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Study of Structure-property Relationships of Poly(benzobisthiazole) and it's Derivatives

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Summary

Poly(*p*-phenylene benzobisthiazole) (**PBZT**) and a series of new derivatives, poly (benzobisthiazole-1,4-diphenylene etherylene) (**PBTPE**), poly(bisbenzothiazole-2,2'-phenelyene-6,6'-(4-*tert*-butyl)cyclohexylidene) (**PBTPBCH**) and poly(bisbenzothiazole-2,2'-phenelyene etherylene-6,6'-(4-*tert*-butyl)cyclohexylidene) (**PBTPEBCH**), were synthesized by polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (**DABDT·2HCl)** or 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride (**BAMPBCH·2HCl**) with terephthalic acid or 4,4'-dicarboxydiphenyl ether in poly (phosphoric acid) (**PPA**). The inherent viscosity, thermal stability, solubility, morphology and photophysical properties of them were investigated and compared in detail. The introduction of etherylene or 4-*tert*-butylcyclohexylidene both decreased the inherent viscosity of **PBZT**. Although the decomposition temperatures of these derivatives were lower than **PBZT**, they still had good thermal stability. In addition, the thermogravimetric analysis showed **PBTPBCH** and **PBTPEBCH** containing 4-*tert*-butylcyclohexylidene had the lower thermal stability than **PBTPE** containing etherylene. The solubility of them was all enhanced. Especially, **PBTPBCH** and **PBTPEBCH** showed better solubility. X-ray diffractograms of all the derivatives showed that they were amorphous. Compared with **PBZT**, the absorption maximum (λ_{max}) of all the derivatives prepared was blue shifted in different degree according to their structure respectively. The excitation and emission peaks were also blue shifted. Furthermore, both of the substituting groups incorporated into the polymer backbone could improve the photoluminescence quantum yield to a certain extent. Finally we established the structure-property relationships of this class of poly(benzothiazole)s by investigating and comparing these properties in detail.

Introduction

The poly(benzazole) family has been studied since the early 1980s [1,2]. It includes poly(benzobisthiazole)s (**PBT**s), poly(benzobisoxazole)s (**PBO**s) and poly(benzimidazole)s (**PBI**s). These polymers have attracted much research interest in the past two decades. **PBT**s have been found to be particularly interesting in the poly(benzazole) family. They exhibit many advantageous physical properties such as high tensile strength, high modulus and outstanding thermal and environment stability [3]. But these rigid-rod polymers were found to be only soluble in strong protic acids such as methanesulfonic acid and sulfuric acid, which adversely affected processability. The common methods to improve the solubility of heterocyclic polymers were to introduce flexibilizing linkages into the main chain [4-6], incorporate fluorinated groups into the polymer backbone [7-9] or synthesize soluble precursor polymers [10,11]. Another successful approach to increase solubility and processability of heterocyclic polymers without sacrificing their high thermal stability was the introduction of a bulky pendent group into the polymer backbone [12-16]. This class of polymers is also considered to be the materials for applications in electronic, photoelectronic and optoelectronic areas such as light emitting diodes (LEDs). Recently, many conjugated poly(benzothiazole)s have been synthesized and their optical and electronic properties have been investigated in detail. In the earlier studies, Jenekhe and Osaheni [17-20] synthesized and studied the new heterocyclic polymers including poly(benzobisthiazole-2,6-diylvinylene) (**PBTV**), poly(benzobisthiazole-2,6-diyldivinylene) (**PBTDV**) and poly(benzobisthiazole-1,4-phenylene-bisvinylene) (**PBTPV**) based on the structure of Poly(*p*-phenylene benzobisthiazole) **PBZT**. Compared with **PBZT**, all of these polymers had the smaller optical bandgap. The wide optical property variations obtained in these polymers provided a useful means of studying structure-property relationships in this class of polymers. The studies [21,22] on how to improve the photoluminescence quantum yield and control the degree of aggregation of this class of polymers would be important to the utilization of them in LEDs. Therefore various efforts have focused on the design and synthesis of new **PBT**s with many advantageous properties.

In our previous studies, we have synthesized a series of novel poly(bisbenzothiazole)s bearing 4-*tert*-butylcyclohexylidene pendent group [23]. They exhibited different properties in many aspects. In order to investigate the effect on properties by introducing different substituents into the backbone, in the present article, we synthesized **PBZT** and poly(benzobisthiazole-2,6-diphenylene etherylene) (**PBTPE**). We compared the thermostability, solubility, morphology and photophysical properties of them with poly(bisbenzothiazole-2,2’-phenelyene-6,6’-(4-*tert*-butyl) cyclohexylidene) (**PBTPBCH**) and poly(bisbenzothiazole-2,2’-phenelyene etherylene-6,6’-(4-*tert*-butyl)cyclohexylidene) (**PBTPEBCH**) in detail and established the structure-property relationships of this class of poly(benzothiazole)s. We hope this work could lay the foundation for the molecular design to a certain extent.

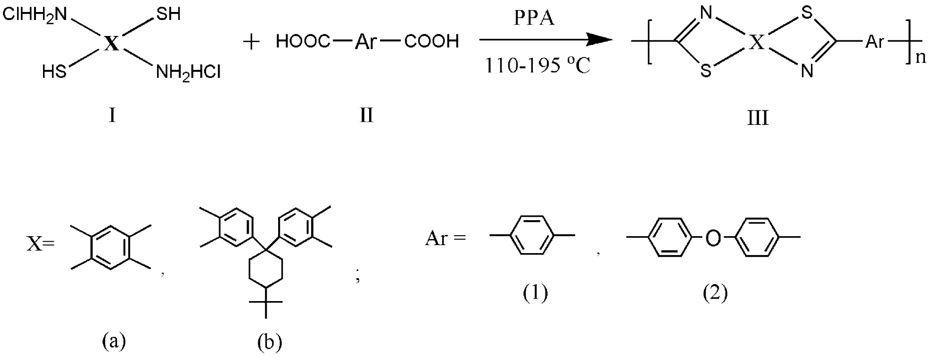
Experimental

Material

2,5-diamino-1,4-benzenedithiol dihydrochloride (**DABDT·2HCl)** was prepared according to the procedure described by Wolfe [3], 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride (**BAMPBCH·2HCl**) was synthesized according to the method reported by our previous study [23], terephthalic acid (from Yi Zheng Chemical Company), 4,4’-dicarboxydiphenyl ether (from Peakchem Company), poly(phosphoric acid) (PPA) (from Medicine group of China), methanesulfonic acid (MSA) (from Ke Wang Chemical Company) and other chemicals are of analytical grade except as noted.

Polymer synthesis

PBZT (**PBT III$_{a1}$**), **PBTPE** (**PBT III$_{a2}$**), **PBTPBCH** (**PBT III$_{b1}$**) and **PBTPEBCH** (**PBT III$_{b2}$**) were synthesized and characterized successfully. The synthetic route used for the preparation of poly(benzothiazole)s is shown in Scheme 1.



Scheme 1. Preparation of the poly(benzothiazole)s.

The poly(benzothiazole)s, were synthesized by direct polycondensation method. A typical procedure for polymerization of **PBT III$_{a2}$** was as follows. Into a three-neck flask were accurately weighed **DABDT·2HCl** (1.0g, 4.08mmol) and freshly prepared phosphoric acid (PPA, 80.8%, 13.51g). The reaction flask was fitted with a mechanical stirrer and argon inlet and outlet adaptors. The mixture was initially flushed with argon and then stirred at room temperature for 24h, at 70 °C for 36h in an argon atmosphere. Then the pressure was reduced until the hydrogen chloride evolution ceased and the solution became clear. 4,4'-dicarboxydiphenyl ether (1.05g, 4.08mmol) and additional phosphorus pentoxide (4.25g) were added to the clear amber solution. The temperature was increased to 110 °C quickly and gradually to 165 °C in 10h. The following temperature profile was used during polymerization: 12h at 165 °C, 10h at 180 °C and 8h at 195 °C. The hazy green-brown solution was poured into a large volume of water. The precipitated polymer was washed with diluted $NaHCO_3$ solution and methanol repeatedly. The green-brown polymer was dried at vacuum at 120 °C for 2 days. **PBT III$_{a2}$** 1.34g (91.7% yield). ^1H NMR (D_2SO_4): δ(ppm)=8.06 (br s, 6H, aromatic), 8.65 (br s, 4H, aromatic). IR (KBr): 3056, 3030 (m, ⌬), 1593 (C=N), 1257 cm^{-1} (C-O-C). ELEM. ANAL. Calcd. for $(C_{20}H_{10}N_2OS_2)_n$: C, 67.02%; H, 2.81%; N, 7.82%. Found: C, 66.74%; H, 2.93%; N, 7.61%.

Measurements

^1H NMR spectrum was recorded on a Mercury Plus 400Hz spectrometer using perdeutero sulfuric acid (D_2SO_4) as solvent. FT-IR spectra were recorded on a Perkin-Elmer Paragon1000 FTIR spectrometer. The samples were prepared as KBr pellets.

Elemental analysis was conducted on an Elementar Varioel apparatus. The inherent viscosity was measured with an Ubbelohde viscometer at 30 ºC in methanesulfonic acid (MSA), c=0.5g/dL. Differential scanning calorimetric (DSC) analysis was conducted on a Perkin-Elmer Pyris I DSC under the protection of N_2. The scan rate was 10 ºC/min. Thermogravimetric analyses (TGA) were recorded on a Perkin-Elmer TGA7 under the protection of N_2. The scan rate was 10 ºC/min. The wide-angle X-ray diffraction (WAXD) patterns for powder polymer samples were obtained with Bruker-AXS D8 Advance X-ray diffractometer with nickel-filtered Cu Kα radiation (λ=0.154178 nm). UV-vis spectra were recorded in methanesulfonic acid (MSA) solution by Perkin-Elmer Lambda 20 UV-vis spectrophotometer. Photoluminescence spectra were recorded in methanesulfonic acid (MSA) solution by Perkin-Elmer LS50B luminescence spectrophotometer. The relative photoluminescence quantum yield in MSA was determined by using a quinine sulfate (10^{-6} mol/L in 0.1 N H_2SO_4).

Results and discussion

Polymer Synthesis

The poly(benzobisthiazole), **PBT $\mathbf{III_{a2}}$,** was synthesized by the direct polycondensation of the monomer (**DABDT·2HCl**) (**$\mathbf{I_a}$**) with 4,4'-dicarboxydiphenyl ether (**$\mathbf{II_2}$**) in poly(phosphoric acid) (PPA) under an argon atmosphere. It was necessary for the removal of HCl from the monomer by dehydrochlorination prior to polymerization. PPA was used as both condensing agent and solvent. The final polymer concentration was controlled at about 7.5% and the P_2O_5 content was maintained at about 85%. It was important to maintain the content of P_2O_5 in order to improve the viscosity of **PBT**s **III**. The reaction time in different temperature was different because the reaction activities of these monomers and aromatic dicarboxylic acids were not the same. The monomer **DABDT·2HCl** was more active than **BAMPBCH·2HCl**, and the solubility of terephthalic acid in PPA is lower than 4,4'-dicarboxydiphenyl ether, which also affect the reaction activities. Consequently, compared with **PBT**s **$\mathbf{III_a}$**, **PBT**s **$\mathbf{III_b}$** should be produced at higher temperature for more time. The reaction time is summarized in Table 1.

Table 1. Synthesis of poly(benzothiazole)s

Monomer code		Polymer							
		Code	η_{inh}[a] (dL/g)	Yields (%)	Reaction Time (h)				
					110-165 (ºC)	165 (ºC)	180 (ºC)	195 (ºC)	205 (ºC)
$\mathbf{I_a}$	**$\mathbf{II_1}$**	**$\mathbf{III_{a1}}$**	19.8	93.4	8	12	12	10	0
$\mathbf{I_a}$	**$\mathbf{II_2}$**	**$\mathbf{III_{a2}}$**	4.23	91.7	10	12	10	8	0
$\mathbf{I_b}$	**$\mathbf{II_1}$**	**$\mathbf{III_{b1}}$**	2.17	92.3	5	18	12	12	5
$\mathbf{I_b}$	**$\mathbf{II_2}$**	**$\mathbf{III_{b2}}$**	0.63	91.6	5	12	12	12	5

[a] Inherent viscosity of **PBT**s **III** was measured at a concentration of 0.5g/dL in methanesulfonic acid (MSA) at 30 ºC

The molecular structures of all the synthesized **PBT**s **III** were characterized by ^{1}H NMR, FT-IR and elemental analysis. Figure 1 shows the ^{1}H NMR spectra of **PBT III$_{a2}$** and **PBT III$_{b2}$**. In Figure 1(A), the hydrogen resonance at 8.06 ppm was assigned to the hydrogen atoms of benzothiazole and the hydrogen atoms of diphenylene meta to O. The resonance at 8.65 ppm was attributed to the hydrogen atoms of diphenylene ortho to O. In Figure 1(B), the resonance at 0.53 ppm was assigned to 4-tert-butyl, and the resonances between 1.44 and 2.28 ppm were attributed to hydrogen atoms of cyclohexylidene. The resonances between 7.24 and 7.86 ppm were assigned to hydrogen atoms of the benzothiazole and diphenylene. In the FT-IR spectra of all the synthesized **PBT**s **III**, the absorptions between 1615 and 1593cm^{-1} were attributed to C=N stretching. The absorptions of NH and SH disappeared in comparison with the FT-IR spectroscopy of **DABDT·2HCl** or **BAMPBCH·2HCl**. The elemental analysis values were consistent well with those calculated for the proposed structures. All of these results showed a complete cyclization of intermediate open structure to benzothiazole rings.

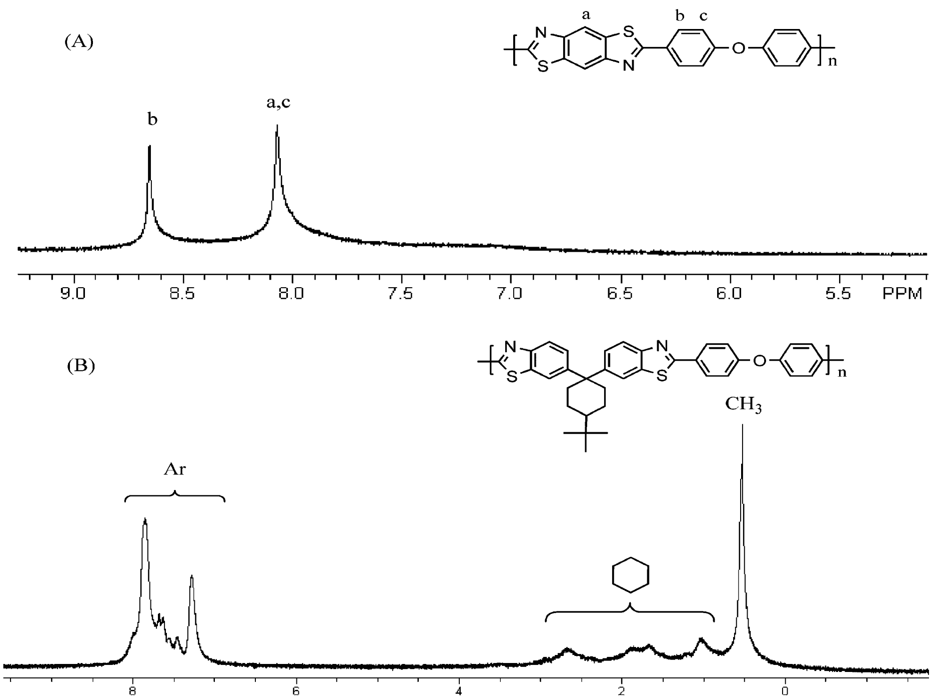


Figure 1. ^{1}H NMR spectra of **PBT III$_{a2}$** **(A)** and **PBT III$_{b2}$** (B) in D_2SO_4.

Inherent viscosity, thermal stability, solubility and morphology

The results of polymerization and the thermal stabilities are also summarized in Table 1. The inherent viscosities of the **PBT**s **III** were in the range of 0.63-19.8 dL/g. The viscosity values showed big difference because of the different molecular structure. The inherent viscosity of **PBT III$_{a1}$** was much higher than the other **PBT**s **III**. The inherent viscosities of **PBT III$_{b1}$** and **PBT III$_{b2}$** were decreased dramatically by introducing the bulky pendant group, 4-*tert*-butylcyclohexylidene. The flow behavior of polymer could be ascribed to the relative slip between polymer chains. **PBT III$_{a1}$** was termed as a rigid-rod polymer having strong intermolecular interactions because the molecular were collinearly arranged and the only possible conformational flexibility arose from the rotation of bonds between phenylene and heterocyclic groups. As a result, the inherent viscosity of **PBT III$_{a1}$** was the highest. As to **PBT III$_{a2}$**, the introduction of ether linkage increased the rotational flexibility in the backbone and decreased the molecular rigidity, which led to much lower inherent viscosity. The bulky pendant group, 4-*tert*-butylcyclohexylidene in the backbone of **PBT III$_{b1}$** and **PBT III$_{b2}$** destroyed the collinear arrangement of polymer chains and decreased the intermolecular interactions greatly. Consequently, **PBT III$_{b1}$** and **PBT III$_{b2}$** had the lowest inherent viscosities. Compared with **PBT III$_{b1}$**, **PBT III$_{b2}$** had lower inherent viscosities, which was consistent with the result found in **PBT**s **III$_a$**.

The thermal stabilities of **PBT**s **III** were characterized by differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) under nitrogen atmosphere. No glass-transition temperatures were observed from the DSC (10°C/min) curves for all **PBT**s **III** prepared. This was expected because the overwhelming effect of the fused-ring structures resisted segmental movement of the benzobisazole-based polymer [24]. All the **PBT**s **III** showed the good thermal stability. TGA curves of **PBT**s **III** are shown in Figure 2.

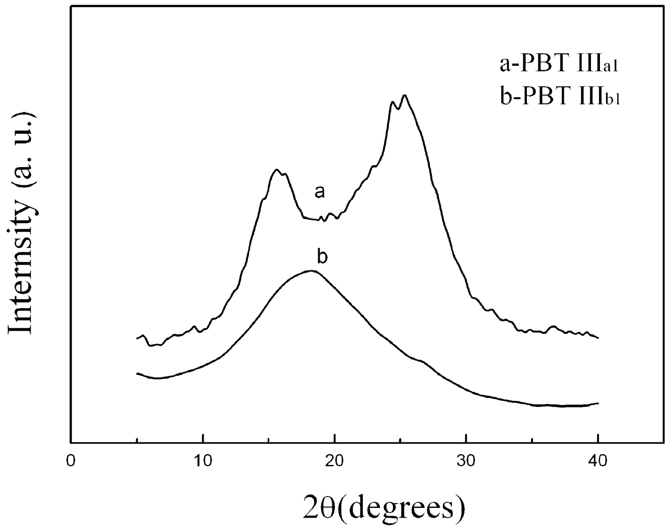


Figure 2. TGA curves of **PBT**s **III** with a heating rate of 10 °C/min in nitrogen.

The temperatures at 10% weight loss and the char yields at 800 °C in nitrogen atmosphere are reported in Table 2.

The 10% weight lost temperatures (T_d) were between 508 and 718 °C and the onsets of weight loss were higher than 475 °C. Furthermore, they afforded an anaerobic char yields of 43-75% at 800 °C in nitrogen atmosphere. Although **PBT**s **III$_b$** had good thermal behavior, they showed lower thermal stability in comparison with **PBT**s **III$_a$**. Temperature at 10% weight loss and the onset temperatures of **PBT**s **III$_b$** were almost the same, which were much lower than **PBT**s **III$_a$**. This phenomenon could be

Table 2. Thermal behavior of poly(benzothiazole)s.

Polymer code	T_d[a]	Char Yield[b]
	°C	%
PBT III_{a1}	718(675)	75
PBT III_{a2}	629(598)	67
PBT III_{b1}	502(475)	52
PBT III_{b2}	508(491)	43

[a] Temperature at 10% weight loss was determined by TGA in nitrogen at a heating rate of 10 °C/min; the onset temperatures are reported in brackets.

[b] Residual weight at 800 °C in nitrogen.

ascribed to the introduction of the bulky pendant group, which reduced the conjugation and rigidity of the polymer chain and increased the flexibility. The onset of degradation of **PBT III_{a1}** in nitrogen atmosphere was 675 °C. The char yield of **PBT III_{a1}** was 75%. Compared with **PBT III_{a2}**, **PBT III_{a1}** showed the higher thermal stability due to the highly regular molecular structure and high chain rigidity. As to **PBT III_{a2}** containing flexible linkage, the diphenylene etherylene was easier to degrade than phenylene. Just like **PBT**s **III_a**, **PBT III_{b1}** showed the higher char yield than **PBT III_{b2}**. Above all, the thermal stability order of **PBT**s **III** was as follows: **PBT III_{a1}>PBT III_{a2}>PBT III_{b1}>PBT III_{b2}**; **PBT**s **III_a**> **PBT**s **III_b**; **PBT**s **III_1**> **PBT**s **III_2**. The introduction of the flexible linkage and bulky pendant group would decreased the thermal stability of the **PBT**s. Comparing **PBT III_{b1}** with **PBT III_{a2}**, it could be observed that the affection of bulky pendant group to the thermal stability was greater than that of flexible linkage.

Qualitative solubilities of **PBT**s **III** toward various organic solvents are reported in Table 3.

Table 3. Solubility of poly(benzothiazole)s **III** in various solvents[a]

Polymer code	Solvents[b]						
	MSA	Conc H_2SO_4	NMP	DMF	DMAc	DMSO	THF
PBT III_{a1}	++	++	–	–	–	–	–
PBT III_{a2}	++	++	+	–	–	–	–
PBT III_{b1}	++	++	+	–	–	–	–
PBT III_{b2}	++	++	++	–	+	–	+

[a] ++, soluble; +, partially soluble and/or swelling; –, insoluble

[b] Abbreviations: MSA, Methanesulfonic acid; NMP, N-methyl-2-pyrrolidone; DMF, N,N-dimethylformamide; DMAc, N,N-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

All **PBT**s **III** were soluble in MSA and concentrated sulfuric acid easily. **PBT III_{a1}** was insoluble in the aprotic polar solvents such as N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). **PBT III_{a2}** and **PBT**s **III_b** showed better solubility than **PBT III_{a1}**.

PBT III$_{a2}$ could be swelling in NMP and **PBT III$_{b1}$** could be partially soluble in NMP. As to **PBT III$_{b1}$**, on one hand, the 4-*tert*-butylcyclohexylidene group decreased intermolecular forces between polymer chains of rigid aromatic repeating units and loosed the packing of them; On the other hand, the introduction of 4-*tert*-butylcyclohexylidene decreased the influence of the charge transfer in conjugated PBTs, which was the reason for coloration and poor fabricability, and increased the solubility of the poly(benzothiazole)s. As to **PBT III$_{a2}$**, the oxygen birdged benzothiazole moieties, the flexible linkage increased the solubility. From the result, it could be also observed that the bulky pendant group was more advantageous to increase the solubility of polybenzothiazole than the flexible linkages was. In comparison with other **PBT**s **III**, **PBT III$_{b2}$** containing the bulky pendant group and flexible linkage showed much better solubility. It could not only be soluble in NMP but also be partially soluble in DMAc and tetrahydrofuran (THF). The improved solubility could be ascribed to the two reasons we mentioned above. In general, the solubility order of **PBT**s **III** was **PBT III$_{b2}$ > PBT III$_{b1}$ > PBT III$_{a2}$ > PBT III$_{a1}$**.

An attempt was made to estimate the crystallinity of all the **PBT**s **III** by means of X-ray diffractograms. The typical wide-angle X-ray diffractograms of **PBT**s **III$_{a1}$** and **PBT**s **III$_{b1}$** are presented in Figure 3. Except for **PBT**s **III$_{a1}$**, which had two obvious broad peaks, all the other **PBT**s **III** exhibited an amorphous nature. The results of diffraction studies indicated the presence of ether linkage or the bulky-pendant group destroyed the ordered arrangement polymer chains and hampered close-packing of the polymer chains, as a result, crystallinity of **PBT III$_{a2}$** and **PBT III$_{b}$** was decreased.

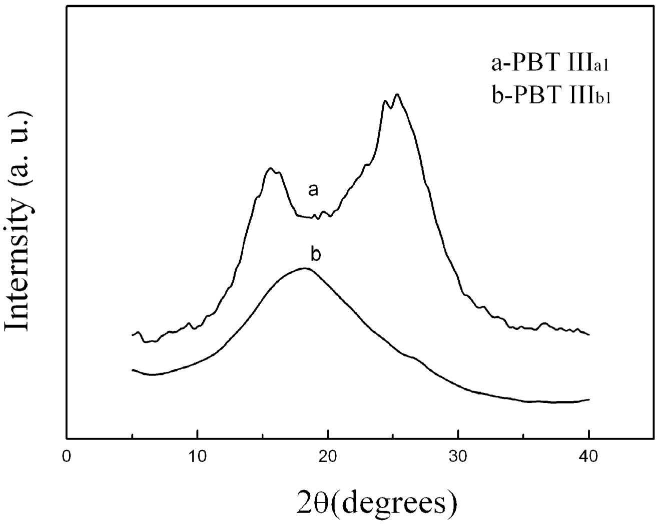


Figure 3. X-ray diffraction patterns of **PBT III$_{a1}$** and **PBT III$_{b1}$**.

Photophysical properties

UV-Vis absorption spectra of the **PBT III$_{a1}$**, **PBT III$_{a2}$**, **PBT V$_{b1}$** and **PBT V$_{b2}$** in MSA are shown in Figure 4. Although the optical absorption spectra of **PBT**s **III** prepared had the similar peak shape, it was obvious that the vibronic peak shifts of the absorption spectra of **PBT**s **III** were different. Compared with **PBT III$_{a1}$**, the

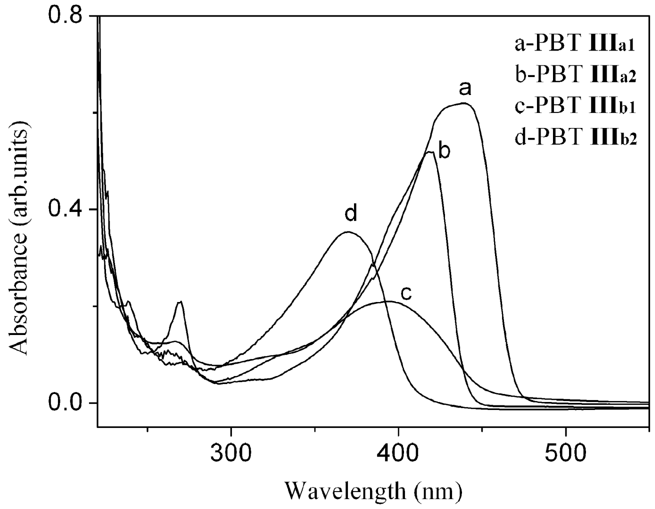


Figure 4. UV-Vis absorption spectra of **PBT**s **III** in MSA.

absorption maxima (λ_{max}) of **PBT** $\mathbf{III_{a2}}$, **PBT** $\mathbf{III_{b1}}$ and **PBT** $\mathbf{III_{b2}}$ were blue shifted from **PBT** $\mathbf{III_{a1}}$ (λ_{max}=439nm) to the position of 418, 394 and 370nm, respectively. This result was due to the introduction of etherylene or 4-*tert*-butylcyclohexylidene into polymers. Both of the groups destroyed the coplanar structure of repeating unit of **PBT** $\mathbf{III_{a1}}$ and decreased conjugation of the polymer, which led λ_{max} of **PBT** $\mathbf{III_{a2}}$ and **PBT**s $\mathbf{III_{b}}$ blue shifted. Compared with **PBT** $\mathbf{III_{a2}}$, **PBT** $\mathbf{III_{b1}}$ showed the larger blue shift, which could be ascribed to two reasons. On one hand, **PBT** $\mathbf{III_{b1}}$ was poly(bisbenzothiazole) which was different from **PBT** $\mathbf{III_{a2}}$, the poly(benzobisthiazole). 4-*tert*-butylcyclohexylidene changed the original coplanar structure of benzobisthiazole repeating unit to the nonplanar structure of bisbenzobisthiazole, and destroyed π-delocalization over the repeating units more greatly. The etherylene only decreased the conjugation between phenylene and benzobisthiazole unit. On the other hand, the lone pairs on an etheric oxygen could be conjugated with phenylene in some degree. As a result, the degree of conjugation of **PBT** $\mathbf{III_{b1}}$ was much lower than **PBT** $\mathbf{III_{a2}}$. These two types of groups also increased the optical bandgap (E_g) of poly(benzothiazole). The optical bandgap order of **PBT III** was as follows: **PBT** $\mathbf{III_{b2}}$ (E_g=2.99eV)> **PBT** $\mathbf{III_{a2}}$ (E_g=2.81eV) >**PBT** $\mathbf{III_{b1}}$ (E_g=2.73eV)>**PBT** $\mathbf{III_{a1}}$ (E_g=2.48eV).

Figure 5 shows the photoluminescence emission spectra of **PBT**s **III**. In comparison with **PBT**s $\mathbf{III_{a1}}$, the emission peaks of other **PBT**s **III** all showed the blue shift. The emission wavelength was in the range of 424-475 nm. From Figure 5, it could be found that the emission intensities of them were different. We also measured the relative photoluminescence quantum yields of all the **PBT**s **III**. The results showed the following orders: **PBT** $\mathbf{III_{b2}}$ (1.22)> **PBT** $\mathbf{III_{b1}}$ (1.18)> $\mathbf{PBTIII_{a2}}$ (0.56)> **PBT** $\mathbf{III_{a1}}$ (0.52). The relative PL quantum yield of **PBT** $\mathbf{III_{b1}}$ was much higher than that of **PBT** $\mathbf{III_{a2}}$. This result indicated it was more advantageous for 4-*tert*-butylcyclohexylidene to decrease the aggregation and improve the PL quantum yield. Compared with **PBT** $\mathbf{III_{a1}}$, **PBT** $\mathbf{III_{a2}}$ had the stronger intensities and higher PL

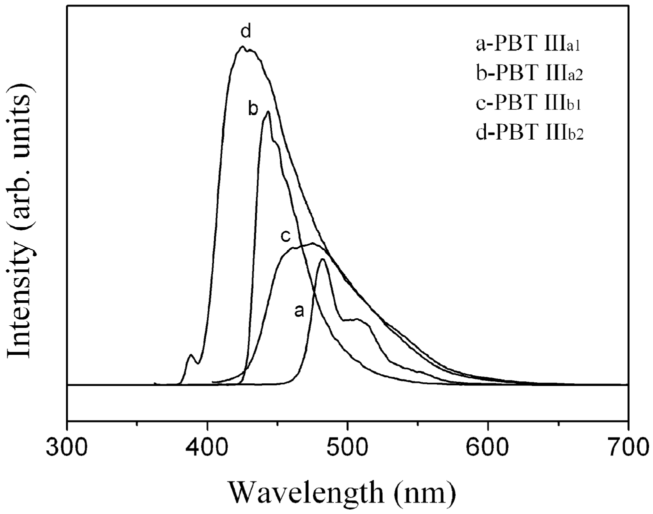


Figure 5. Photoluminescence emission spectra of **PBT**s **III.**

quantum yield as well. The same result was also found in **PBT**s **III**$_b$. This phenomenon was due to the introduction of etherylene and it might be explained by two factors. On one hand, the ether linkage increased the flexibility of polymer backbone and meanwhile it decreased intermolecular interactions between the chains as well. As a result, the interchain aggregation was decreased, which improved the PL quantum yield. On the other hand, the lone pairs on etheric oxygen occupied "lone-pair" orbitals, which could be involved in bonding with the aromatic system. The electronic transition could be thought as a π-π^* transition with significant intramolecular charge-transfer character [25]. Consequently the PL quantum yield was enhanced. As to **PBT**s **III**$_a$, the higher relative PL quantum yield of **PBT III**$_{a2}$, which could be mainly ascribed to the first reason we mentioned above. As to **PBT III**$_b$, the improved relative PL quantum yield of **PBT III**$_{b2}$ was mainly due to the second reason we mentioned because the decreased aggregation in **PBT**s **III**$_b$ was mainly decided by 4-*tert*-butylcyclohexylidene. It was also obvious that the relative PL quantum yields of **PBT**s **III**$_b$ were much higher than the corresponding polymers of **PBT**s **III**$_a$. The bulky pendant group, 4-*tert*-butylcyclohexylidene, in the backbone of **PBT**s **III**$_b$ decreased the aggregation of polymer chains efficiently and improved the photoluminescence quantum yield. Although the rigidity and the degree of π-delocalization were lower than the corresponding polymers of **PBT**s **III**$_a$, **PBT**s **III**$_b$ still had the higher relative photoluminescence quantum yields.

Conclusions

In this study we synthesized and characterized a series of poly(benzothiazole)s containing ether linkage or 4-*tert*-butylcyclohexylidene group. We compared the properties such as inherent viscosity, thermal stability, solubility, morphology and photophysical properties of these poly(benzothiazole)s in detail and established the structure-property relationships in this class of polymers. The introduction of ether linkage and the 4-*tert*-butylcyclohexylidene group into the polymer backbone led to the lower inherent viscosity of these derivatives of **PBZT**. Especially, the dramatically decreased inherent viscosities of **PBT**s **III$_b$** were due to the introduction of 4-*tert*-butylcyclohexylidene. The thermal stability of these **PBT**s was decreased and the solubility of them was enhanced. Furthermore the affection of bulky pendant group to the thermail stability and solubility was greater than that of flexible linkage. Except for **PBT III$_{a1}$**, all the other **PBT**s **III** exhibited an amorphous nature. Compared with the absorption maximum (λ_{max}) of **PBT III$_{a1}$**, λ_{max} of all the other **PBT**s **III** we investigated was blue shifted and their optical bandgap was increased. **PBT**s **III$_b$** showed larger blue shift because the introduction of aliphatic groups decreased π-delocalization over the repeating units in larger degree than ether linkage did. The emission peaks of them showed the blue shift as well. The peak intensities and the relative PL quantum yields of them were improved. The bulky pendant group of **PBT**s **III$_b$** could reduce the aggregation, which was more efficient to improve the relative PL quantum yield than the etherylene did.

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