Synthesis and Characterization of New Cardo Poly(bisbenzothiazole)s from 1,1-Bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane Dihydrochloride

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ABSTRACT: A new monomer 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride, bearing the bulky pendant 4-*tert*-butylcyclohexylidene group, was synthesized from 4-*tert*-butylcyclohexanone in three steps. Its chemical structure was characterized by ^{1}H NMR, ^{13}C NMR, MS, FTIR, and EA. Aromatic poly(bisbenzothiazole)s (PBTs **V**) were prepared from the new monomer and five aromatic dicarboxylic acids by direct polycondensation. The inherent viscosities were in the range of 0.63–2.17 dL/g. These polymers exhibited good solubility and thermal stability. Most of the prepared PBTs **V** were soluble in various polar solvents. Thermogravimetric analysis showed the decomposition temperatures at 10% weight loss that were in the range of 495–534°C in nitrogen. All the PBTs **V**, characterized by X-ray diffraction, were amorphous. The UV absorption spectra of PBTs **V** showed a range of λ_{max} from 334 to 394 nm. All the PBTs **V** prepared had evident fluorescence emission peaks, ranging from 423 to 475 nm with different intensity. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2000–2008, 2006

Key words: poly(bisbenzothiazole); 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride (BAMPBCH·2HCl); polycondensation; solubility; thermal stability

INTRODUCTION

Aromatic poly(benzothiazole)s (PBTs) constantly attract much interest because of their excellent high-temperature resistance, thermooxidative stability, high mechanical properties, and outstanding environmental resistance.[1] They are also known to have the third order nonlinear optical susceptibility.[2,3] Such exceptional properties due to its unique rigid backbone and π-conjugated structure offer a high potential for electrical and optical applications.[4–6] But these rigid-rod polymers were found to be only soluble in strong protic acids, such as methanesulfonic acid (MSA) and sulfuric acid, which adversely affected the processability, so that the potential utility of the PBTs had been restricted in many applications. Therefore, various efforts were aimed at establishing the structure–property relationships in this class of polymers, to improve the solubility of PBTs.[7,8]

The common methods to improve the solubility of aromatic heterocyclic polymers were to introduce flexible linkages in the main chain,[9–11] to reduce the packing force, or to introduce fluorine and chlorine groups.[12–14] Another successful approach was in introducing bulky pendent groups into the polymer backbone.[15–17] The 4-*tert*-butylcyclohexylidene group could be considered as a bulky cardo group. It was reported that the incorporation of 4-*tert*-butylcyclohexylidene groups into the backbone of polycarbonates, polyesters, and polyimides resulted in polymers with enhanced solubility, processability, and high heat resistance.[18–20] However, there is few literature on the characteristics of introducing 4-*tert*-butylcyclohexylidene unit into PBTs by modifying the monomer structure of diaminobenzenethiol.

In the present article, we report the synthesis of a series of novel poly(bisbenzothiazole)s (PBTs **V**) bearing 4-*tert*-butylcyclohexylidene pendent group. A new monomer, 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride (BAMPBCH·2HCl), was synthesized. The polymers were prepared from BAMPBCH·2HCl and conventional aromatic dicarboxylic acids. The properties of these polymers were also investigated.

EXPERIMENTAL

Material

4-*tert*-Butylcyclohexanone (Aldrich Chemical Company), 4,4'-sulfonyldibenzoic acid (Aldrich), 4,4'-

(hexafluoroisopropylidene)bis(benzoic acid) (TCI Chemical Company), benzophenone-4,4'-dicarboxylic acid (TCI Chemical Co.), 4,4'-dicarboxydiphenyl ether (Peakchem Company), terephthalic acid (Yi Zheng Chemical Company), potassium thiocyanate, bromine, acetic acid, tetrahydrofuran (THF), poly(phosphoric acid) (PPA) (Medicine group of China), and other chemicals were of analytical grade, except as noted.

Monomer synthesis

1,1-Bis(4-aminophenyl)-4-*tert*-butylcyclohexane

A three-necked flask fitted with a mechanical stirrer and an argon inlet was charged with a mixture of aniline (102.4 g, 1.1 mol) and aniline hydrochloride 51.8 g (0.4 mol). The mixture was stirred at 60°C. 4-*tert*-butylcyclohexanone (15.4 g, 0.1 mol) was added when the solution became clear. The mixture was stirred at 140°C for 36 h. After being cooled to room temperature, the solution was treated with NaOH aqueous solution to a pH of 10, and the oily layer was separated, washed with water to pH 7, dried by anhydrous magnesium sulfate, and distilled to remove the excess aniline. The resulting crude product was recrystallized from benzene to give 1,1-bis(4-amino-phenyl)-4-*tert*-butylcyclohexane (**I**) (18.1 g, 56.1% yield); mp: 147–148°C. ^{1}H NMR (DMSO-d_6): δ (ppm) = 0.71 (s, 9H, CH$_3$), 1.07–1.09 (br s, 3H, cyclohexylidene), 1.56–1.62 (br m, 4H, cyclohexylidene), 2.54–2.57 (br d, 2H, cyclohexylidene), 4.77 (br s, 4H, NH$_2$), 6.34–6.48 (dd, 4H, aromatic ortho to amine), 6.78–6.96 (dd, 4H, aromatic ortho to cyclohexylidene).

1,1-Bis(2-aminobenzothiazole-6-yl)-4-*tert*-butylcyclohexane

A three-necked flask fitted with a mechanical stirrer, an addition funnel, and an argon inlet was charged with potassium thiocyanate (29.2 g, 0.3 mol), **I** (16.1 g, 0.05 mol), and 240 mL of acetic acid. The mixture was stirred and cooled. A solution of bromine (19.2 g, 0.12 mol) in 5 mL of acetic acid was added to the solution dropwise. During bromine addition, an orange-red solid appeared, and was stirred at room temperature for 12 h. Three hundred and thirty milliliters of water was added, and then the mixture was heated to reflux for 2 h, cooled to room temperature, and filtered. The resulting solution was poured into large amount of water, and the white precipitate was collected by filtration. The crude product was washed with 200 mL of concentrated ammonia water and washed with water to a pH of 7. It was recrystallized from tetrahydrofuran to afford 1,1'-bis(2-aminobenzothiazole-6-yl)-4-*tert*-butylcyclohexane (**II**) (15.7 g, 72.0% yield) mp: 281–282°C. ^{1}H NMR(DMSO-d_6): δ (ppm) = 0.71 (s, 9H, CH$_3$), 1.07–1.10 (br s, 3H, cyclohexylidene), 1.63–1.79

(br m, 4H, cyclohexylidene), 2.81–2.84 (br d, 2H, cyclohexylidene), 7.02–7.05 (dd, 2H, aromatic para to S), 7.23 (s, 2H, aromatic ortho to N), 7.30–7.35 (ss, 4H, NH$_2$), 7.35–7.66 (dd, 2H, aromatic ortho to S). ^{13}C NMR (DMSO-d_6): δ (ppm) = 24.20, 28.00, 32.72, 37.56, 45.60, 48.22, 117.62, 117.98, 118.58, 120.53, 124.35, 125.75, 131.22, 131.71, 139.12, 145.63, 150.43, 150.46, 166.88, 167.10. MALDI-TOF-MS: m/z = 437 (M$^+$+1). IR (KBr): 3367 (m, N—H), 2941, 2864 (m, cyclohexylidene), 1615cm^{-1} (m, C=N).

1,1-Bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride

A three-necked flask fitted with a condenser and an inlet for argon was charged with a mixture of potassium hydroxide (29.6 g, 529 mmol) and 35 mL of deaerated water. The solution was stirred and heated at 100°C. Compound **II** (10 g, 23 mmol) was then added while the flask was swept with a stream of argon. The mixture was gradually heated up to 170°C in an argon atmosphere and refluxed for 5 h, until the evolution of carbon dioxide and ammonia ceased. The resulting yellow solution was allowed to cool, with stirring at room temperature, overnight. The mixture was added to 28 mL of deaerated water, and a clear solution was obtained by heating up to 100°C. After being cooled to room temperature, 100 mL 8N HCl was added to the solution dropwise in an argon atmosphere. The white precipitate was collected and recrystallized from 6N HCl containing Zn to afford BAMPBCH·2HCl (**III**) (5.8 g, 55.2% yield) mp: 157–158°C. ^{1}H NMR(CD$_3$OD): δ (ppm) = 0.78 (s, 9H, CH$_3$), 1.13–1.1.21 (br s, 3H, cyclohexylidene),1.76–1.91 (br m, 4H, cyclohexylidene), 2.84–2.87 (br d, 2H, cyclohexylidene), 7.25–7.32 (dd, aromatic para to SH), 7.42–7.47 (d, 2H, aromatic ortho to SH), 7.70–7.73 (d, 2H, d, 2H, aromatic ortho to NH$_3$Cl). ^{13}C NMR (CD$_3$OD): δ (ppm) = 23.62, 26.68, 31.97, 36.62, 45.70, 48.01, 123.92, 124.36, 125.96, 126.59, 126.60, 127.72, 128.05, 128.19, 131.65, 133.35, 147.00,152.12. MS (70 eV): m/z = 386 (M$^+$—2HCl). IR (KBr): 3367 (m, N—H), 2941, 2864 (m, cyclohexylidene), 2557cm^{-1} (s, SH). Elem. Anal. Calcd. for C$_{22}$H$_{32}$Cl$_2$N$_2$S$_2$: C, 57.50%; H, 7.02%; N, 6.10%. Found: C, 57.78%; H, 6.81%; N, 6.01%.

Polymer synthesis

A typical procedure for polymerization was as follows: Into a three-necked reaction flask were added accurately weighed **III** (0.50 g, 1.09 mmol) and freshly prepared PPA (80.8%, 5.63 g). The reaction flask was fitted with a mechanical stirrer and an argon inlet and outlet adaptors. The mixture was initially flushed with argon and then stirred at room temperature for 24 h, at 70°C for 36 h, in an argon atmosphere. Then the pressure was reduced until the hydrogen chloride evolu-

tion ceased, and the solution became clear. 4,4′-dicarboxydiphenyl ether (**IV$_b$**) (0.28 g, 1.09 mmol) and additional phosphorus pentoxide (2.02 g) were added to the clear amber solution. The temperature was increased to 110°C quickly and gradually to 165°C in 5 h. The following temperature profile was used during polymerization: 12 h at 165°C, 12 h at 180°C, 12 h 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 then methanol repeatedly. The brown polymer was dried at vacuum at 120°C for 2 days. PBT **V$_b$** 0.57 g (91.6% yield). ^{1}H NMR (D$_2$SO$_4$): δ (ppm) = 0.53 (s, 9H, CH$_3$), 0.81–1.20 (br s, 3H, cyclohexane), 1.39–2.12 (br d, 4H, cyclohexylidene), 2.43–3.13 (br d, 2H, cyclohexylidene), 7.1–8.24 (m,14H, aromatic). IR (KBr): 2936, 2862 (m, cyclohexylidene), 1595 (C=N), 1239 cm^{-1} (C—O—C). Elem. Anal. Calcd. for (C$_{36}$H$_{32}$N$_2$OS$_2$)$_n$: C, 75.49%; H, 5.63%; N, 4.89%. Found: C, 74.31%; H, 5.81%; N, 4.63%.

Other polymers were synthesized by an analogous procedure. Because of the high inherent viscosity in D$_2$SO$_4$, almost all the polymers were hard to be analyzed by ^{13}C NMR, except PBT **V$_e$** which can be dissolved in THF well. ^{13}C NMR(THF-d_8) of PBT **V$_e$**: δ (ppm) = 24.16, 27.05, 32.21, 37.74, 46.59, 48.47, 64.40, 64.66, 64.96, 65.28, 65.59, 118.82, 118.85, 121.33, 123.01, 123.43, 123.51, 125.97, 127.15, 127.33, 130.96, 131.22, 134.92, 135.00, 135.24, 135.40, 135.56, 136.04, 143.67, 149.61, 152.48, 152.66, 165.58, 165.80.

Measurements

NMR spectra were recorded on a Mercury Plus 400Hz spectrometer, using deutero chloroform (CDCl$_3$), perdeuterodimethyl sulfoxide (DMSO-d_6), perdeuterotetrahydrofuran (THF-d_8), or perdeutero sulfuric acid (D$_2$SO$_4$) as solvent. Mass spectra were determined on an Agilent 5973N Msd-EI mass spectrometer and an Agilent HP1100 matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF). FTIR 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°C in MSA, c = 0.5 g/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°C/min. Thermogravimetric analyses (TGA) were recorded on a Perkin–Elmer TGA7 under the protection of N$_2$. The scan rate was 10°C/min. The wide-angle X-ray diffraction 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 MSA solution by Perkin–Elmer Lambda 20

UV–vis spectrophotometer. Fluorescence spectra were recorded in MSA solution by Perkin–Elmer LS50B luminescence spectrophotometer.

RESULTS AND DISCUSSION

Monomer synthesis

The synthetic route used for the preparation of the new monomer **III** is reported in Scheme 1. It was synthesized in a three-step procedure from 4-*tert*-butylcyclohexanone. The diamine compound **I** was synthesized from the reaction of cyclohexanone, with excess aniline and aniline hydrochloride. The intermediate **II** was prepared by nucleophilic addition from **I** with thiocyanate, followed by the nucleophilic ring closure reaction between the thiourea and ortho-bromine groups.[21] Compound **II** was hydrolyzed with concentrated aqueous potassium hydroxide at 170°C, under the protection of argon. The air-sensitive dipotassium salt of 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane was acidified with 8N hydrochloric acid to give **III**. The molecular structure of **II** was confirmed by ^{1}H NMR and ^{13}C NMR spectrum. The hydrogen resonances between 0.71 and 2.84 ppm were attributed to the hydrogen atoms of 4-*tert*-butylcyclohexylidene. The resonances between 7.02 and 7.66 ppm were assigned to the hydrogen atoms of the benzothiazole. The resonances at 7.30 and 7.35 ppm assigned to hydrogen atoms of the amino group indicated that the group was connected with benzothiazole. Owing to the steric hindrance of bulky pendent group, the structure of **II** was not symmetrical completely. ^{13}C NMR showed that the chemical shift of the corresponding carbons of two benzothiazole rings were not at the same site completely. The resonances at 166.88 and 167.10 ppm were assigned to carbons of thiazole ring, which confirmed that the benzothiazole ring was formed. The molecular ion peak was found in MALDI-TOF-MS. The characteristic absorption of amino group of **II** was shown at 3367 cm^{-1} in the IR spectrum, and the absorption at 1615 cm^{-1} attributed to C=N stretching. The ^{1}H NMR and ^{13}C NMR spectra of **III** are shown in Figure 1. The resonances between 7.25 and 7.73 ppm were assigned to the hydrogen atoms of the phenyl moiety, which indicated that **II** was hydrolyzed completely. In the ^{13}C NMR spectrum, the resonances between 123.92 and 152.12 ppm were assigned to the carbons of the phenyl moiety, and the resonances of carbons of thiazole ring disappeared. The IR spectrum of **III** showed a characteristic absorption at 2557 cm^{-1} attributed to S—H. The elemental analysis value was consistent, well with those calculated for the proposed structure. These results clearly confirmed the structure of **III**.
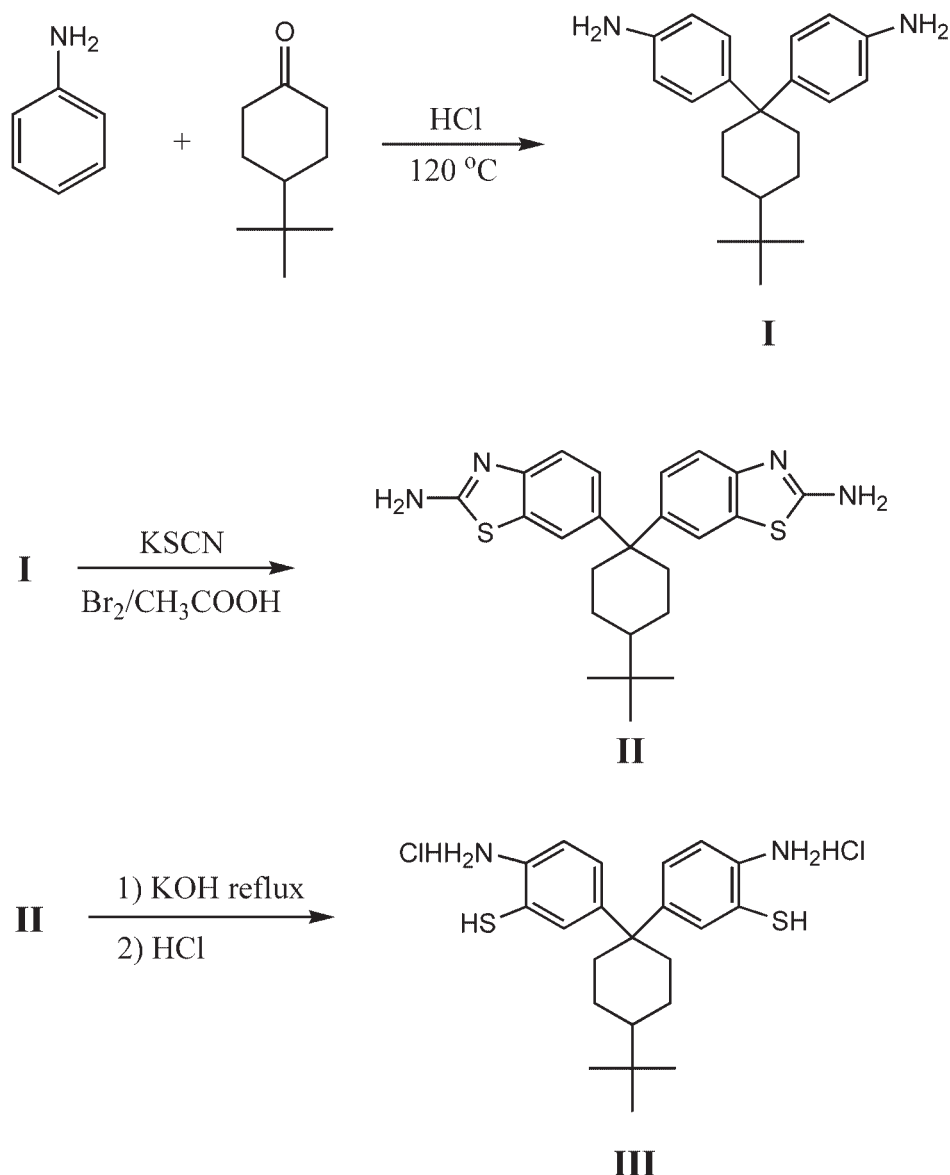
Scheme 1 Synthesis of 1,1-bis(4-amino-3-mercaptophenyl)-4-*tert*-butylcyclohexane dihydrochloride (BAMPBCH·2HCl).

Preparation of PBTs V

Scheme 2 outlines the synthetic route for the preparation of the new PBTs **V**. They were synthesized by the direct polycondensation of **III** with aromatic dicarboxylic acids (**IV**) in PPA, under an argon atmosphere. To obtain the high molecular weight polymers, it was necessary for the removal of HCl from **III** 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 is important to maintain the content of P_2O_5 to improve the viscosity of PBTs **V**. The results of polymerization are summarized in Table I. The inherent viscosities of the PBTs **V** were in the range of 0.63–2.17 dL/g.

The molecular structures of all the synthesized PBTs **V** were characterized by ^{1}H NMR, IR, and elemental analysis. Figure 2 shows the ^{1}H NMR and ^{13}C NMR spectra of PBT **V_e**. The resonances between 0.79 and 3.04 ppm were assigned to the hydrogen atoms of 4-*tert*-butylcyclohexylidene moiety, and resonances between 7.42 and 8.18 ppm were assigned to the hydrogen atoms of the phenyl moiety. A further confirmation of the polymer structure was obtained by analyzing the ^{13}C NMR spectrum of PBT **V_e**, which could be dissolved in THF-d_8. The other PBTs **V** exhibited a poor signal–noise ratio[22] in the ^{13}C NMR spectrum in D_2SO_4. The carbon resonance of PBT **V_e** at 165.58 and 165.80 ppm attributed to the carbons of thiazole ring indicated the successful formation of the thiazole ring; the resonances at
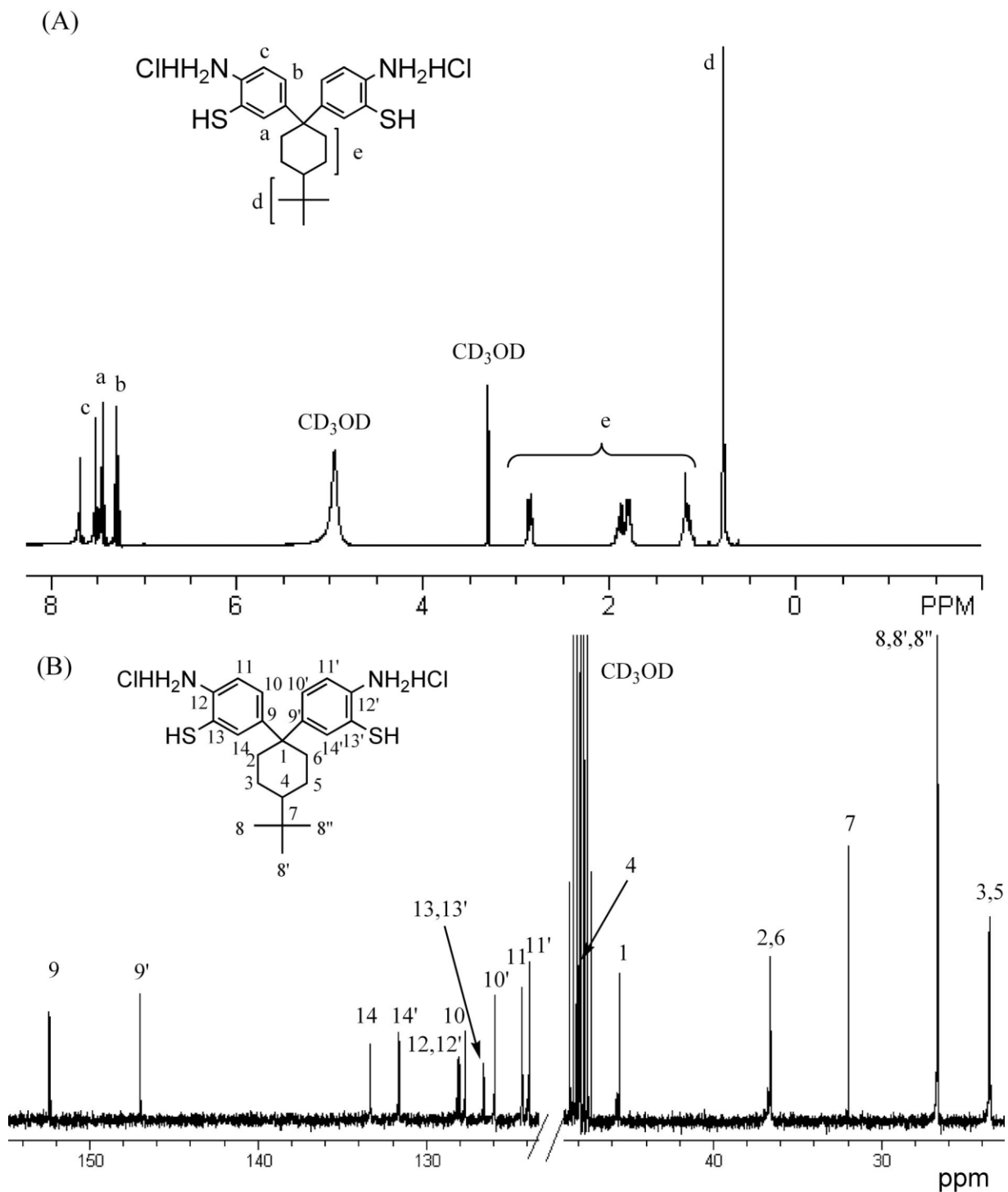
(A)

(B)

Figure 1 NMR spectra of BAMPBCH·2HCl in CD₃OD. (A) ¹H NMR and (B) ¹³C NMR.

134.92 and 135.00 ppm were assigned to the phenyl carbons attached to the thiazole. The other aromatic carbons were shown between 118.82 and 152.66 ppm. The resonances between 24.16 and 48.47 ppm were assigned to the carbons of cyclohexylidene. These results were in good agreement with the expected structure of the polymer. The molecular structures of all the synthesized PBTs **V** were

checked by FTIR spectroscopy. The characteristic absorptions of cyclohexane were shown at 2864–2941 cm⁻¹. The absorptions at 1615 and 819 cm⁻¹ were attributed to C=N stretching. The absorptions of NH and SH disappeared in comparison with the FTIR spectroscopy of **III**. The elemental analysis values were consistent, well with those calculated for the proposed structures. All of these results
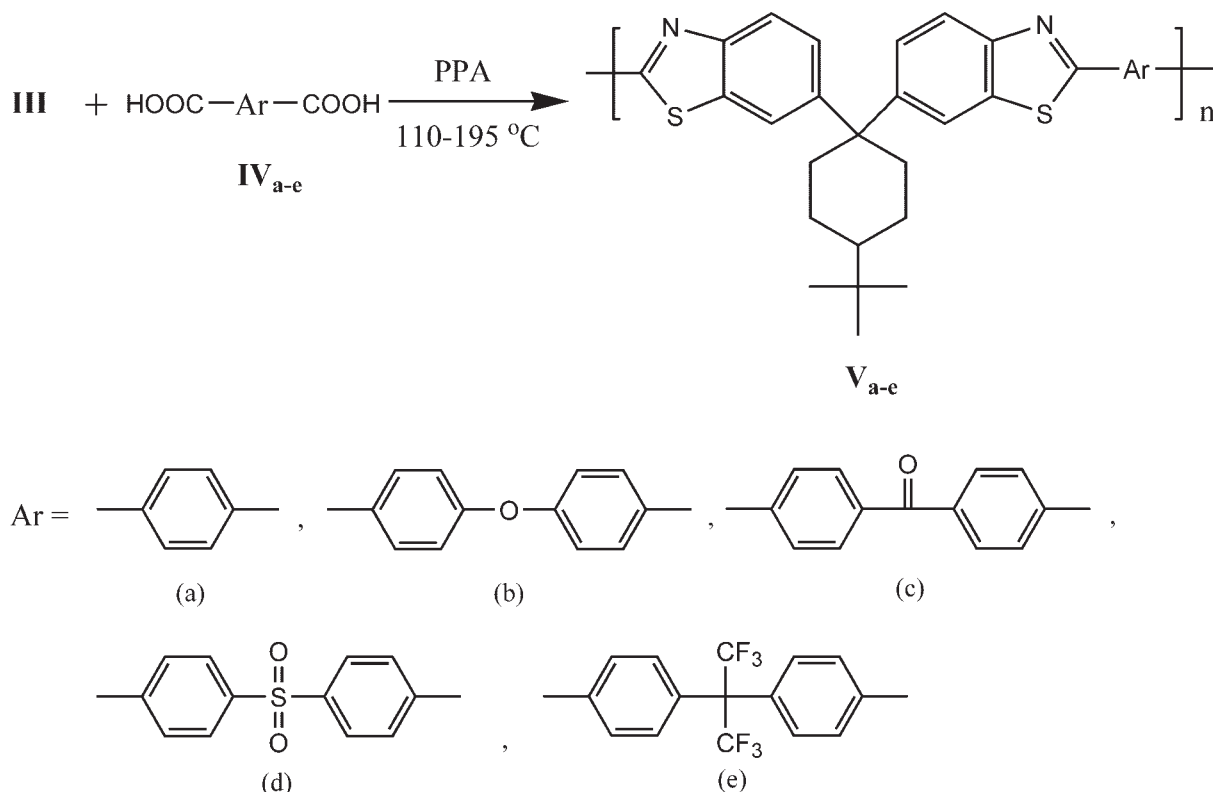
Scheme 2 Preparation of the poly(bisbenzothiazole)s.

showed a complete cyclization of intermediate open structure to benzothiazole rings.

Properties of polymers

Solubility

Qualitative solubilities of PBT **V** toward various organic solvents are reported in Table II. All PBTs **V** were soluble in MSA and concentrated sulfuric acid easily. PBT **V_a** was almost insoluble in common polar organic solvents while it could be swelled in polar organic solvent N-methyl-2-pyrrolidone (NMP). PBT **V_b**-**V_e** could be soluble in NMP and most of them were partially soluble in the aprotic polar solvents, such as N,N-dimethylformamide (DMF), dimethylacet-

amide (DMAc), and dimethyl sulfoxide (DMSO), with the exception of PBT **V_d** containing sulfone linkages which were soluble in DMAc. In less polar THF, PBT **V_e** incorporated with hexafluoroisopropylidene group showing better solubility than the other PBTs **V** prepared. In general, the solubility order of PBTs **V** is PBT **V_e** > PBT **V_d** > PBT **V_c** > PBT **V_b** > PBT **V_a**. Compared with the other PBTs **V**, the increased solubility of PBT **V_e** and PBT **V_d** was ascribed to the introduction of the sulfonyl and hexafluoroisopropylidene, which decreased the intermolecular forces between polymer chains. In addition, the highly distorted diphenylsulfonyl and diphenylhexafluoroisopropylidene units loosed the packing of the chains. Compared with the analogous polymer of PBT **V_e** reported in the literature,[12] which was prepared from 2,5-diamino-1,4-benzenedithiol dihydrochloride with aromatic dicarboxylic acids (**IV_e**), PBT **V_e** showed better solubility (see Table II). It might be explained that the bulky pendent group hampered the close packing of the chains and decreased the interchain interactions of rigid aromatic repeating units, resulting in improved solubility.

Thermal stability

The thermal stabilities of PBTs **V** were characterized by DSC and TGA, under a nitrogen atmosphere. No

TABLE I
Synthesis of Poly(bisbenzothiazole)s

Monomer code for BAMPBCH·2HCl	Polymer code	$\eta_{inh}{}^a$ (dL/g)	Yields (%)
IV_a	**V_a**	2.17	92.3
IV_b	**V_b**	0.63	91.6
IV_c	**V_c**	0.91	95.7
IV_d	**V_d**	0.65	92.5
IV_e	**V_e**	0.98	94.8

[a] Inherent viscosity of PBT **V** was measured at a concentration of 0.5 g/dL in MSA at 30°C.

(A)

(B)

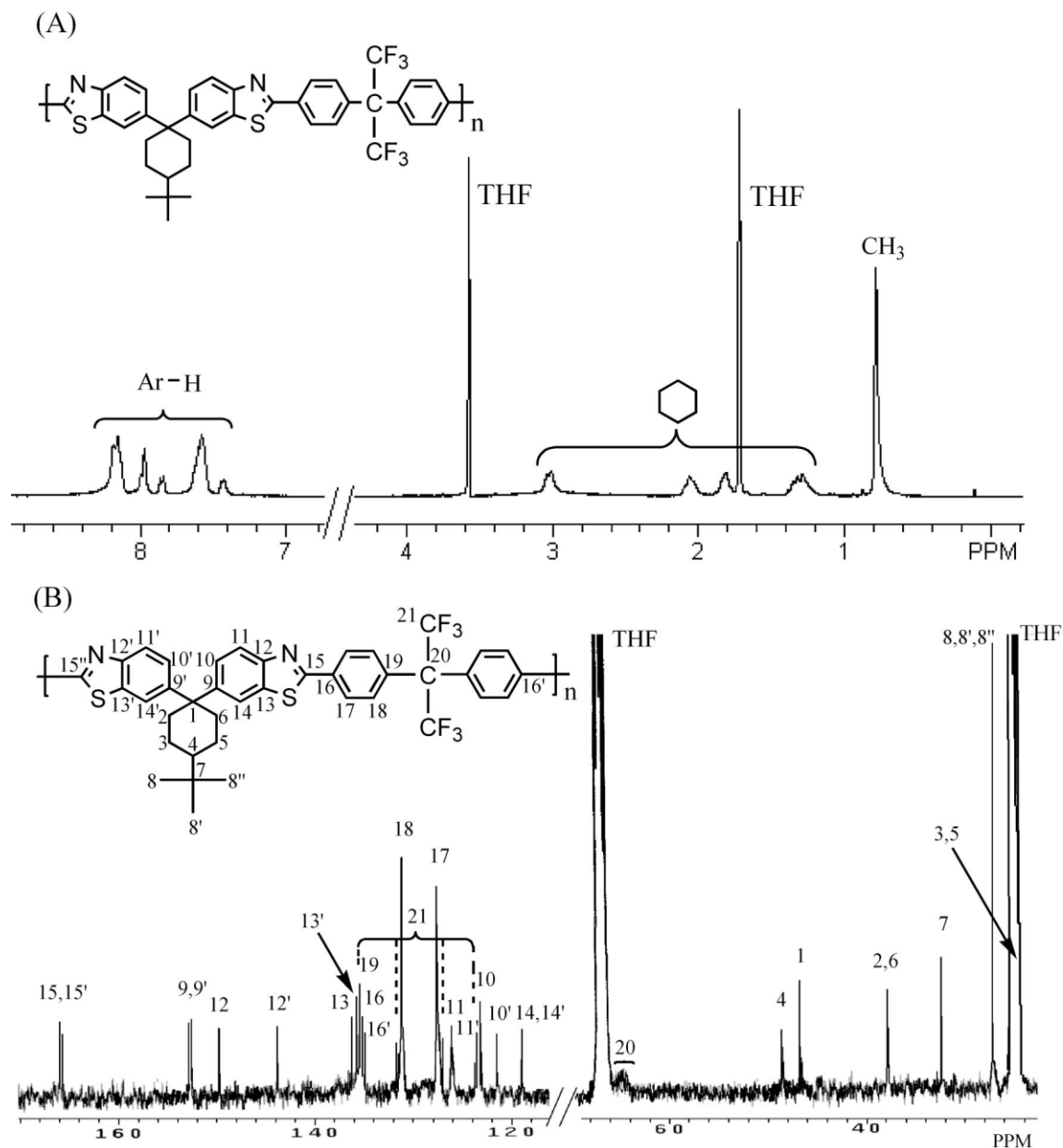**Figure 2** NMR spectrum of PBT V_e in THF-d_8. (A) ^{1}H NMR and (B) ^{13}C NMR.

glass transition temperature was observed from the DSC (10°C/min) curves for all PBTs **V** prepared. This is expected, because the overwhelming effect of the fused-ring structures resisted the segmental movement of the benzobisazole-based polymer.[23] The typical TGA curve of PBT V_e is shown in Figure 3. All PBTs **V** showed similar thermal behaviors. The temperatures at 10% weight loss and the char yields at 800°C in nitrogen atmosphere are reported in Table III. All the polymers showed excellent thermal stability. The lower thermal stability of PBT V_d might be ascribed to the degradation of diphenylsulfonyl moiety, which was cleaved to form SO_2 easily. They were stable up to 450°C, the 10% weight loss temperatures

(T_d) were between 495 and 534°C, and furthermore, they afforded an anaerobic char yield of 43–68% at 800°C in a nitrogen atmosphere. These indicated that although an aliphatic group was introduced in the polymer backbone, all PBTs **V** had good thermal stability.

XRD study

An attempt was made to estimate the crystallinity of all the PBTs **V** by means of X-ray diffractograms. All of them exhibited an amorphous nature. On one hand, the amorphous behavior of the PBTs **V** was due to the bulky-pendent group disrupting the symmetry of

TABLE II
Solubility of Poly(bisbenzothiazole)s V in Various Solvents[a]

Polymer code	Solvents[b]						
	MSA	Conc. H$_2$SO$_4$	NMP	DMF	DMAc	DMSO	THF
PBT V$_a$	++	++	+	−	−	−	−
PBT V$_b$	++	++	++	−	+	−	+
PBT V$_c$	++	++	++	+	+	+	−
PBT V$_d$	++	++	++	+	++	+	+
PBT V$_e$	++	++	++	+	+	−	++
Ref.[c]	++	++	+	○	−	−	−

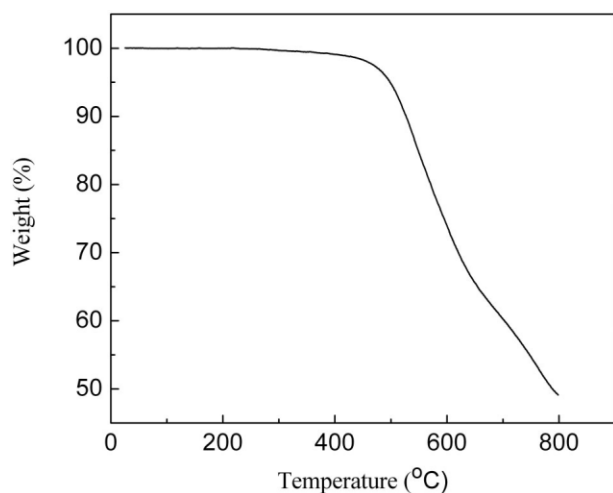[a] ++, soluble; +, partially soluble and/or swelling; −, insoluble; ○, not reported.
[b] MSA, methanesulfonic acid; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.
[c] Analogous poly(benzobisthiazoles) of PBT V$_e$ Ref. cyclohexylidene

TABLE III
Thermal Behavior of Poly(bisbenzothiazole)s

Polymer code	$T_d{}^a$ (°C)	Char yield[b] (%)
PBTV$_a$	502	52
PBTV$_b$	508	43
PBTV$_c$	534	68
PBTV$_d$	495	45
PBTV$_e$	526	46

[a] Temperature at 10% weight loss was determined by TGA in nitrogen at a heating rate of 10°C/min.
[b] Residual weight at 800°C in nitrogen.

their structures and hampering their ordering. On the other hand, the bulky-pendent group inhibited close-packing of the polymer chains, and the intermolecular force between them was reduced. As a result, crystallinity of PBTs **V** was decreased. These results were consistent with the solubility behavior.

UV–vis and fluorescence spectra

UV–vis absorption spectra of the PBTs **V** in MSA are shown in Figure 4. Though the optical absorption spectra of PBTs **V** prepared had a similar peak shape, it was obvious that the vibronic peak shift of the absorption spectrums of PBTs **V** was different. Because PBTs **V** were prepared from different dicarboxylic acids, the conjugation degree of PBTs **V$_b$**–**V$_e$** were

lower than that of PBT **V$_a$** and with the increasing ability of electron withdrawing group, the peaks were blue-shifted. Consequently, in comparison with PBT **V$_a$**, λ_{max} of PBT **V$_b$** containing ether group was blue-shifted from 394 nm (PBT **V$_a$**) to 370 nm and λ_{max} of the PBTs **V$_c$**–**V$_e$** containing electron withdrawing groups was shifted to 352, 334, and 342 nm respectively.

Figure 5 shows the fluorescence emission spectra of PBTs **V$_a$**–**V$_e$**. It was obvious that the emission intensities were different. The fluorescence intensities of PBT **V$_c$** and PBT **V$_d$** were much weaker than the other PBTs **V**. It might be ascribed to carbonyl and sulfonyl in the polymer structures influencing the luminescence behavior. The low-lying singlet excited states of carbonyl and sulfonyl compounds were (n, π*). The dominant decay mode of $S_1{}^*$ was intersystem crossing to the triplet manifold. Thus, many molecules in which $S_1{}^*$ was (n, π*) in nature exhibited very small fluorescence quantum yields. Unlike the lone-pair of electrons in a carbonyl group, in which the electrons occupied a "σ-type" orbital orthogonal to the system of the aromatic nucleus, the lone pairs on an etheric oxygen occupied "lone-pair" orbitals, which could be in-

Figure 3 TGA curve of PBT **V$_e$** with a heating rate of 10°C/min in nitrogen.
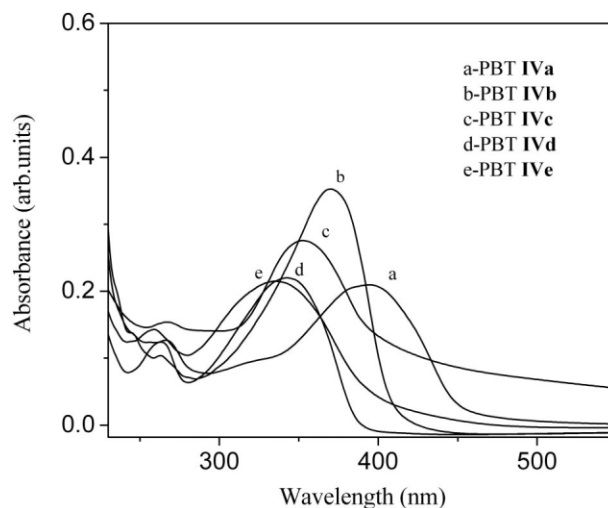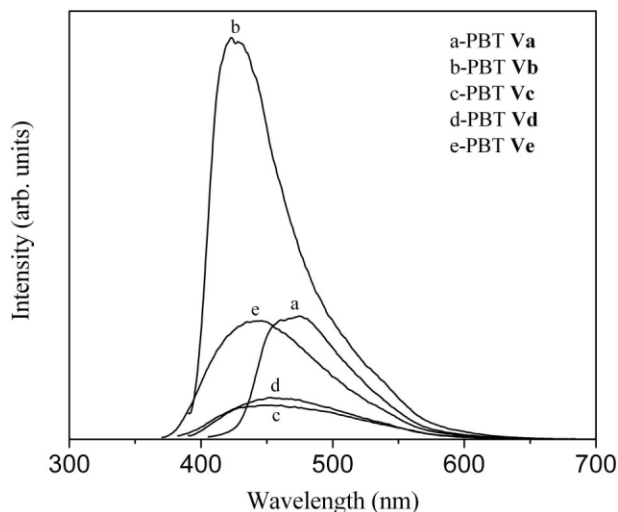

Figure 4 UV–vis absorption spectra of PBTs **V** in MSA at concentration of 4×10^{-4} gdl^{-1}.

Figure 5 FL emission spectra of PBTs **V** in MSA at concentration of 4×10^{-4} gdl^{-1}.

volved in bonding with the aromatic system. The electronic transition could be thought as a π–π* transition with significant intramolecular charge-transfer character.[24] Consequently the fluorescence intensity of PBT **V$_b$** was much enhanced. The fluorescence emission wavelength was in the range of 423–475 nm. In general, the electron withdrawing groups made the wavelength blue-shifted.

CONCLUSIONS

In this study, we had synthesized a new monomer **III** containing bulky pendant 4-*tert*-butylcyclohexylidene group in three steps successfully. A new series of PBTs **V** were prepared from this monomer and various aromatic dicarboxylic acids. The introduction of bulky pendant 4-*tert*-butylcyclohexylidene groups into the backbone of PBTs enhanced the solubility of PBTs, and some PBTs **V** possessed wider solubility, particularly in polar solvents, such as NMP, DMAc, and THF. All the PBTs **V** obtained exhibited an amorphous nature

and maintained good thermal stability. The photophysical properties of them were changed corresponding to changes in structures of the PBTs **V** prepared. Thus, these new PBTs **V** could be considered as new processible high-performance polymeric materials.

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