

Diacid architecture effect on the synthesis and microstructure of rigid-rod poly(benzobisthiazole)s

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Abstract: Six poly(benzobisthiazole)s (PBTs) have been synthesized by the solution polycondensation of 2,5-diamino-1,4-benzenedithiol in poly(phosphoric acid) (PPA) with systematically varied diacids to demonstrate the diacid architecture effect of the aromatic heterocyclic rigid-rod polymers. The role of PPA is identified and the effects of phosphorus pentoxide and water on PBT during polycondensation are discussed. Polymer properties such as the inherent viscosity and decomposition temperature are correlated to the diacid chemistry. The effect of diacid architecture on the synthesis and microstructure of PBT is studied. The results are discussed in terms of resonance, symmetry, and solubilization of the diacids.

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Keywords: poly(benzobisthiazole)s; synthesis; microstructure; rigid-rod polymers

INTRODUCTION

The conjugated rigid-rod aromatic heterocyclic benzazo polymers, typically known as PBX, have attracted much attention in both academia and industry.^{1–3} The historical development of PBX started in 1961 from the synthesis and processing of poly(benzobisimidazole) (PBI); however, major advances in the last two decades have been centered on poly(benzobisthiazole) (PBT) and poly(benzobisoxazole) (PBO). In particular, fibers, films, or molecular composites of PBT and PBO have been commercially realized.^{4–6} PBT and PBO have very high tensile strength and tensile modulus, but poor performance under compression. While the original motivation for PBX concentrated on the development of mechanical, thermal, and oxidative stability,^{7,8} current interests have shifted to the tremendous potential in optical and electronics applications, such as third-order nonlinear optical (NLO) materials or polymer electrolytes used in secondary lithium-ion batteries.^{9–14}

PBTs can be prepared directly by means of polycondensation of 2,5-diamino-1,4-benzenedithiol with certain diacids in poly(phosphoric acid).^{7,15} However, they are generally insoluble in common organic solvents, giving them limited potential utility in spite of many targeted applications. Methods to improve the solubility of aromatic heterocyclic rigid-rod polymers have been proposed. A novel

two-step synthesis via polyamide precursors to prepare PBTs was proposed,^{16–18} utilizing the better solubility of polyamides to improve the ease of processing; the precursor is then converted to PBTs via thermal cyclization. The complex formation with Lewis acids in aprotic organic solvents is another successful approach;^{8,19} it is very suitable for thin-film applications but the products are less thermally stable due to residual Lewis acid in the films. Chemical modifications with organic-soluble dopants of the final aromatic heterocyclic polymers were also mentioned, i.e., sulfonated PBIs. Fluorine-containing aromatic polybenzothiazole was also synthesized; the amorphous structures showed good solubility in organic solvents with high thermal stability.²⁰

In our previous work on PBIs,²¹ the diacid architecture effects on the microstructure, thermal, and optical properties of PBIs were reported. The present paper deals with a diacid architecture effect on the microstructure, thermal and optical properties of PBTs. Six PBTs with diacids of different degrees of flexibility in the main chain were synthesized. The chemical structure of the diacids was varied mainly in the main chain of the PBTs, different from that reported on side-chain variation of PBI. The results are discussed in detail in terms of conjugation, symmetry, and electrophilicity of the diacids.

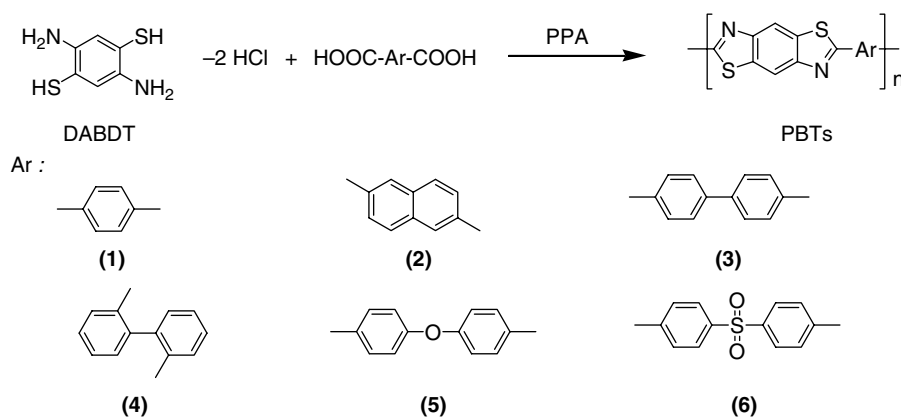
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Scheme 1. Chemical structure of diacids and the polycondensation.

EXPERIMENTAL

Materials

2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT) was synthesized according to the reported method,^{7,15} and recrystallized from concentrated aqueous hydrochloride solution before reacting with the following acids: terephthalic acid (**1**, from Riedel-Haen), 2,6-naphthalene dicarboxylic acid (**2**, from Aldrich), 4,4'-biphenyl dicarboxylic acid (**3**, from Aldrich), 2,2'-biphenyl dicarboxylic acid (**4**, from Aldrich), 4,4'-oxybis(benzoic acid) (**5**, from TCI), and 4,4'-sulfonyl bis(benzoic acid) (**6**, from TCI). The chemical structures of the diacids are depicted in Scheme 1, along with the polycondensation reaction. Phosphorus pentoxide (P_2O_5) was obtained from Acros. Phosphoric acid (H_3PO_4 , 85%, from Tedia) and phosphorus pentoxide (P_2O_5 , from Showa) were used as received to prepare 77% fresh poly(phosphoric acid)s (PPAs) in the dehydrochlorination of DABDT. The PPAs were prepared at 150 °C for 6 h under argon atmosphere before use. Methanesulfonic acid (MSA, from Lancaster) was used as solvent for dissolving PBTs for the preparation of thin films.

Polycondensation

PBTs were prepared according to the reported method.^{7,15} It is described in brief here to emphasize the materials and processing parameters used. DABDT was dissolved in 77% PPA under argon atmosphere with mechanical stirring at room temperature for 24 h; the solution was then heated to 65 °C for dehydrochlorination. After dehydrochlorination, an equimolar amount of diacid was added together with an appropriately adjusted amount of P_2O_5 to control the water content in the final solution. The polymer concentration was 1.1 wt% and the polycondensation conditions were 140 °C for 8 h, 165 °C for 12 h, then 180 °C for 12 h, and finally 195 °C for 12 h. The corresponding polymers synthesized using the diacids depicted in Scheme 1 are abbreviated as PBT-1 to PBT-6. The polymerization dope in PPA was washed and precipitated in deionized water. The PBTs were further purified using a Soxhlet extractor

for 72 h to remove completely PPA. The product was then dried in a vacuum oven at 65 °C for 48 h.

The polymerization dope in PPA was precipitated and washed in deionized water. However, PPA was possibly trapped in the PBT when the viscous PBT/PPA solution was poured into the deionized water. A TGA trace of PPA residue indicates an abrupt weight drop at ~250 °C as compared to the degradation temperature of PBT at ~650 °C. Further purification of PBT using the Soxhlet extraction apparatus for 72 h was required for complete removal of PPA, as is evidenced from the TGA trace.

Preparation of thin films

To prepare thin films of PBTs, the polymerization dope was first dissolved in methanesulfonic acid, cast onto a glass plate to form a thin film, and extracted in water for typically 2–3 days to free the film of acid. After evaporation of methanesulfonic acid, the film was washed with the basic organic solvent methanol and dried in a vacuum oven at 65 °C for 48 h.

Characterization

Inherent viscosity η_{inh} of the PBTs was measured with a concentration of 0.3 g dL⁻¹ in methanesulfonic acid at 30 °C using a Cannon Ubbelohde capillary viscometer. Fourier transform infrared (FTIR) spectra were recorded (Perkin Elmer 2000) with a resolution of 4 cm⁻¹, scanning from 4000 to 400 cm⁻¹. PBT thin films were measured directly, while powders of PBTs were mixed with KBr as thin pellets and measured. TGA was carried out with a Perkin-Elmer TGA-7 thermogravimetric analyzer, scanning from 50 to 800 °C with a scanning rate 10 °C min⁻¹. XRD analysis, to determine crystalline phase and growth directions, was carried out using a Siemens D5000 (Germany) X-ray diffractometer with Cu K α radiation operated at 40 kV and 30 mA. The 2θ scan range was set to be 4–80° using a step scan of 0.05° s⁻¹. Optical UV-visible absorption spectra of PBTs in methanesulfonic acid were obtained (Simadzu UV-160A spectrophotometer) in the wavelength range 190–600 nm.

RESULTS AND DISCUSSION

Resonance effect

To illustrate the resonance effect of diacid monomers, a comparison was made among PBT-1, PBT-2, and PBT-3. It is expected that the naphthalenyl unit (PBT-2) is more conjugated and coplanar than the benzyl unit (PBT-1). The biphenyl unit (PBT-3), with free rotation of the C–C bond between the two benzene rings, is the least conjugated among the three PBTs. The inherent viscosity η_{inh} listed in Table 1 indicates that the absolute molecular weights of PBT-1 and PBT-2 are higher, by about two times, than that of PBT-3. In general, η_{inh} of all the PBTs synthesized in this study was in the right range, as reported previously.⁷

Table 1. Inherent viscosity and thermal properties of PBTs

Sample	η_{inh}^a (dL g ⁻¹)	T_d (°C)	5% weight loss temperature (°C)	Char yield (%) at 800 °C
PBT-1	3.01	750	751	89.5
PBT-2	3.52	740	739	92.0
PBT-3	1.68	627	686	87.4
PBT-4	1.38	623	606	83.7
PBT-5	2.7	649	646	81.4
PBT-6	0.8	588	607	71.5

^a Concentration $C = 0.30$ g dL⁻¹, measured at 30 °C.

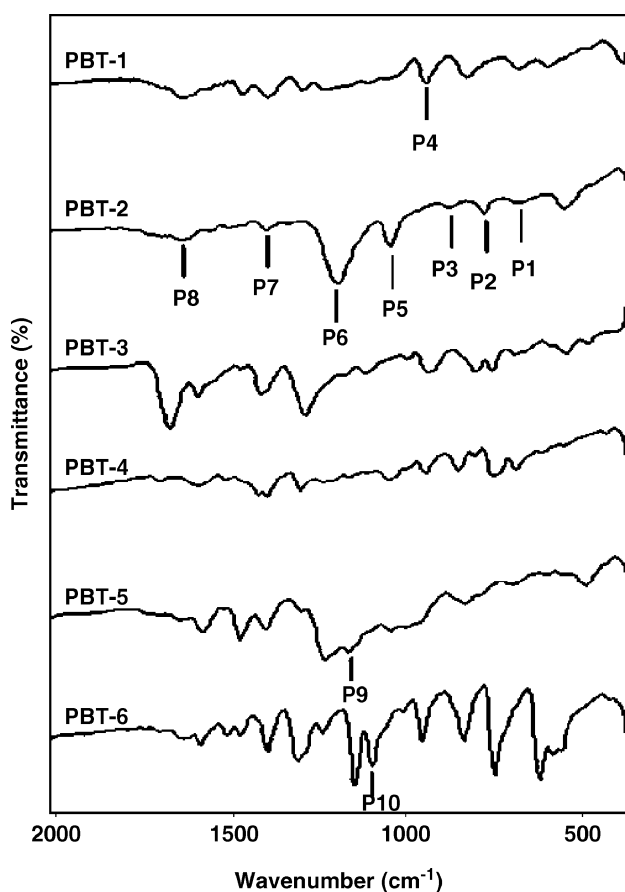


Figure 1. FTIR spectra of PBTs.

Several characteristic FTIR bands of the PBTs, shown in Fig. 1 and assigned P1–P8 for both PBT-1 and PBT-2, can be observed. These include, in their numerical order, the out-of-plane hetero-ring deformation at ~ 684 cm⁻¹ (P1), the band associated with the diacid portion for the C₆H₄–ring at 828 cm⁻¹ (P2), the C₆H₄–ring stretching (in fact, C₆H₃) appearing at 880 cm⁻¹ (P3), the hetero-ring breathing at ~ 946 cm⁻¹ (P4), the benzene ring 1,2,4,5-C₆H₄– at 1044 cm⁻¹ (P5), the C–C stretching at 1233 cm⁻¹ (P6), the hetero-ring stretching at ~ 1395 cm⁻¹ (P7), and the hetero-ring stretching associated with the thiazole ring by the strong C=N band at 1635 cm⁻¹ (P8). In essence, the FTIR spectra are consistent with previous reports on PBT series.⁵ The frequency of the out-of-plane hetero-ring deformation at ~ 684 cm⁻¹ (P1) of PBT-1 is shifted in PBT-2 to 680 cm⁻¹. This represents an increase in frequency (or in force constant) of this resonance vibration motion due entirely to the substitution of the benzene ring by the naphthalene ring.

Plotted in Fig. 2 are TGA curves showing the weight loss *versus* temperature of the PBTs. For a typical rigid-rod PBT, T_d as high as 750 °C and char yield $\sim 89.5\%$ are attainable. It is worth noting that there is a relation between the thermal stability and the viscosity. From the thermal stability point of view, there is no significant difference among the benzyl, naphthalenyl, and biphenyl units for their all-aromatic structures. However, the T_d values of both PBT-1 and PBT-2 are higher than that of PBT-3; this result can be explained by the lower viscosity of PBT-3. The optical absorption spectra are shown in Fig. 3 and the results for the maximum absorption peak λ_{max} summarized in Table 2. The PBTs synthesized here have λ_{max} values comparable to previously reported ones and are typically higher than those of corresponding PBIs;²¹ this means the PBTs have stronger conjugation than PBIs. Similar to the thermal analysis, no significant difference can be found between PBT-1 and PBT-2.

Schematic representations of the PBTs are given in Fig. 4 to demonstrate their molecular structure. Molecular mechanics were utilized to investigate the minimization by incorporating an empirical force field, the consistent valence force field, and the minimum

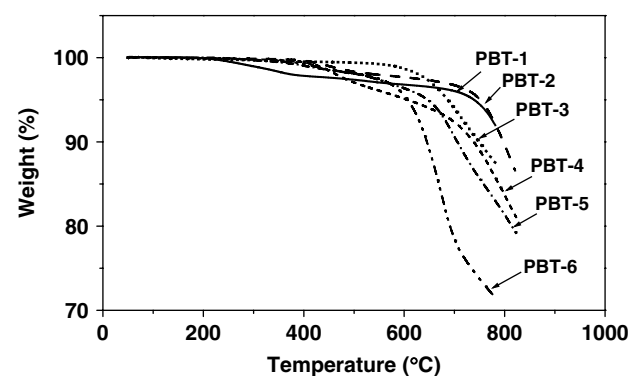


Figure 2. TGA of PBTs.

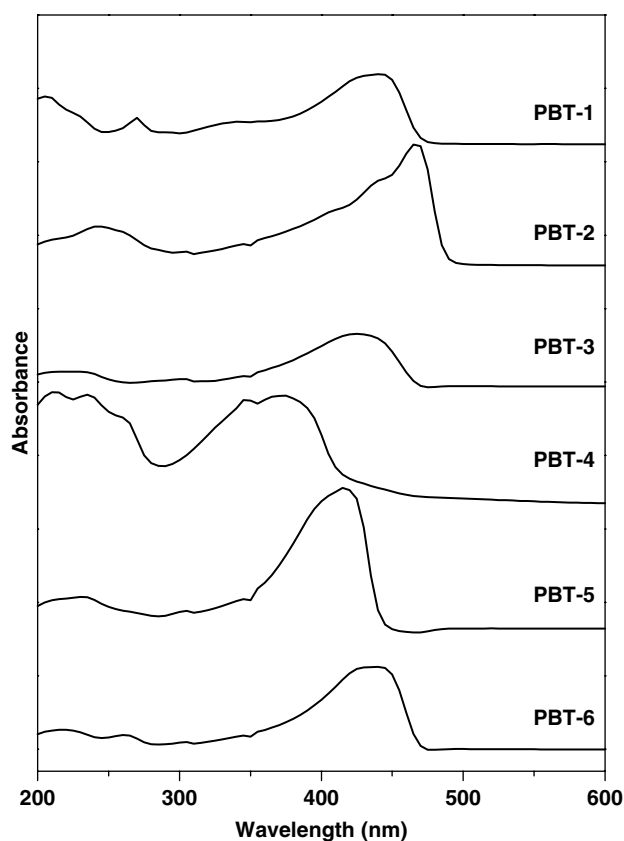


Figure 3. UV-visible absorption spectra of six PBTs.

Table 2. Effect of diacid architecture on the structure of PBTs

Sample	λ_{\max} (nm)	2θ ($^{\circ}$)	d -spacing (nm)
PBT-1	440	15.46	0.573
		–	–
PBT-2	465	13.27	0.646
		26.00	0.343
PBT-3	425	14.23	0.622
		–	–
PBT-4	375	13.46	0.657
		22.85	0.389
PBT-5	415	13.15	0.673
		–	–
PBT-6	435	13.00	0.681
		25.10	0.355

energy was calculated (MSI Insight II/Discover, version 95.0/2.97, MSI Technologies Inc., San Diego, CA). Corresponding XRD results are summarized in Table 2, and the XRD traces shown in Fig. 5. In general, there are two major peaks for a typical PBT. Taking PBT-2 as an example, the (200) peak at $2\theta = 13.27^{\circ}$ is assigned to the side-to-side packing and the (010) peak at $2\theta = 26.00^{\circ}$ is assigned to the face-to-face packing, consistent with previously reported data.^{22,23} This corresponds to $a = 1.292$ nm and $b = 0.343$ nm in a non-primitive monoclinic unit cell. One may note from Table 2 that the d -spacing in the b -direction is only about one quarter of that in the a -direction.

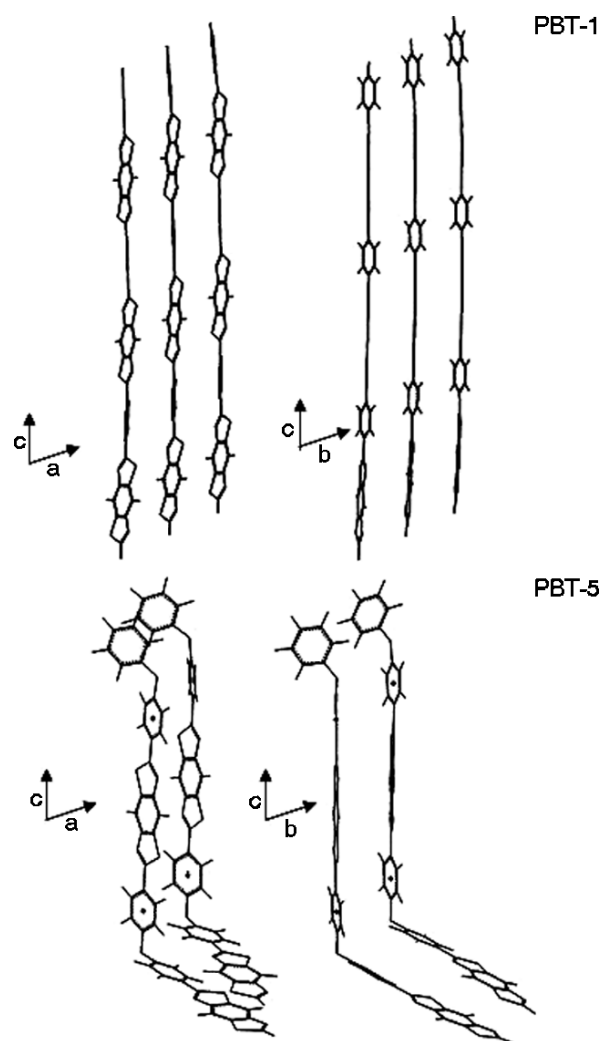


Figure 4. Schematic representation showing the face-to-face (left) and side-to-side (right) packing of PBTs.

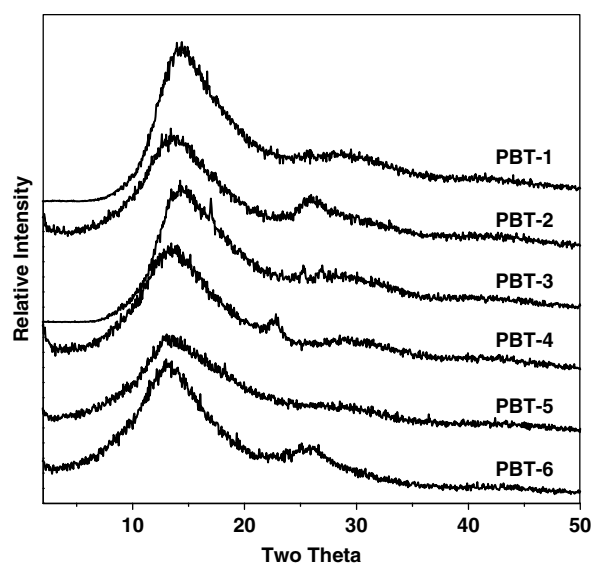


Figure 5. XRD traces of PBTs.

Substitution of the benzyl by the diphenyl unit in PBT-3 gives an almost identical XRD trace, but PBT-2 shows a different XRD trace (Fig. 5 and Table 2).

The naphthalene ring in PBT-2 leads to a wider *d*-spacing than for PBT-1 and PBT-3 in side-to-side packing (0.646 nm *versus* 0.573 nm in PBT-1). Naphthalene ring substitution of PBT-2 results in a more discernable (010) peak and a longer *b*-axis ($b = 0.343$ nm). This implies that the naphthalene unit combined with the benzo [1,2-*d*:4,5-*d'*] bisthiazole unit lines up straight more in the *c*-axis direction. The other PBTs are less ordered; PBT-6 also exhibits (010) peak with $b = 0.355$ nm but its inherent viscosity is too low (0.80 dL g⁻¹).

Due to additional π electrons, the strongly conjugated naphthalene ring apparently offers conjugation, rendering itself a less confined vibration space, and also leading to the neighboring hetero-ring and the C=N bond undergoing more easily resonance stretching and vibration. This resonance effect can be identified from the red shift for PBT-2 by 25 nm in the UV absorption spectrum (Fig. 3). The XRD trace indicates a less compact side-to-side packing of (200) for PBT-3 ($a = 0.622$ nm as compared to 0.573 nm of PBT-1), suggesting a less rigid-rod-like molecular assembly. Thus, there is a strong tendency for coplanarity in the *a*-direction.

Symmetry effect

In contrast to the naphthalene ring, the biphenyl unit imposes a restriction for free vibration. The asymmetric PBT-4 is thermally very unstable as compared to the symmetrical PBT-3 (Fig. 2 and Table 1). This may result from incomplete polycondensation as evidenced from the FTIR spectra in Fig. 1 where carboxyl groups –COOH at ~ 1700 cm⁻¹ can be identified. A large ‘blue shift’ of 50 nm is found for the asymmetric PBT-4 as compared to the symmetric PBT-3 (Fig. 3). It is interesting to compare the XRD traces of PBT-3 and PBT-4. The molecular order is greatly reduced for the asymmetric PBT-4. The *d*-spacing of PBT-4 ($a = 0.657$ nm) is larger than that of PBT-3 ($a = 0.622$ nm). This suggests that the molecular structure of PBT-4 is less ordered in the *a*-axis direction due to free rotation between the benzene ring of the biphenyl moiety. The asymmetric molecular structure of PBT-4 makes itself more difficult to vibrate freely, yielding a reduced conjugation and coplanarity; thus compared to PBT-3, a large ‘blue shift’ for PBT-4 in the UV absorption spectra can be identified (Table 2 and Fig. 3). Other effects include a wider (010) alignment (Fig. 5), a large reduction of weight loss (Table 1), and poorer thermal properties (80 °C lower in T_d , Table 1). Yet the (200) alignment is not altered, a strong indication of the coplanarity of PBTs in the *a*-axis direction.

Solubilization effect

The viscosity data shown in Table 1 indicate that η_{inh} increases with the incorporation of the ‘softer’ ether moiety in the biphenyl unit when comparing PBT-5 and PBT-6 to PBT-3 (Table 1). Their FTIR spectra are very similar to that of PBT-1, with the only

exception of a lower C=N stretching by ~ 10 cm⁻¹. With the incorporation of the ‘softer’ ether or sulfone in the biphenyl unit, both PBT-5 and PBT-6 show a greatly reduced thermal performance indicated in Table 1. The same ‘blue shift’ can also be found when comparing PBT-1 with PBT-4, PBT-5, and PBT-6 (Fig. 3); in addition, the absorption peaks become broader and lower, indicating a larger dispersion of the optical constituent in the PBT molecular structure.

PBT-5 and PBT-6 with flexible linkages, however, show a larger *d*-spacing in the *a*-axis direction (Table 2) as compared to PBT-3. Apparently, the flexible oxygen atom and sulfone units allow a looser molecular packing in the *a*-direction. Problems associated with the electrophilicity caused by ether and sulfone groups cannot be ignored. A tremendous ‘blue shift’ in the UV absorption spectra (Table 2 and Fig. 3) is found.

CONCLUSIONS

The synthesis and microstructure of six PBTs have been studied. The role of PPA is identified as the solvent, the dehydrochlorinating agent, and the dehydrating agent. Additional phosphorus pentoxide is needed to remove extra water as the polycondensation byproduct. The results were then discussed in terms of the effects of resonance and symmetry. For the resonance effect, the strongly conjugated naphthalene ring offers resonance by additional π electrons, rendering itself a less confined vibration space, and also leading to the neighboring hetero-ring and the C=C bond undergoing more easily resonance stretching and vibration. This resonance effect can further be identified from the red shift in the UV absorption spectrum. XRD traces indicate a less compact side-to-side packing of (200) for PBT-3 ($a = 0.622$ nm as compared to 0.573 nm for PBT-1), suggesting a less rigid-rod-like molecular assembly. The naphthalene unit combined with benzo[1,2-*d*:4,5-*d'*] bisthiazole unit in PBT-2 lines up straight more in the *c*-axis direction; the other PBTs are less ordered. Study of the symmetry effect indicates a decrease of vibration frequency in FTIR spectra and a ‘blue shift’ in UV-visible spectra due to the asymmetry of PBT-4. This is also accompanied by a large reduction of molecular weight and poorer thermal properties. For the solubility effect, the flexible linkage of oxygen atom and sulfone unit allows a reduced thermal performance, a tremendous ‘blue shift’ in the UV-visible absorption spectra, and a looser molecular packing in the *a*-direction.

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