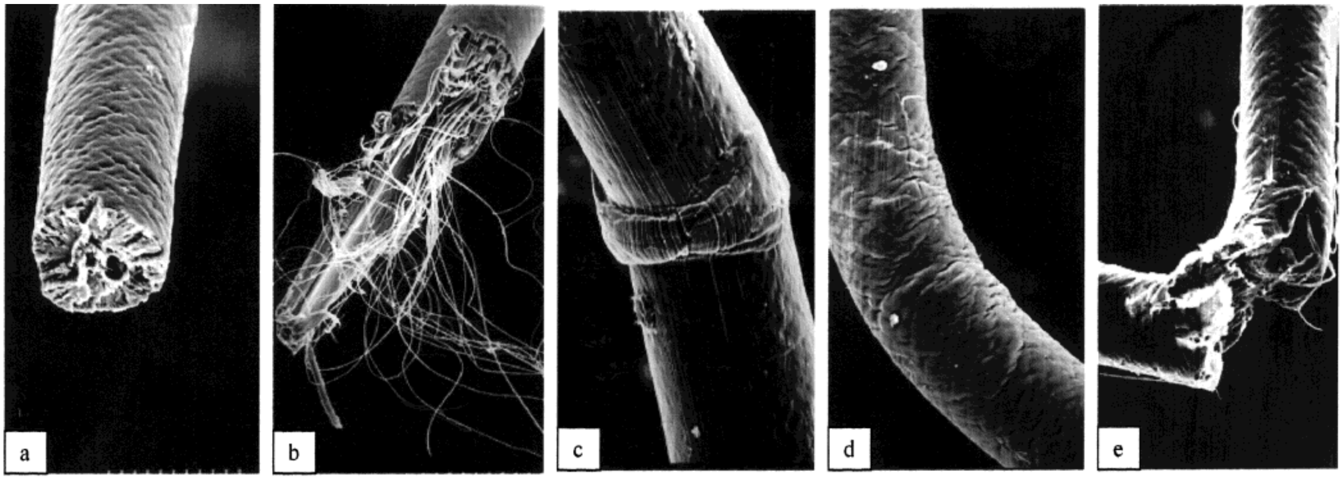


Figure 6. Scanning electron micrographs of tetramethylbiphenyl PBZT/PBZT (25/75) copolymer fibers: (a) tensile test on the fiber free annealed at 550 °C for 10 min in nitrogen, (b) tensile test on the fiber tension annealed at 500 °C in nitrogen, (c) kink in the recoil test in the as-spun fiber, (d) no kink in the recoil test in the fiber free annealed at 500 °C for 10 min in nitrogen, and (e) failure in the tension side and no failure on the compression side in the recoil test in the fiber free annealed at 550 °C in nitrogen for 10 min. Photographs were taken at varying magnifications—all fiber diameters are approximately 75 μm.

annealed at 550 °C failed in tension and not in compression. These visual observations are consistent with the tensile and compression test data, suggesting that the compressive strength of this fiber is higher than the tensile strength. For compressive strength comparison with other high performance fibers and polymeric resins, the reader is referred to the reviews on these subjects in refs 3 and 26, respectively.

Experimental Section

Materials. Poly(phosphoric acid) was purchased from the Aldrich Chemical Co. and used as received. Thionyl chloride was purchased from the Aldrich Chemical Co. as well, but distilled before use. 2,5-Diamino-1,4-benzenedithiol dihydrochloride (**1**)[1] and 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarboxylic acid[22,23] were prepared according to the literature procedures.

Instruments. Thermal analyses were performed at 10 °C/min on a Seiko 220 thermogravimetric analyzer. Solid-state ^{13}C NMR spectra were obtained on a noncommercial spectrometer operating[13] at 2.35 T (25.2 MHz). Generally, 13 200 scans were taken.

Synthesis of Monomer 2. A mixture of 15 g of 2,2′,6,6′-tetramethylbiphenyl-4,4′-dicarboxylic acid, 5 drops of pyridine, and 50 mL of distilled thionyl chloride was heated at reflux for 2 h to form a clear solution. After evaporation of excess thionyl chloride, the residue was treated with 200 mL of anhydrous benzene. The solution was filtered, and the filtrate was evaporated to dryness. The product was recrystallized from a mixture of anhydrous benzene-hexane (7:3 in volume) to give 12.3 g of slightly yellow crystals (73% yield). Mp: 209−210 °C. Mass spectrum: *m/e* 334 M$^+$, 299 (M − Cl)$^+$ (base peak), 283 (M − ClO)$^+$. FTIR: 1756 cm^{-1} (carbonyl), and disappearance of broad bands above 3100 cm^{-1} associated with the carboxylic acid OH of the starting reactant. ^{1}H NMR (benzene-d_6): δ 7.46 (s, integral 2.49) and 1.84 (s, integral 8.64) ppm;^{13}C NMR (benzene-d_6) δ 167.99, 146.06, 136.18, 132.74, 131.01, 18.97 ppm. Anal. Calcd for $C_{18}H_{16}O_2Cl_2$: C, 64.49; H, 4.81; Cl, 21.15. Found: C, 64.55; H, 4.84; Cl, 21.24.

Polymer Synthesis. Table 1 shows the detailed conditions for the PBZT polymer syntheses. The synthesis of co-polymer is described as the general procedure. In trial number 11 (Table 1), into a 250 mL three-neck flask was placed 4.095 g (16.70 mmol) of **1** and 45 g of PPA. The mixture was stirred at room temperature under a stream of nitrogen for 24 h and then at 70 °C for another 24 h. The clear yellow solution was allowed to cool to 50 °C. To the solution was added 1.398 g (4.170 mmol) of **2** in 10 g of anhydrous benzene, and the mixture was maintained at 50 °C for 3 h under stirring. The benzene was removed cautiously under reduced pressure. The temperature was raised to 80 °C, and 2.543 g (12.53 mmol) of terephthaloyl chloride was added to the flask. After 3 h at 80 °C, the mixture was heated to 110 °C for 12 h, 140 °C for 24 h, and 165 °C for 10 h. A small portion of the reaction solution was precipitated in water, collected by filtration, washed thoroughly with dilute ammonium hydroxide aqueous solution and hot water, and finally dried in vacuo at 100 °C for 20 h. The precipitated polymer was a bright brown color and was soluble in methanesulfonic acid. The intrinsic viscosity was 14.0 dL/g in methanesulfonic acid at 30 °C. The remaining solution was bottled for the fiber-spinning process. Anal. Calcd for $(C_{24}H_{18}N_2S_2)_{0.25}(C_{14}H_6N_2S_2)_{0.75}$: C, 66.19; H, 3.03; N, 9.36; S, 21.42. Found: C, 65.73; H, 3.13; N, 8.96; S, 20.22.

Fiber Spinning. The polymerization solutions were directly spun into fibers by the dry-jet wet spinning process. Before spinning, the polymer solution in PPA underwent a filtration at 90 °C, using a 75 μm dimension filter screen. Fiber spinning was carried out at 110 °C using a 0.25 mm diameter spinneret. A 200 mm long air gap was used, and the coagulation bath contained water at room temperature. The as-spun fiber was washed in running water for 1 week, and was subsequently dried in air. For ^{13}C solid-state NMR study, the fiber was further dried in vacuo at 100 °C overnight.

Structure and Properties. The fiber tensile tests were performed on an Instron universal tester (model 5567) at 1 in. gage length. Fiber compressive strength was measured using the recoil compression technique.[3,24] Scanning electron microscopy was carried out on various samples using a Hitachi S800 microscope operated at 15 kV. The WAXS flat plate photographs were obtained on a Statton-Warhus camera mounted on a Rigaku rotating anode generator using Cu Kα radiation.

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