Pseudo-ladder rigid-rod polymers: dihydroxy pendent benzothiazole aromatic heterocyclic polymer and copolymers

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Anisotropic homopolymerization of 2,5-dihydroxyterephthalic acid (DHTA) and 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT.2HCl), and copolymerization of DHTA, terephthalic acid and DABDT.2HCl in polyphosphoric acid (PPA), afforded high molecular weight rigid-rod polymer and copolymers, with two hydroxyl groups as pendants per repeat unit. In PPA, the lyotropic liquid crystalline behaviour of the homopolymer was distinctly affected by the polymerization temperature. Spectroscopic evidence strongly suggested a completely planar and ribbon-like structure, the consequence of the strong intramolecular hydrogen bonds between the OH moieties and the N atoms of the nearby benzothiazole units. The homopolymer also exhibited the unusual capability, characteristic of BBL-type ladder polymers, to form directly from its precipitate an aggregated film which displayed little or no shrinkage when dried. Anisotropic dopes of the homopolymer (dihydroxy-polybenzothiazole (PBZT)) and certain dihydroxy-PBZT/PBZT copolymers were spun into fibres with typical tensile properties for modified PBZT polymers, but marginal compressive strength (4–30 ksi (1 ksi = 6.9 MPa) for homopolymer and 16–61 ksi for the copolymers). The intrinsic conductivity for the as-spun fibre of the homopolymer was 2.2×10^{-7} S cm^{-1} and that for heat-treated (435°C) fibre was 5.6×10^{-8} S cm^{-1}.

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

INTRODUCTION

Among the new generation of structural polymeric materials, rigid-rod ordered polymers, polybenzazoles (PBX; see *Figure 1*), comprising polybenzimidazoles (PBIs), polybenzothiazoles (PBZTs) and polybenzoxazoles (PBOs), are clearly outstanding, with their superior tensile properties and high-temperature tolerance under extremely harsh conditions. However, their compressive characteristics are less than ideal for certain aerospace applications. Accordingly, recent efforts from our laboratories are directed towards the improvement of the compressive strength of PBX polymers. It was thought that the origin of the compressive failure might be the lack of lateral support amongst the PBX microfibrils. Conceivably, the necessary support might be provided if a mechanism were to be installed so as to increase the lateral interactions among the microfibrils. In a theoretical study[1], it was shown that high compressive strength could be achieved with lateral chain supports, such as an interdigitation network formed by suitable side chains at regular intervals along the rigid polymer backbone. An obvious approach to rendering such lateral support at the molecular level is to crosslink the rigid-rod polymer chains. Research along this line, using potentially

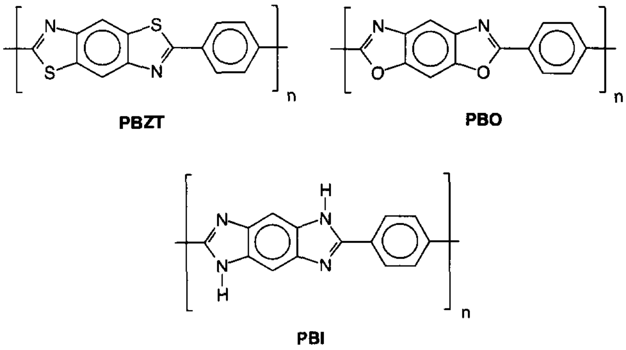

Figure 1 Molecular structures of poly{(benzo-[1,2-d;4,5-d']-bisthiazole-2,6-diyl)-1,4-phenylene} (PBZT), poly{(benzo-[1,2-d;4,5-d']-bisoxazole-2,6-diyl)-1,4-phenylene} (PBO) and poly{(benzo-[1,2-d;4.5-d']-bisimidazole-2,6-diyl)-1,4-phenylene} (PBI)

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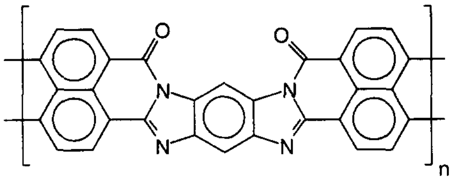
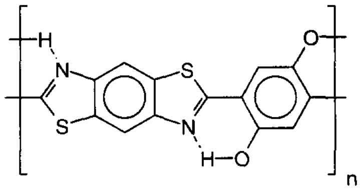
crosslinkable functions such as methyl[2–5], fluorene[6], halo-[7] and benzocyclobutene[8] groups, has been reported. Crosslinking of PBZT and PBO fibres via high-energy radiation has also been explored[9]. Another approach to provide a mechanism for interchain buttressing would be the synthetic creation of some sites for specific interactions along the all-*para*-polymeric backbone. Hydroxyl (OH) function was selected because of its ability to form hydrogen bond and coordination bonds, and to undergo some nucleophilic substitution reactions. It was later found to be relatively inert under the polymerization conditions required to form high molecular weight PBZT polymers. Upon synthesizing the dihydroxy-PBZT homopolymer, we discovered that it has the propensity to form a ladder structure, driven by strong intramolecular hydrogen bonding between the hydroxyl moieties and the neighbouring nitrogen atoms of the benzothiazole units. The ladder structure is similar to that of the classical ladder polymer, poly[(7-oxo-7,10-*H*-benz[de]imidazo[4′,5′:5,6]-benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL)[10–12] (see *Figure 2*). In our preliminary report[13,14], we have referred to such structures as pseudo-ladder, rigid-rod structures, because of the fact that hydrogen bonds are much weaker than their covalent counterparts and are therefore more easily broken thermally, with the polymeric structures reverting to those comprising single strands.

This paper describes in detail the syntheses and characterization of the dihydroxy-PBZT homopolymer and dihydroxy-PBZT/PBZT copolymers as well as their processing and fibre properties.



BBL



Dihydroxy-PBZT

Figure 2 Molecular structures of poly[(7-oxo-7,10-*H*-benz[de]imidazo-[4′,5′:5,6]-benzimidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl] (BBL) and poly{(benzo[1,2-d;4,5-d′]-bisthiazole-2,6-diyl)-(2,5-dihydroxy-1,4-phenylene)} (dihydroxy-PBZT)

RESULTS AND DISCUSSION

Model compounds

One of the required monomers, 2,5-dihydroxyterephthalic acid (DHTA) was initially prepared in a two-step synthetic sequence[15]. Thus, diethyl-1,4-cyclohexanedione-2,5-dicarboxylate (Et_2CHDA; also known as diethyl succinylosuccinate) was treated with bromine in cold H_2SO_4 to yield the aromatized product, diethyl 2,5-dihydroxyterephthalate (Et_2DHTA), which could be easily hydrolysed with refluxing aqueous NaOH, followed by acidification to form DHTA. The overall yield was about 40%. Subsequently, a more convenient method of synthesizing Et_2DHTA that entailed the refluxing of Et_2CHDA in diethylbenzene (DEB) in the presence of elemental sulfur and a catalytic amount of Pd/C was developed[16] (see *Figure 3*).

Three model compounds, **1**–**3**, were prepared in polyphosphoric acid (PPA) in essentially quantitative yields (*Figure 4*). They were all characterized and authenticated by conventional spectroscopic methods and elemental analysis. Model compounds **2** and **3** were too insoluble in common deuterated solvents to permit their n.m.r. characterization. The composite i.r. (KBr) spectra of these model compounds are depicted in *Figure 5*. As expected, none of them showed any strong and broad band around 3300–3200 cm^{-1} where the stretches of normal intermolecularly bonded OH groups of phenols would appear[17]. Instead, they showed complex sets of weak and broad absorption bands in the region 2700–3000 cm^{-1}, which has been attributed to intramolecular hydrogen bonding in this type of organic molecules[18]. It is also noteworthy that they are highly fluorescent. In fact, **1** is an important u.v. absorber[19].

Polymerization

The preparation of the dihydroxy-PBZT homopolymer from DHTA and 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT.2HCl) was performed in polyphosphoric acid (PPA) (*Figure 6*), following the adjusted P_2O_5 content anisotropic polymerization process[20]. The homopolymer prepared under various conditions had intrinsic viscosity values of 17.6–31.2 $dl\,g^{-1}$ (as measured in methanesulfonic acid (MSA) at 30°C; see *Table 1*).

It is noteworthy that the lyotropic liquid-crystalline behaviour of the polymerization dope was distinctly affected by the reaction temperature. A polymerization dope with polymer content of 10% or greater sustained its anisotropic character, as evidenced by the persistent stir-opalescence throughout the polymerization period (17–30 h), provided that the heating (oil bath) temperature did not exceed 140°C. As soon as the heating temperature was raised above 140°C, the loss of stir-opalescence began to occur. Its complete disappearance took place at approximately 190°C, attended by the precipitation of higher molecular weight polymer and some gelation.

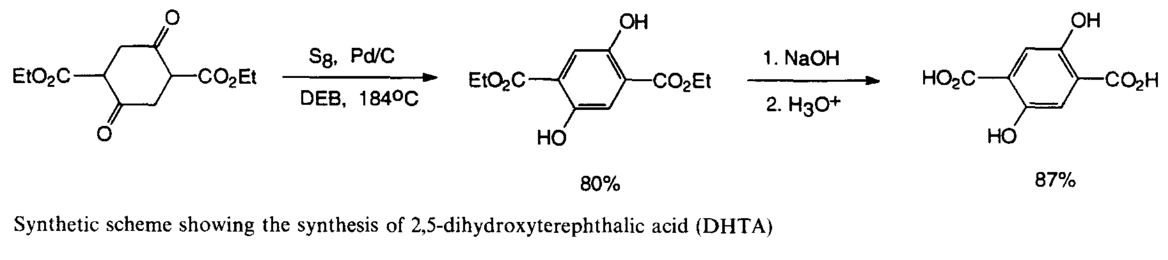
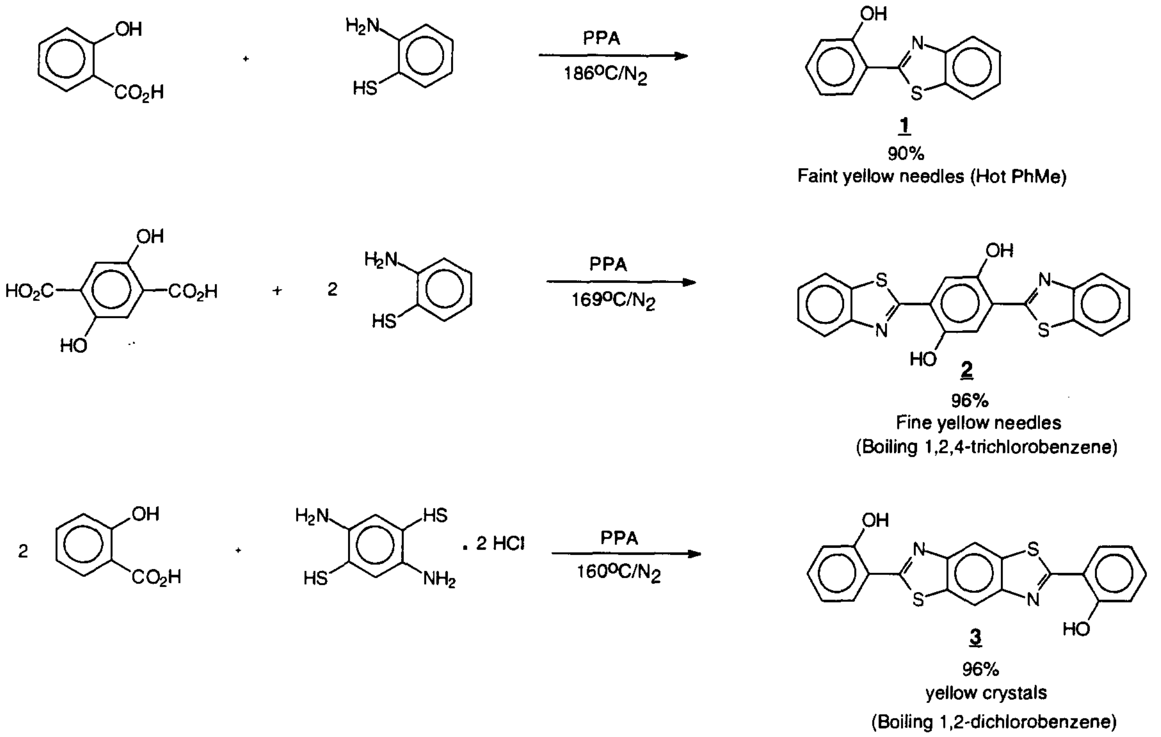


Figure 3 Synthetic scheme showing the synthesis of 2,5-dihydroxyterephthalic acid (DHTA)



1
90%
Faint yellow needles (Hot PhMe)

2
96%
Fine yellow needles
(Boiling 1,2,4-trichlorobenzene)

3
96%
yellow crystals
(Boiling 1,2-dichlorobenzene)

Figure 4 Syntheses of the model compounds: 2-(2-hydroxyphenyl)benzothiazole (**1**), 2,5-bis(2-benzothiazolyl)-dihydroquinone (**2**) and 2,6-bis(2-hydroxyphenyl)benzo[1,2-d:4,5-d′]bisthiazole (**3**)

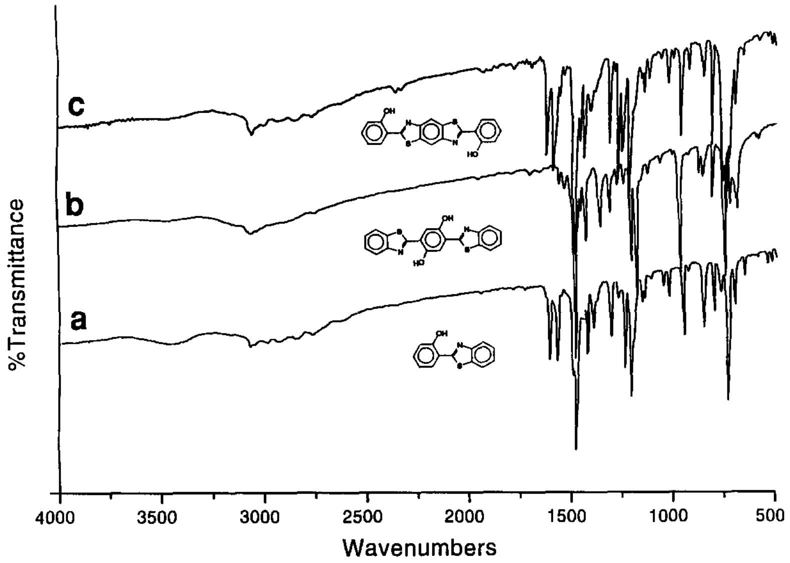


Figure 5 Composite i.r. (KBr) spectra of the model compounds: (a) 2-(2-hydroxyphenyl)benzothiazole, (**1**); (b) 2,5-bis(2-benzothiazolyl)-dihydroquinone (**2**); (c) 2,6-bis(2-hydroxyphenyl)benzo[1,2-d:4,5-d′]bisthiazole (**3**)

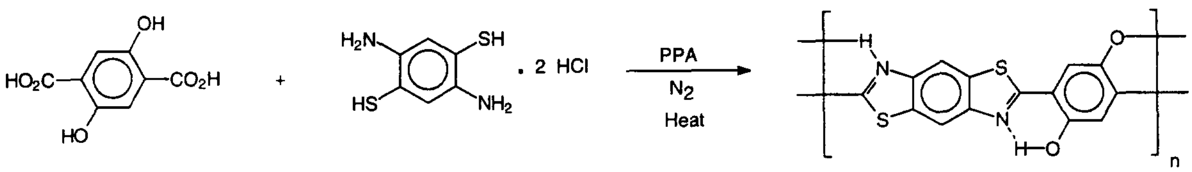


Figure 6 Preparation of poly{(benzo-[1,2-d;4,5-d′]-bisthiazole-2,6-diyl)-(2,5-dihydroxy-1,4-phenylene)}(dihydroxy-PBZT) from 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT.2HCl) and 2,5-dihydroxyterephthalic acid (DHTA) in polyphosphoric acid (PPA)

Upon cooling to 140°C or below, there was no anisotropic resilience. Such an irreversible phase transition was normally not observed during the polymerization processes of PBZT or other pendent-PBZT polymers[21]. It is suggested that the loss of anisotropic mesophase may be the consequence of a decrease in the polymer solution concentration. At reaction temperatures higher than 140°C, apparently the precipitation and gelation of the polymer with higher molecular weights were taking place to such an extent that the effective polymer concentration fell below the critical concentration. It is known that at high temperatures, an unendcapped PBZT polymer can

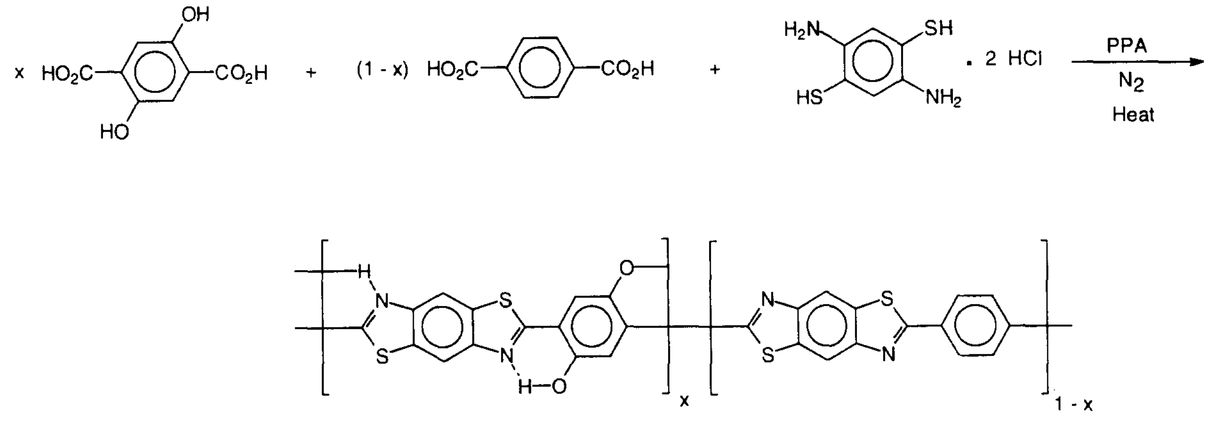


Figure 7 Preparation of dihydroxy-PBZT/PBZT copolymers from 2,5-dihydroxyterephthalic acid (DHTA), terephthalic acid, and 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT.2HCl)

continue to build up its molecular weight in the liquid-crystalline state to result in some insolubility in PPA or MSA. However, the origin of the gelation remains uncertain. It is possible that at 140–190°C, some reaction between the hydroxyl group and PPA might have occurred, resulting in some crosslinking, which was subsequently destroyed during the aqueous work-up. This explanation is supported by the fact that a very high molecular weight polymer ($[\eta] = 31.2\,\mathrm{dl\,g^{-1}}$) was obtained from an isotropic dope (see run 2, *Table 1*). It was completely soluble in MSA, which is a better solvent than PPA, albeit at a more diluted concentration than polymers from runs 3–5.

As a simple way to delineate the effect of solubility of dihydroxy-PBZT in PPA on its lyotropic behaviour during polymerization, we conducted copolymerization experiments of DHTA, terephthalic acid and DABDT.2HCl using various compositions (*Figure 7*). *Table 2* displays a summary of the preparative conditions for the copolymers with intrinsic viscosity values ranging from 19.2 to $30.8\,\mathrm{dl\,g^{-1}}$. Indeed, the polymerization process was similar to that of unsubstituted PBZT with respect to the reaction temperature (190°C), polymer dope texture (anisotropic) and the molecular weights (typical intrinsic viscosity values). Particularly noteworthy is that the 50/50 copolymer dope still maintained its homogeneity and anisotropic texture even at 190°C (run 3). This seemingly reaffirmed the inference that the unfunctionalized PBZT possesses a greater solubility in PPA than dihydroxy-PBZT, based on the previous observations made on the homopolymerization process.

Table 1 Summary of homopolymerization conditions and intrinsic viscosity data

Run	Polymer concentration (wt%)	Polymerization temperature (°C)	Anisotropic polymer dope?	Intrinsic viscosity in MSA, 30°C ($\mathrm{dl\,g^{-1}}$)
1	10	190	no	17.6
2	15	190	no	31.2
3	15	140	yes	27.9
4	10	140	yes	20.6
5	10	140	yes	28.6

Evidence for ladder structure

PBX polymers belong to a special class of rigid-rod polymers, which, by definition, have catenation angles of 180° along the backbone structure. The only freedom of molecular motion available to them is axial rotation, namely around the carbon–carbon single bonds. This degree of freedom could be severely restricted if a 'bridge' were to exist over each of the skeletal C–C single bonds. The resultant polymer would be a bona fide ladder (ribbon-like) polymer related to BBL[10–12]. We found that hydroxyl bridges can indeed transform a rigid-rod polymer to a rigid-rod, ladder polymer via their strong intramolecular hydrogen bonds with the nitrogen atoms of the nearby benzothiazole units. Several pieces of evidence already exist in the literature to firmly establish the intramolecular hydrogen bonding in the 2-(*o*-hydroxyphenyl)benzothiazolyl (BHT) unit. First, Stentson[22] reported an X-ray crystal structure of BHT compound (i.e. model compound **1**) which showed a completely planar structure, whereas Wellman *et al.*[23] found that the structure of 2,6-diphenylbenzo[1,2-d:4,5-d′]bisthiazole, a model compound of unsubstituted PBZT polymer, was not planar. The plane defined by the benzobisthiazole unit and the phenyl plane is at a twist

Table 2 Summary of copolymerization conditions and intrinsic viscosity data

Run	Comonomer molar ratio *x*	Comonomer molar ratio (1−*x*)	Polymer concentration (wt%)	Polymerization temperature (°C)	Anisotropic polymer dope?	Intrinsic viscosity in MSA, 30°C ($\mathrm{dl\,g^{-1}}$)
1	0.10	0.90	10	190	yes	28.0
2	0.30	0.70	10	190	yes	25.9
3	0.50	0.50	15	190	yes	30.8
4	0.50	0.50	10	140	yes	19.2

angle of 23.2°. Secondly, other spectroscopic techniques, such as n.m.r.[24] and i.r.[25] have also confirmed the existence of a hydrogen bridge in the BHT molecule. Last, but not least, an X-ray crystallographic study of the model compound **3** revealed that it was indeed a planar molecule, due to the strong intramolecular hydrogen bonding (details of the study will be published elsewhere)[26]. Also pertinent is the report[27] that a strong intramolecular hydrogen bond, as detected by picosecond laser-pulse i.r. spectroscopy, also exists in the excited state of BHT molecule (see *Figure 8*).

Another piece of strong evidence rests on the fact that the dihydroxy-PBZT polymer possesses an unusual characteristic that allows its small precipitates (from relatively dilute MSA solution, e.g. 0.25 g dl^{-1}) to coalesce into a continuous film with a metallic lustre upon filtration using a fritted filter funnel. The resultant metallic green film showed very little or no shrinkage when completely dried. The capability to form such aggregated film is unique to the ribbon-like ladder polymers[11,12]. Although the copolymers (e.g. 30/70 dihydroxy-PBZT/PBZT) could also form similar films, their metallic lustre and dimensional stability (upon drying) corresponded proportionally with dihydroxy-PBZT content. The i.r. spectrum of an aggregated film of the homopolymer exhibits a set of strong, broad and complex absorption bands spanning from about 2500 cm^{-1} to about 3300 cm^{-1}. These bands are undoubtedly due to the extensive intramolecular hydrogen bonding of the polymer chains.

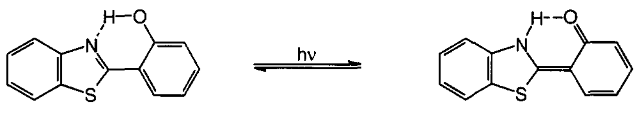


Figure 8 Intramolecular hydrogen bonding in the excited state (ortho-quinonoid form) of 2-(*o*-hydroxyphenyl)benzothiazole

In addition, comparison of the electronic absorption spectra of both PBZT (extruded film) and dihydroxy-PBZT (aggregated film) reveals that there is a general shift of the absorption bands towards lower wavelengths (red-shift) for the dihydroxy-PBZT (see *Figure 9*). It is expected that an increase in the extent of conjugation will lower the energy for π–π^* transitions. Such a change may be brought about by the coplanarity of all the phenyl rings and the aromatic benzobisthiazole segments, assisted by the intramolecular hydrogen bonding. Rather surprisingly, however, in MSA solutions the dihydroxy-PBZT polymer still shows absorption at longer wavelengths beyond the cutoff wavelength of PBZT (~475 nm). In fact, its absorption behaviour is quite similar to that of BBL in this region of the electromagnetic spectrum (see *Figure 10*). This appears to suggest that the intramolecular hydrogen bonding in the protonated form of dihydroxy-PBZT remains intact even in an acidic solvent, although it is well known that intramolecular hydrogen bonding in simple organic molecules can be easily disrupted by polar solvents which are capable of intermolecular hydrogen bonding[28–30]. A proposed structure of protonated dihydroxy-PBZT is depicted in *Figure 11*.

We made three attempts to chemically rupture the hydrogen bonds in the dihydroxy-PBZT polymer. Reagents/reaction conditions were as follows: (1) molten $SbCl_3$ in excess/100–140°C, 26 h; (2) CH_3SO_2Cl, MSA/100°C, 48 h; (3) chlorosulfonic acid/100°C, 48 h. In the first two cases, there was apparently little or no reaction as the recovered polymers were almost identical to the starting ones in their intrinsic viscosity values and other physical properties. In the last case, there was a change in the colour of the reaction mixture. However, the precipitated polymer still retained the ability to form a coalesced film, whose i.r. spectrum was similar to that of the original polymer and did not show any stretching bands assignable to the sulfonyl group. There was, nevertheless, a substantial reduction in the molecular

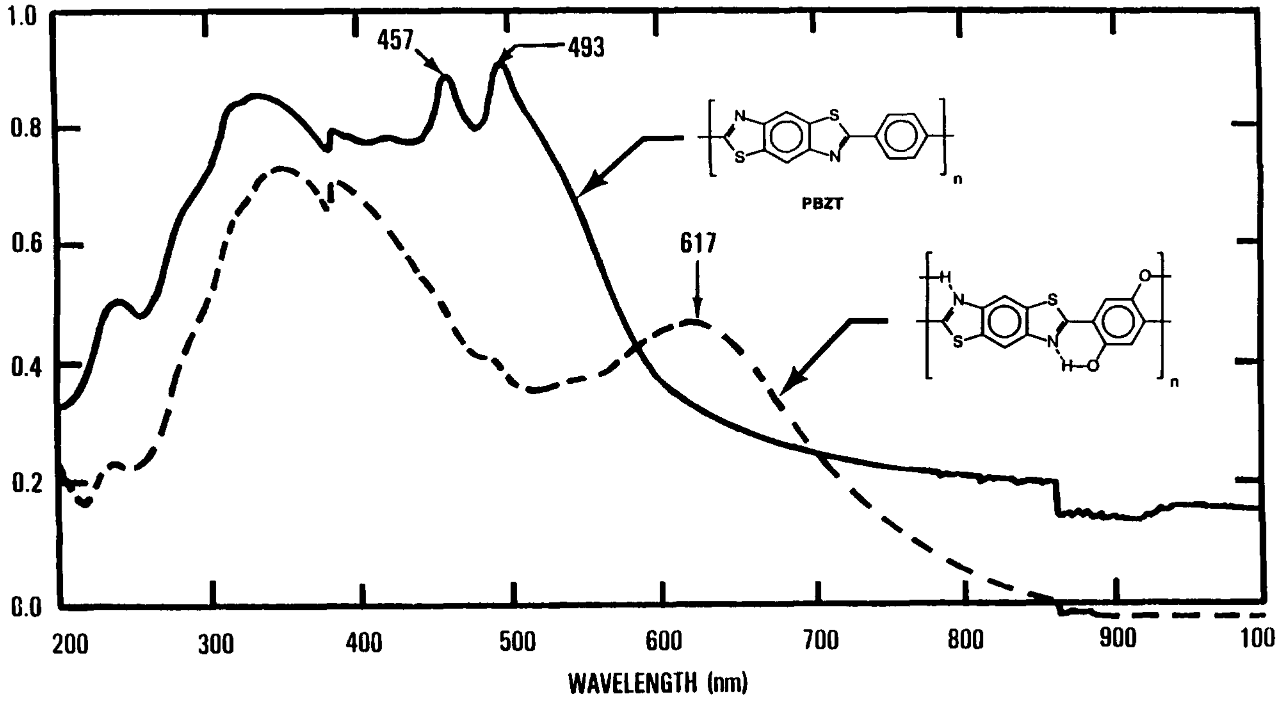


Figure 9 U.v.–vis.–n.i.r. spectra of PBZT (extruded film) and dihydroxy-PBZT (aggregated film)

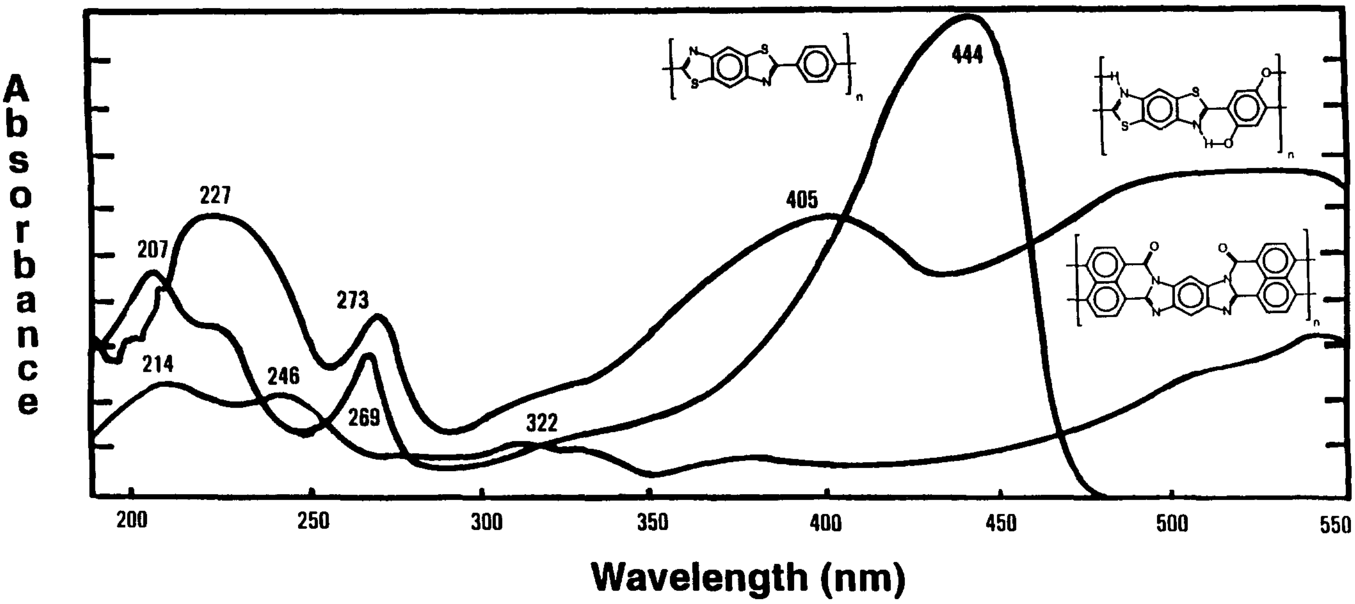


Figure 10 U.v.–vis. spectra of PBZT, dihydroxy-PBZT and BBL in methanesulfonic acid (MSA) solutions

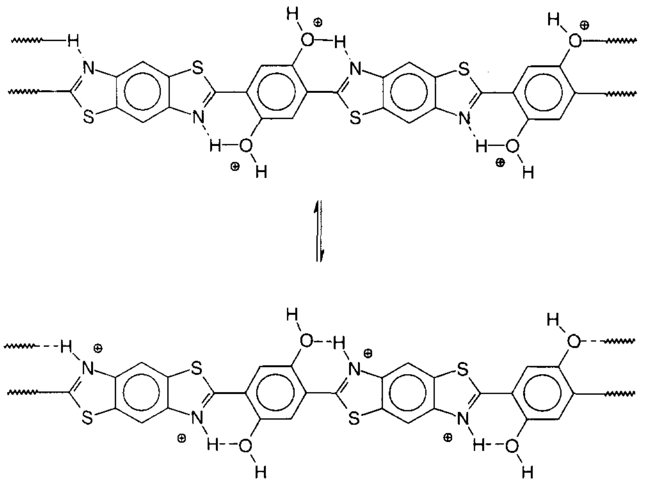


Figure 11 Proposed molecular structure of dihydroxy-PBZT in methanesulfonic acid (MSA) showing the tautomeric structures of oxygen-protonated form (top) and nitrogen-protonated form (bottom)

weight, as indicated by the drop in the intrinsic viscosity value from 20.6 to 12.0 dl g^{-1}, as measured in MSA at 30°C.

Thermal properties

As expected, none of the homopolymer or copolymers displayed any softening or melting behaviour before the decomposition temperatures as determined by differential scanning calorimetry (d.s.c.) under nitrogen atmosphere. All the polymers exhibited single-step thermal degradation profiles in both air and helium by thermogravimetric analysis (t.g.a.). In air, the extrapolated onset-of-degradation temperature for dihydroxy-PBZT was 515°C, about 95°C less than that of PBZT; the corresponding temperatures for the 10, 30 and 50 mol% dihydroxy-PBZT/PBZT copolymers were 608, 572 and 557°C, respectively, consistent with the hydroxyl group content in the polymers. In helium, the extrapolated onset-of-degradation temperature for the homopolymer was about the same as that in air, and those for the copolymers ranged from 677°C for 10 mol% dihydroxy-PBZT to 602°C for 50 mol% dihydroxy-PBZT. These observations are in agreement with previous studies on the thermal properties of PBX polymers modified with a variety of simple pendent groups[31].

Processing and mechanical properties

The homopolymer and copolymers were processed from the PPA dopes into monofilament fibres for evaluation of mechanical properties using a dry-jet wet-spinning method[32]. From our previous work, we found that rigid-rod polymers could form crystal solvates with the acid solvent as a function of time when they were exposed to moist air. This caused a dramatic increase in the dope bulk viscosity, rendering it unspinnable. Therefore, spinning of these polymers was performed immediately after the completion of polymerization, and care was taken to preclude the exposure of the dope to moist air by conducting the transfer of the dope from the polymerization vessel to the spinning chamber in a dry box.

Prior to spinning, the dopes were filtered and deaerated to reduce void formation and to improve the quality of the fibres. The combined filtration–deaeration system was actually a set of two stainless steel cylindrical chambers placed on top of each other. The top chamber was used to filter the dope, which was heated to 100°C and pushed through a 20 μm porous stainless steel plate with a plunger. Beneath the porous steel plate was a slit die. Therefore, the dope exited the filter as a thin film with high surface area and fell into the bottom spinning chamber while vacuum was applied to deaerate it. After filtration and deaeration, the top chamber was removed and a plunger was inserted into the bottom chamber for spinning. This operation was also done in a dry box.

The dope was then spun into monofilament fibres through a 0.25 mm diameter spinnerette, coagulated in distilled water bath and wound on a 254 mm diameter drum. The air gap between the spinnerette and the coagulation bath, where the fibre was stretched, was maintained at 203 mm. The ratio between the speed of stretching the dope in the air gap and the speed of dope

Table 3 Processing conditions and mechanical properties of dihydroxy-PBZT and copolymers

	Processing conditions				Mechanical properties			
Polymer	Temp. (°C)	Pressure (psi)	Spin draw ratio	Heat treatment (°C)	Modulus (Msi)	Tensile strength (ksi)	E_h (%)	Compressive strength (ksi)
100 mol%, 140°C[a]	100	1200	20	350	22±2	248±25	1.2±0.1	4–30
100 mol%, 140°C[a]	100	1240	24	435	25±2	304±20	1.3±0.1	16–59
50 mol%	120	950	30	435	14	166	1.4±0.1	61
30 mol%	130	1350	20	435	16	120	0.8±0.1	16–26
30 mol%	130	1350	38	435	39	360	1.0±0.1	20

[a] Homopolymer prepared at 140°C. Homopolymer synthesized at 190°C was unspinnable due to too high bulk viscosity

emerging from the spinnerette was defined as the spin draw ratio. After coagulation, the wet fibre was neutralized with 3% NH_4OH solution, and heat treated in a tube furnace with 30 s residence time. The values for spinning temperatures, spin draw ratios and heat treatment temperatures are shown in *Table 3*.

Tensile properties were measured using an Instron tensile tester with gauge lengths of 25.4, 76.2 and 127 mm, and were corrected for machine compliance. Compressive strength values were determined at a gauge length of 25.4 mm using a recoil method[33].

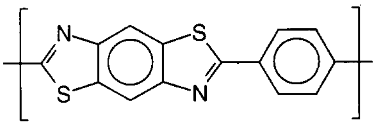
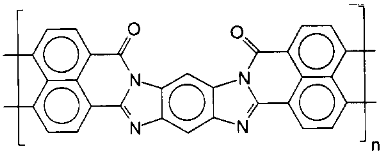
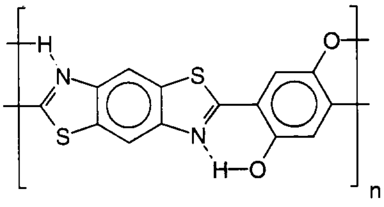
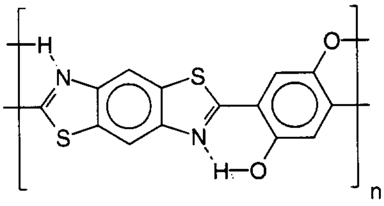
The tensile modulus values of the dihydroxy-PBZT homopolymer were 22–25 Msi (1 Msi = 6.9 GPa), much lower than the typical 40 Msi modulus found in PBZT rigid-rod fibres. The lower modulus was probably due to the lower orientation of these fibres with spin draw ratios of 20 and 24, respectively, rather than to the introduction of pendent groups to the rigid-rod chains. This rationale is supported by the fact that in the 30 mol% dihydroxy-PBZT copolymer, the modulus of a fibre with a spin draw ratio of 20 was 16 Msi, and it increased to 39 Msi when the spin draw ratio was increased to 38. Such high modulus would not be possible if the dihydroxy-PBZT had an inherently low modulus from the rule-of-mixture standpoint. Similarly, lower tensile strength values of 248 and 304 ksi (1 ksi = 6.9 MPa) were found in the homopolymer fibres with low spin draw ratios.

One of the main purposes of introducing hydroxyl groups was to improve the axial compressive strength of PBZT fibres. We have found that the pendent OH groups did not help at all. On the contrary, the homopolymer and the dihydroxy-PBZT/PBZT copolymers exhibited somewhat lower compressive strength. The measured strengths had a large variation within each group of fibres. The homopolymer fibres ranged from poor to slightly better (4–59 ksi) than the unsubstituted PBZT fibres. Similar results were found in the copolymers. The failure of the dihydroxy pendent groups to improve the compressive strength was, in hindsight, due to hydrogen bonding occurring in an intrachain fashion, to form a pseudo-ladder structure, rather than in an interchain manner, which could provide lateral support to the neighbouring chains, as we had envisaged.

ELECTRICAL CONDUCTIVITY

Because of the assumption that the pseudo-ladder, rigid-rod structure of the dihydroxy-PBZT is a wholly aromatic, conjugated and ordered system, we suspected that it might exhibit some interesting intrinsic conductivity. It is also known that conductivity can be enhanced by ordering the already conducting polymer chains. Fibre spinning of an anisotropic polymer dope is one of the most effective methods of achieving a high level of order, especially for the lyotropic liquid-crystalline polymers. Therefore, the conductivity of the as-spun and heat

Table 4 Comparison of intrinsic conductivities of PBZT, BBL and dihydroxy-PBZT polymer fibres

Polymer fibres	Conductivity ($S\,cm^{-1}$)[a]
 PBZT	4.9×10^{-12}[b]
 BBL	1.4×10^{-8}[b]
 Dihydroxy-PBZT (AS)[c]	2.2×10^{-7}
 Dihydroxy-PBZT (HT)[d]	5.6×10^{-8}

[a] Conductivity values are for axial direction

[b] Courtesy of Professor R. E. Barker, University of Virginia, Charlottesville, VA

[c] As-spun fibre dried at 200°C; 3.7% P

[d] Heat treated (435°C) fibre; 4.4% P

treated (435°C) fibres was briefly studied and compared with that of related polymer fibres (*Table 4*). As anticipated, the dihydroxy-PBZT fibre showed conductivity in the same range as that for the BBL fibre and about four to five orders of magnitude higher than that of unsubstituted PBZT fibre. However, it was quite contrary to our expectation that heat treated dihydroxy-PBZT fibre would have a conductivity value slightly lower than that of the as-spun fibre. Heat treatment should provide a higher level of order and closer packing of the polymer chains with a consequent increase in conductivity, in addition to the enhancement of the mechanical properties. Another point that needs to be clarified in our future study is the effect of the residual phosphorus, about 4% as determined by elemental analysis, on the conductivity of the dihydroxy-PBZT polymer.

CONCLUSION

We have demonstrated that the homopolymerization of 2,5-dihydroxyterephthalic acid (DHTA) and 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT.2HCl) and copolymerization of DHTA, terephthalic acid and DABDT.2HCl in polyphosphoric acid (PPA) in the anisotropic state afforded high molecular weight rigid-rod polymer and copolymers, with two hydroxyl groups as pendants per repeat unit. In PPA, the lyotropic liquid crystalline behaviour of the homopolymer was sensitive to the polymerization temperature, and the optimal temperature was 140°C. Spectroscopic evidence suggested a completely planar and ribbon-like structure, a consequence of the strong intramolecular hydrogen bonds between the OH moieties and the N atoms of the nearby benzothiazole units. The homopolymer also exhibited the unusual capability, characteristic of BBL-type ladder polymers, to form directly from its precipitates in methanol an aggregated film which displayed little or no shrinkage when dried. Although the compressive strength of dihydroxy-PBZT polymer (4–30 ksi) was poor compared to that of PBZT (54–64 ksi), this is the first indication that the presence of a pendant has actually imposed a negative effect on the compressive strength. Previously reported modified PBZT polymers with a variety of pendent groups showed values of compressive strength about the same, or slightly better, than that of PBZT. Therefore, this system may provide clues as to the mechanism of compressive failure in the rigid-rod ordered polymers. On the other hand, its ribbon-like ladder structure with a unidirectional character is expected to lend itself to other areas of application, namely electronic and photonic transports. Also, the reported light-induced tautomerism (hydrogen transfer) phenomenon, as illustrated by the model compound **1** (2-(*o*-hydroxyphenyl)benzothiazole)[23] and other intramolecularly hydrogen-bonded organic systems[34,35], suggests a variety of potential applications based on photochromism[36]. Preliminary measurement of the dihydroxy-PBZT fibre showed an intrinsic conductivity of 5.6×10^{-8}–$2.2 \times 10^{-7}\,\mathrm{S\,cm^{-1}}$. In a recent conductivity study from our laboratories, it was demonstrated that the conductivity of dihydroxy-PBZT aggregated film ($1.8 \times 10^{-12}\,\mathrm{S\,cm^{-1}}$), could be dramatically elevated to 2.4–$1800 \times 10^{3}\,\mathrm{S\,cm^{-1}}$ after Kr ion implantation[37]. Our current work to exploit these features of pseudo-ladder, rigid-rod structures is progressing along these lines.

EXPERIMENTAL

Diethyl-2,5-dihydroxyterephthalate[16]

Diethyl-2,5-dioxo-1,4-cyclohexanedicarboxylate (25.6 g, 0.10 mol) was dissolved in 180 ml of 95% diethylbenzene at about 100°C. To the resultant light yellow solution was added 3.52 g (0.11 mol) of sulfur and 0.20 g of 10% Pd/C. The reaction mixture was subsequently heated to reflux overnight. While it was still hot, the reaction mixture was filtered through a cake of Celite. Yellow precipitates formed as the filtrate cooled down. After chilling in an ice bath for about 6 h, the product was collected and washed with hexane. Recrystallization of the crude product from ethanol afforded 20.4 g of yellow crystalline diethylester, m.p. 178°C. I.r. (KBr; in $\mathrm{cm^{-1}}$): 3304 ms, 2991 w, 2968 vw, 2941 vw, 1689 vs, 1626 vw, 1496 s, 1470 s, 1447 w, 1406 m, 1371 ms, 1342 m, sh, 1320 vs, 1289 w, 1220 ms, sh, 1198 vs, 1178 s, 1131 w, 1100 m, 1069 w, 1020 m, 887 m, 877 sh, 802 ms, 795 ms, 662 m, 602 vw, 512 w. ^{1}H n.m.r. (270 MHz, $CDCl_3$; δ in ppm): 1.42, (triplet, CH_3, 2H); 4.42 (quartet, CH_2, 4H); 7.48 (singlet, aromatic protons, 2H); ~10.14 (singlet, OH, 2H). ^{13}C n.m.r. ($CDCl_3$; δ in ppm): 14.05, 62.02, 117.65, 118.46, 152.95, 169.08. Mass spectrum: 254 (M^+; 28.07%); 208 (M-EtO; 100%). Analysis: calcd for $C_{12}H_{14}O_6$: C 56.69%; H 5.50%. Found: C 56.26%; H 5.52%.

2,5-Dihydroxyterephthalic acid[16,38]

Diethylester (10.0 g, 39.3 mmol) and 10 g of sodium hydroxide pellets were placed in a 500 ml round-bottomed flask, followed by addition of 200 ml of distilled water. The reaction mixture was stirred magnetically at room temperature for about 30 min and then heated to reflux under nitrogen overnight. The resultant solution was filtered to remove some minute amount of insolubles. The orange filtrate was chilled in an ice bath followed by dropwise addition of concentrated HCl until the pH of the yellow mixture was about 1. The yellow slurry was then filtered, washed with water until the filtrate was neutral, and air-dried with suction overnight. The yellow product was then treated with minimal amount of methanol, filtered and finally dried in vacuum at 110°C for 20 h. Yield 6.80 g (87%); m.p. 349–350°C. I.r. (KBr; in $\mathrm{cm^{-1}}$): 3567–3084 v, br, 2881 br, 2686 br, 2566 br, 1649 vs, 1496 ms, 1481 sh, 1428 vs, 1360 w, 1295 w, 1183 vs, 901 w, 849 m, 799 vw, 758 m, 708 vw, 527 vw, 498 w. ^{1}H n.m.r. (270 MHz, DMSO-d_6; δ in ppm): 7.31 (aromatic protons, s, 2H); ~10.95 (OH and COOH, br, 4H). ^{13}C n.m.r. (DMSO-d_6; δ in ppm): 117.59, 119.37, 152.43, 170.00. Mass spectrum: 198 (M^+; 26%); 162 (M-2H_2O; 100%). Analysis: calcd for $C_8H_6O_6$: C 48.49%; H 3.05%. Found: C 48.48%; H 3.06%.

2-(2-Hydroxyphenyl)benzothiazole

2-Hydroxybenzoic acid (salicylic acid) (13.8 g, 100 mmol) and 13.46 g (107 mmol) of 2-aminothiophenol were placed in a 150 ml polymerization vessel, followed by the addition of 180 g of PPA (83% P_2O_5 content). The resultant mixture was heated within 3 h to 166°C in an oil bath under a nitrogen atmosphere. At 63°C, the reaction mixture was grey and heterogeneous. At 130°C, it became green with most of the solids dissolved. At 166°C, it became completely homogeneous and dark brown. The reaction mixture was heated at this temperature for another 17 h. Then it was allowed to cool to about 60°C and poured into 2 l of ice/water. Light green solid precipitated. It was collected by filtration and washed with water (5 × 200 ml).

The resultant yellow-green crude product was finally air-dried (with suction) at room temperature overnight. The yield was 22.30 g. The crude product was recrystallized twice from boiling toluene to afford light yellow solid. Yield 20.38 g (90%); m.p. 129–131°C. I.r. (KBr; in cm^{-1}): 3059 vw, 2770 vw, 2540 vw, 1622 ms, 1589 ms, 1485 vs, 1458 w, 1438 m, 1407 w, 1386 vw, 1315 m, 1272 ms, 1253 m, 1219 ms, 1151 w, 1129 w, 1035 m, 973 w, 933 w, 860 w, 818 m, 756 s, 743 s, 728 ms, 701 m, 499 vw, 458 vw. ^1H n.m.r. (270 MHz, $CDCl_3$; δ in ppm): ~1.38 (v, br, OH); 6.88 (triplet); 7.08 (doublet); 7.35 (triplet); 7.45 (triplet); 7.63 (doublet); 7.83 (doublet); 7.93 (doublet). ^{13}C n.m.r. ($CDCl_3$; δ in ppm): 116.73, 117.83, 119.44, 121.45, 122.14, 125.48, 126.64, 128.36, 132.57, 132.68, 151.80, 157.91, 169.31. Mass spectrum: 227 (M^+; 100%). Analysis: calcd for $C_{13}H_9NOS$: C 68.70%; H 3.99%; N 6.16%; S 14.10%. Found: C 68.28%; H 4.04%; N 6.08%; S 14.61%.

2,5-Bis(2-benzothiazolyl)-dihydroquinone

2,5-Dihydroxyterephthalic acid (3.00 g, 15.14 mmol), 48 g of PPA and 4.00 g (31.95 mmol) of 2-aminothiophenol were placed in a 150 ml polymerization vessel equipped with nitrogen adapters and a mechanical stirrer. The resultant yellow-green heterogeneous mixture was heated in an oil bath with slow stirring under nitrogen. The reaction temperature was increased from 70 to 170°C over a period of 4 h. The resultant dark red mixture (at this stage there was still some undissolved orange solid present) was heated at 170°C for another 16 h. The final dark red and homogeneous solution was allowed to cool to about 65–70°C and poured into 1000 ml of water. The precipitated light brown material was collected by suction filtration, washed with water, ammonium hydroxide (2 × 40 ml), and finally water again until the pH of the filtrate was neutral. The crude product was air-dried with suction for 3 days. Recrystallization of the crude product from 1,2,4-trichlorobenzene (450 ml) afforded fine yellow crystals, which were washed with methanol and dried in vacuum (0.10 torr at 140°C). Yield 5.49 g (96%); m.p. 354.4–356.4°C. I.r. (KBr; in cm^{-1}): 3123 vw, 1561 w, 1533 w, 1492 vs, 1457 w, 1434 m, 1363 m, 1315 m, 1277 w, 1247 w, 1213 ms, 1190 s, 1131 vw, 1072 vw, 977 s, 935 sh, 881 w, 860 w, 812 m, 756 s, 723 m, 689 m, 586 vw. Mass spectrum: 376 (M^+; 100%). Analysis: calcd for $C_{20}H_{12}N_2O_2S_2$: C 63.81%; H 3.21%; N 7.44%; S 17.03%. Found: C 63.72%; H 3.16%; N 7.29%; S 16.91%.

2,6-Bis(2-hydroxyphenyl)benzo[1,2-d:4,5-d']bisthiazole

Salicylic acid (2.76 g, 0.020 mol), 2.45 g (0.010 mol) of DABDT.2HCl and 75.0 g of PPA (83% P_2O_5 content) were placed into the bottom of a three-necked resin flask equipped with a mechanical stirrer and nitrogen adaptors. The resultant mixture was placed in an oil bath and agitated at room temperature for 1 h. Subsequently, it was slowly heated to 80°C and maintained at that temperature for 24 h. The oil bath temperature was then increased to 160°C and maintained at that temperature for another 24 h. The resultant reaction mixture was poured into water while it was still warm. The crude product was collected by suction filtration, subjected to Soxhlet extraction (water, 24 h) and dried under vacuum at 100°C. Recrystallization of the crude product from *o*-dichlorobenzene afforded 3.60 g (96%) of bright yellow crystals, m.p. 385–386°C. I.r. (KBr; in cm^{-1}): 3070 vw, 2851 vw, 2772 vw, 2639 vw, 1619 m, 1581 m, 1485 vs, 1433 m, 1404 m, 1387 sh, 1317 m, 1279 vw, 1250 ms, 1220 s, 1165 w, 1035 w, 966 m, 868 m, 814 m, 779 w, 749 s, 711 w, 659 w. Mass spectrum: 376 (M^+; 100%). Analysis: calcd for $C_{20}H_{12}O_2N_2S_2$: C 63.81%; H 3.21%; N 7.44%; S 17.03%. Found: C 63.37%; H 3.26%; N 7.09%; S 17.01%.

*Poly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl(2,5-dihydroxy-*p*-phenylene)](dihydroxy-PBZT)*

Into the bottom of a resin flask, equipped with a high-torque mechanical stirrer, a nitrogen adapter, a pressure regulator and a side opening for additions, were placed 4.904 g (20 mmol) of DABDT.2HCl, 3.962 g (20 mmol) of DHTA and 18.74 g of PPA (77% P_2O_5 content). The monomers were blended into the PPA by stirring. The resultant mixture was dehydrochlorinated under reduced pressure (176 mmHg) while slowly heating the mixture to 80°C for 24 h, then cooled to 60°C. P_2O_5 (13.64 g) was added to the mixture, thus raising the final polymer concentration to 15%. The mixture was heated under a positive nitrogen flow at 60°C for 4 h, 100°C for 2 h, and 140°C for 24 h. As the temperature was increased, stir-opalescence began to appear at about 120°C. At the end of the polymerization, most of the polymer dope was used for fibre spinning (see below), and a small but sufficient amount of the polymer dope was precipitated into water. The resultant fibrous polymer was chopped in a Waring blender, collected by suction filtration, washed with ammonium hydroxide, then with a copious amount of water, and finally dried under reduced pressure (0.02 torr) at 110°C. An intrinsic viscosity of 28 dl g^{-1} was obtained in MSA at 30°C.

The anisotropic reaction mixture was spun into monofilament fibre using a dry-jet wet-spinning method with a 0.25 mm diameter spinnerette and coagulated in distilled water. The air gap where the fibre was stretched was maintained at 203 mm. After neutralization with 3% NH_4OH and washing with water, the fibres were tension dried at 150°C, then heat treated in a tube oven under an inert nitrogen atmosphere at 435°C with a 30 s residence time. The resulting fibre had a modulus of 25 Msi, tensile strength of 304 ksi and an elongation at break of 1.3%.

*Poly[benzo[1,2-d:4,5-d']bisthiazole-2,6-diyl-(2,5-dihydroxy-*p*-phenylene) 30 mol%/(1,4-phenylene) 70 mol% (30 mol% dihydroxy-PBZT/70 mol% PBZT copolymer)*

Into the bottom of a resin flask equipped with a high torque mechanical stirrer, a nitrogen adapter, a pressure regulator and a side opening for additions, were placed 4.41 g (18.00 mmol) of DABDT.2HCl, 2.09 g (12.60 mmol) of terephthalic acid, 1.07 g (5.40 mmol) of DHTA and 21.3 g of 77% PPA. The monomers were incorporated into the PPA by stirring, and the resultant mixture was dehydrochlorinated under reduced pressure (176 mmHg) by heating slowly to 80°C in an oil bath, then maintained at that temperature for 24 h. The reaction mixture was cooled to 60°C and 13.8 g of phosphorus pentoxide was added, thereby making the final polymer concentration 15%. Under a positive nitrogen flow, the mixture was heated to 100°C for 2 h, 180°C for 18 h and finally at 190°C for 2 h. At the end of the polymerization, most of the polymer dope was used for fibre spinning (see below), and a small but sufficient amount of the polymer dope was precipitated into water. The resultant fibrous polymer was chopped in a Waring blender, collected by suction filtration, washed with ammonium hydroxide, then with a copious amount of water, and finally dried under reduced pressure (0.02 torr) at 110°C. An intrinsic viscosity of 25.9 dl g^{-1} was measured in MSA at 30°C.

Reaction of dihydroxy-PBZT with antimony trichloride

Dihydroxy-PBZT (2.0 g, 6.70 mmol) and 25 g of distilled $SbCl_3$ (0.11 mol) were placed into the bottom of a resin flask equipped with a mechanical stirrer, nitrogen adaptors and a condenser. The resultant mixture was slowly heated to 100°C and maintained at that temperature for 24 h. The temperature was then raised to 140°C and maintained at that temperature for 2 h. The final reaction mixture was precipitated into nitromethane, collected by suction filtration, Soxhlet extracted with water and dried in vacuum at 120°C for 24 h. The recovered product was identical to the starting polymer in its colour, intrinsic viscosity and other physical properties (i.r., t.g.a. and d.s.c.).

Reaction of dihydroxy-PBZT with methanesulfonyl chloride

Dihydroxy-PBZT (1.0 g, 3.30 mmol) and 200 g distilled MSA were placed into the bottom of a resin flask equipped with a mechanical stirrer, nitrogen adaptors and a condenser. The resultant mixture was slowly heated to 100°C and maintained at that temperature for 24 h. After the complete dissolution of the polymer in MSA was achieved, the reaction temperature was lowered to 40°C and 10.0 g (87.3 mmol) of methanesulfonic chloride was added. The resultant mixture was reheated to 100°C and maintained at that temperature for 24 h. The final reaction mixture was precipitated into water, collected by suction filtration, Soxhlet extracted with water and dried in vacuum at 120°C for 24 h. The recovered product was identical to the starting polymer in its colour, intrinsic viscosity and other physical properties (i.r., t.g.a. and d.s.c.).

Reaction of dihydroxy-PBZT with chlorosulfonic acid

Dihydroxy-PBZT (1.0 g, 3.30 mmol) and 200 g of chlorosulfonic acid were placed into the bottom of a resin flask equipped with a mechanical stirrer, nitrogen adaptors and a condenser. The resultant mixture was stirred at room temperature for 2 h, heated at 40°C for 3 h, 60°C for 4 h, 80°C for 14 h and finally at 100°C for 24 h. There was a change in the colour of the reaction mixture from deep red to orange during the course of heating. The final reaction mixture was precipitated into water, collected by suction filtration, Soxhlet extracted with water and dried in vacuum at 120°C for 24 h. There was a drastic reduction in the intrinsic viscosity, from 20.6 to 12.0 dl g^{-1} as measured in MSA at 30°C. However, the polymer still retained its original colour. Its i.r. spectrum was similar to the original polymer and did not show any stretching bands attributable to the sulfonyl group.

Fibre spinning of the dihydroxy-PBZT polymer

The anisotropic reaction mixture of the dihydroxy-PBZT polymer synthesized at 140°C was spun into monofilament fibres using a dry-jet wet-spinning method with a 0.25 mm diameter spinnerette and coagulated in distilled water. The air gap where the fibre was stretched was maintained at 203 mm. After neutralization with 3% NH_4OH and washing with water, the fibres were tension dried at 150°C, then heat treated in a tube oven under an inert nitrogen atmosphere at 435°C with a 30 s residence time. The resulting fibre with spin draw ratio of 24 had a modulus of 25 Msi, tensile strength of 304 ksi, an elongation at break of 1.3% and compressive strength of 16–59 ksi; the fibre with a spin draw ratio of 20 and heat treatment (N_2) at 350°C, had a modulus of 22 Msi, tensile strength of 248 ksi, an elongation at break of 1.2% and compressive strength of 4–30 ksi.

Fibre spinning of the 30 mol% dihydroxy-PBZT/70 mol% PBZT

The anisotropic reaction mixture of the copolymer-(30 mol% dihydroxy-PBZT/70 mol% PBZT) was spun into monofilament fibres using a dry-jet wet-spinning method with a 0.25 mm diameter spinnerette and coagulated in distilled water. The air gap where the fibre was stretched was maintained at 203 mm. After neutralization with 3% NH_4OH and washing with water, the fibres were tension dried at 150°C, then heat treated in a tube oven under an inert nitrogen atmosphere at 435°C with a 30 s residence time. The resulting fibre with spin draw ratio of 20 had a modulus of 16 Msi, tensile strength of 120 ksi, an elongation at break of 0.82% and compressive strength of 16–26 ksi; the fibre with a spin draw ratio of 38, had a modulus of 16 Msi, tensile strength of 120 ksi, an elongation at break of 0.82% and compressive strength of 16–26 ksi.

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