

# A new class of aromatic polybenzoxazoles containing *ortho*-phenylenedioxy groups

Sheng-Huei Hsiao\*, Ya-Huei Huang

Department of Chemical Engineering, Tatung University, 40 Chungshan North Road, 3rd Section, Taipei 104, Taiwan, ROC

Received 15 September 2003; received in revised form 14 January 2004; accepted 14 January 2004

Available online 12 February 2004

## Abstract

A series of poly(*o*-hydroxy amide)s having both ether and *ortho*-catenated phenylene unit in the main chain were synthesized via the low-temperature solution polycondensation of 4,4'-(1,2-phenylenedioxy)dibenzoyl chloride and 4,4'-(4-*tert*-butyl-1,2-phenylenedioxy)dibenzoyl chloride with three bis(*o*-aminophenol)s including 4,4'-diamino-3,3'-dihydroxybiphenyl, 3,3'-diamino-4,4'-dihydroxybiphenyl, and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane. The poly(*o*-hydroxy amide)s exhibited inherent viscosities in the range of 0.23–0.96 dl/g. Most of the poly(*o*-hydroxy amide)s were soluble in polar organic solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) and could afford flexible and tough films by solution casting. Subsequent thermal cyclodehydration of the poly(*o*-hydroxy amide)s afforded polybenzoxazoles. However, the polybenzoxazoles were organic-insoluble except for those with the hexafluoroisopropylidene group. The polybenzoxazoles exhibited glass-transition temperatures ( $T_g$ ) in the range of 200–232 °C by DSC and softening temperatures ( $T_s$ ) of 250–256 °C by thermomechanical analysis. Thermogravimetric analyses indicated that most polybenzoxazoles were stable up to 500 °C in air or nitrogen. The 10% weight loss temperatures were recorded in the ranges of 546–606 °C in air and 574–631 °C in nitrogen.

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**Keywords:** Polybenzoxazoles; Poly(*o*-hydroxy amide)s; *Ortho*-phenylenedioxy; Thermal properties; Structure–property relations

## 1. Introduction

Aromatic polybenzoxazoles (PBOs) are a class of heterocyclic polymers that have excellent thermal stability, high mechanical properties, good environmental resistance, and superior hydrolytic stability [1–4]. High-modulus fibers can be produced by the spinning of liquid-crystalline solutions of rod-like aromatic PBOs in sulfuric acid or polyphosphoric acid [5,6]. An important example is Zylon commercialized by Toyobo in 1998, which exhibits superior heat and flame resistance and ultra-high strength. The excellence of mechanical property and thermal stability on PBO fibers comes from the

extreme rigidity of PBO molecule. However, most aromatic PBOs cannot be fabricated into flexible and tough films due to the rigid rod polymer nature. This may restrict their applications in some fields. Consequently, much effort has been placed upon modifying properties through the incorporation of flexible linkages in the polymer backbone and/or bulky side group along the main chain [7–14]. It has been reported that polyimides having *ortho*-linked aromatic units in the main chain exhibit a good combination of properties including processability, either by solution or melt processing [15–17]. Recently, we have demonstrated that the combination of *ortho*-phenylene units and the *tert*-butyl group could further improve processability and film toughness in polyamides [18] and polyimides [19]. The present study deals with the synthesis of the *ortho*-linked aromatic poly(*o*-hydroxy amide)s by the polymerization of bis(ether-acyl chloride) monomers,

\* Corresponding author. Tel.: +886-2-25925252x2977; fax: +886-2-25861939.

E-mail address: [shhsiao@ttu.edu.tw](mailto:shhsiao@ttu.edu.tw) (S.-H. Hsiao).

4,4'-(1,2-phenylenedioxy)dibenzoyl chloride (**1**) and 4,4'-(4-*tert*-butyl-1,2-phenylenedioxy)dibenzoyl chloride (*t*-Bu-**1**) with aromatic bis(*o*-aminophenols). The basic properties such as solubility and thermal properties of the obtained poly(*o*-hydroxy amide)s and their thermally converted PBOs were investigated. This study focused on the *ortho*-substitution effect on PBOs' properties, such as film-forming capability and film properties,  $T_g$ 's and softening temperatures, and thermal and thermo-oxidative stability.

## 2. Experimental

### 2.1. Materials

The bis(ether-acyl chloride) monomers, 4,4'-(1,2-phenylenedioxy)dibenzoyl chloride (**1**) (m.p. 101 °C) and 4,4'-(4-*tert*-butyl-1,2-phenylenedioxy)dibenzoyl chloride (*t*-Bu-**1**) (m.p. 127 °C), were prepared by chlorinating the precursor dicarboxylic acids [18,20] with thionyl chloride and a few drops of *N,N*-dimethylformamide (DMF) as the catalyst. The aromatic bis(*o*-aminophenol) monomers, that include 4,4'-diamino-3,3'-dihydroxybiphenyl (**2**), 3,3'-diamino-4,4'-dihydroxybiphenyl (**3**), and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (**4**), were of high purity and used as received (all from TCI). *N*-methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Propylene oxide (PO) (Wako) was used as received.

### 2.2. Synthesis of poly(*o*-hydroxy amide)s

The low-temperature solution polycondensation technique [21] was employed in this study. A typical procedure for the synthesis of poly(*o*-hydroxy amide) **5** is as follows. In a 50 ml flask, a solution of 0.2163 g (1 mmol) of bis(*o*-aminophenol) **2** was dissolved in 5 ml of NMP and maintained at -10 to 0 °C in an ice-acetone bath. To this solution 0.3 ml of PO was added, and then 0.3873 g (1 mmol) of diacyl chloride **1** was added all at once. The reaction was carried out at -10 to 0 °C in the initial 2 h and continued at room temperature overnight. As the polycondensation proceeded, the reaction mixture became increasingly viscous. The resulting viscous polymer solution was poured slowly into 200 ml of methanol to give a pale-brown fiber-like precipitate that was collected by filtration, washed thoroughly with methanol and hot water, and dried. Yields were usually quantitative. The inherent viscosity of the obtained poly(*o*-hydroxy amide) **5** was 0.73 dl/g measured in *N,N*-dimethylacetamide (DMAc) at a concentration of 0.5 g/dl at 30 °C.

### 2.3. Film preparation and thermal cyclodehydration to polybenzoxazoles

A polymer solution for preparing the film was made by dissolving about 0.6 g of the poly(*o*-hydroxy amide) sample in 6 ml of DMAc. The solution was poured into a glass culture dish of 9 cm diameter, which was placed in a 90 °C oven for 12 h for the removal of the solvent. The obtained semidried polymer film was stripped from the glass substrate and further dried in vacuo at 160 °C for 8 h. The conversion of poly(*o*-hydroxy amide)s to polybenzoxazoles was carried out by heating the above fabricated polymer films at 200 °C for 30 min, 250 °C for 30 min, 300 °C for 30 min, and 320 °C for 1 h under a nitrogen atmosphere.

### 2.4. Characterization methods

Inherent viscosities ( $\eta_{inh}$ ) for a polymer solution of 0.5 g/dl in DMAc were determined with a Cannon-Fenske viscometer at 30 °C. IR spectra were recorded using a Horiba FT-720 Fourier-transform infrared (FTIR) spectrophotometer on solution-cast films. An Instron universal tester model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the polymer film samples. A gauge length of 2 cm and a crosshead speed of 5 mm/min were used for this study. Measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and about 50–60  $\mu$ m thick), and an average of at least five individual determinations was used. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered  $\text{Cu-K}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) (operating at 40 kV and 20 mA). The scanning rate was 2°/min over a range of  $2\theta = 5\text{--}45^\circ$ . Differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen.  $T_g$ 's were determined in the temperature range from 40 to 400 °C and with a heating rate of 20 °C/min in a nitrogen atmosphere. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were carried out from 30 to 300 °C at a scan rate of 10 °C/min using a penetration probe of 1.0 mm diameter under an applied constant load of 10 mN. Softening temperatures ( $T_s$ ) were taken as the onset temperature of probe displacement on the TMA traces. Thermogravimetric analysis (TGA) was performed using a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 3–5 mg samples under a nitrogen or air stream (flow rate 20 cm<sup>3</sup>/min) at a heating rate of 20 °C/min.

### 3. Results and discussion

#### 3.1. Polymer synthesis

The PBOs in this study were synthesized in a classical two-step procedure by the initial formation of soluble poly(*o*-hydroxy amide)s through low-temperature solution polycondensation of aromatic diacid chlorides with bis(*o*-aminophenols) followed by thermal cyclodehydration [21]. The structures and codes of the monomers and polymers are shown in Scheme 1.

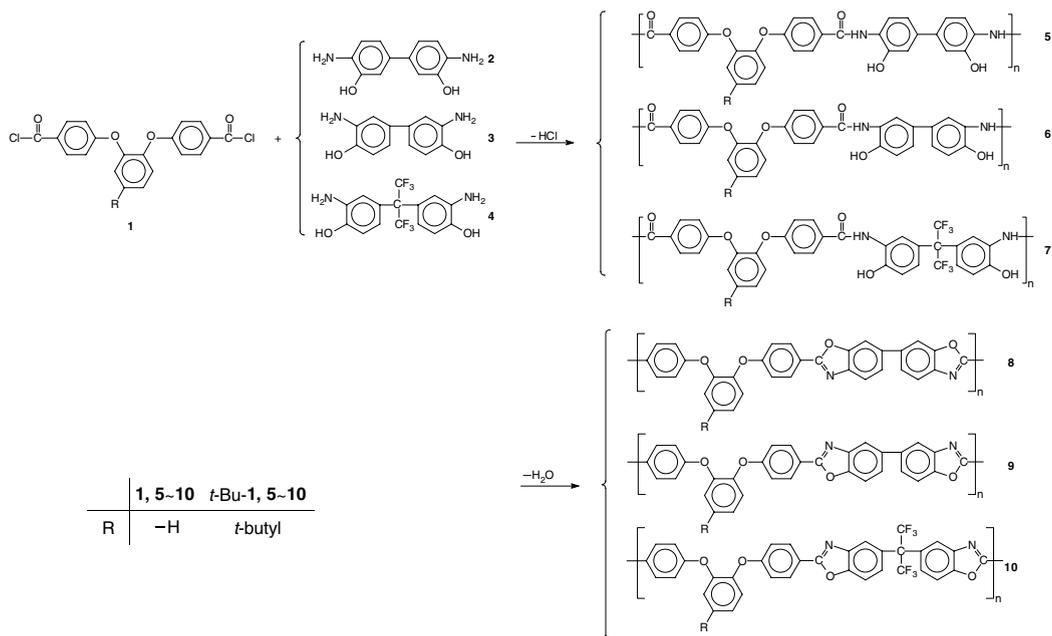
The poly(*o*-hydroxy amide)s as PBO precursors were prepared by the low-temperature solution polycondensation of aromatic diacyl chlorides **1** and *t*-Bu-**1** with three structurally different bis(*o*-aminophenols) **2** to **4** in NMP solution in the presence of PO as the acid acceptor at  $-10$  to  $0$  °C in the initial 2 h and then at room temperature overnight (for  $\approx 10$  h). As shown in Table 1, the inherent viscosities of the poly(*o*-hydroxy amide)s were in the range 0.23–0.96 dl/g. The polymers (**7** and *t*-Bu-**7**) derived from the hexafluoroisopropylidene (6F)-containing bis(*o*-aminophenol) **4** had relatively lower inherent viscosities and afforded brittle films, which may be attributable to low nucleophilicity of the fluorine-containing monomer caused by the presence of electron-withdrawing 6F groups. The other poly(*o*-hydroxy amide)s could be solution cast into strong and flexible films, indicative of high molecular weight polymers.

All of the precursor poly(*o*-hydroxy amide)s could be thermally cyclodehydrated to the corresponding PBOs in the solid state by heating the fabricated films at ele-

vated temperatures. The conversion process could be monitored by means of IR spectroscopy. Fig. 1 shows the IR spectra of a thin-film sample of poly(*o*-hydroxy amide) **5** heated sequentially at 250, 300, and 320 °C. The as-prepared poly(*o*-hydroxy amide) film exhibited the characteristic absorption bands around  $3410$   $\text{cm}^{-1}$  (N–H stretching),  $3000$ – $3400$   $\text{cm}^{-1}$  (O–H stretching),  $1650$   $\text{cm}^{-1}$  (amide C=O stretching), and  $1530$   $\text{cm}^{-1}$  (N–H bending). The peak intensities decreased gradually with increasing curing temperatures and disappeared completely at 320 °C for 1 h, whereas two new characteristic absorptions for benzoxazole at  $1590$   $\text{cm}^{-1}$  (C=N stretching) and  $1055$   $\text{cm}^{-1}$  (C–O stretching) were clearly observed. This conversion also could be confirmed by the DSC and TGA experiments, as discussed subsequently.

#### 3.2. Polymer properties

The solubility behavior of the poly(*o*-hydroxy amide)s and PBOs was qualitatively tested in various organic solvents, and the results are summarized in Table 2. As can be seen, most poly(*o*-hydroxy amide)s were readily soluble at room temperature in polar aprotic solvents such as NMP, DMAc, DMF, and DMSO. Possibly due to lower cohesive force caused by the 6F groups and the lower molecular weights of the polymers, poly(*o*-hydroxy amide) **7** and *t*-Bu-**7** were also soluble in less polar *m*-cresol, sulfolane and tetrahydrofuran (THF). On the other hand, the PBOs revealed a significantly decreased solubility. Except for the



Scheme 1. Synthesis of poly(*o*-hydroxy amide)s and polybenzoxazoles.

Table 1  
Inherent viscosity and film quality of poly(*o*-hydroxy amide)s

Polymer code	$\eta_{inh}^a$ (dl/g)	Film quality <sup>b</sup>
<b>5</b>	0.73	Flexible, dark brown
<b>6</b>	0.81	Flexible, dark brown
<b>7</b>	0.23	Brittle, pale yellow
<i>t</i> -Bu- <b>5</b>	0.77	Flexible, dark brown
<i>t</i> -Bu- <b>6</b>	0.96	Flexible, dark brown
<i>t</i> -Bu- <b>7</b>	0.26	Brittle, pale yellow

<sup>a</sup> Measured at a concentration of 0.5 g/dl in DMAc at 30 °C.

<sup>b</sup> Films were cast by slow evaporation of polymer solutions in DMAc and further dried in vacuo at 160 °C for 8 h.

6F group-containing PBOs **10** and *t*-Bu-**10**, all the other PBOs were insoluble in any test organic solvents because of the existence of rigid rod-like bis(*p*-phenylenebenzoxazole) segments in their polymer backbones.

Crystallinity of all the poly(*o*-hydroxy amide)s and PBO films was measured by WAXD studies. All of these polymers exhibited essentially amorphous WAXD patterns because of the lateral arrangement of *ortho*-phenylene units. Most of the *tert*-butyl group-containing polymers showed almost completely amorphous patterns due to the fact that the bulky side groups increased the disorder in the repeating unit and interfered with the

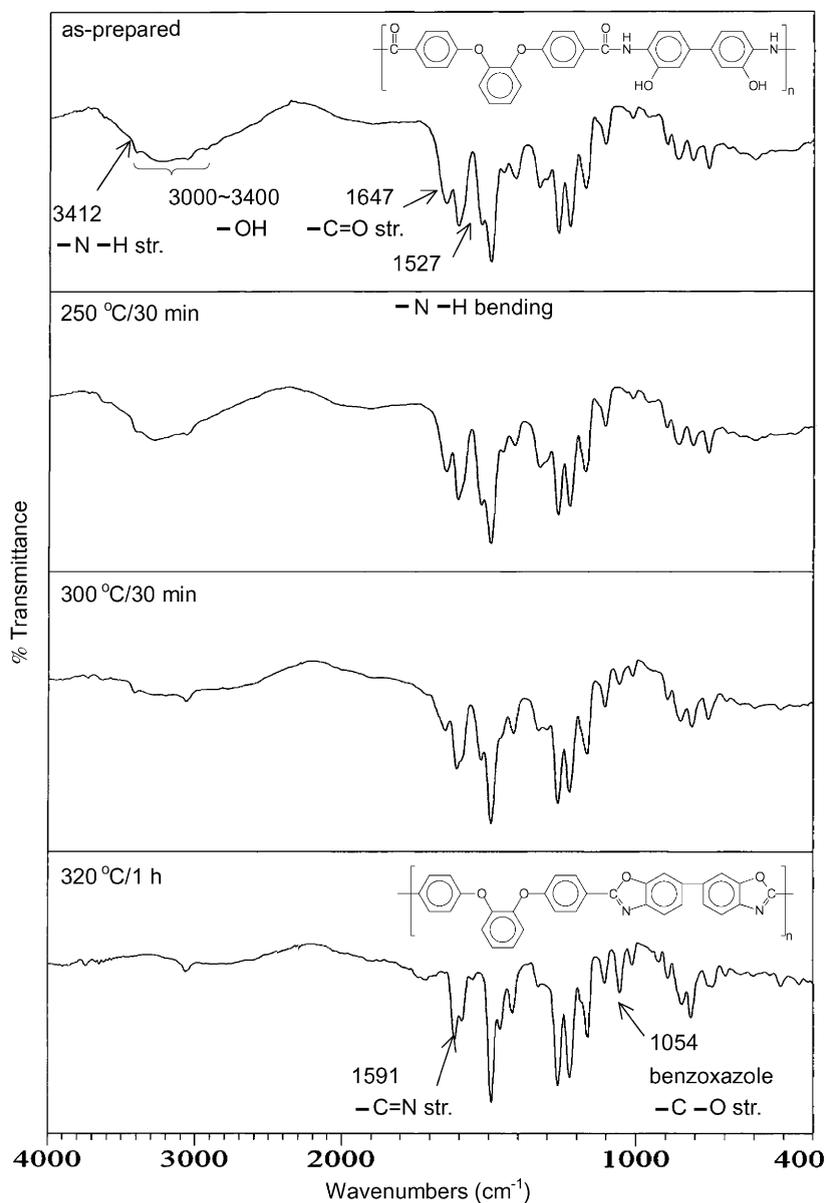


Fig. 1. IR spectra of poly(*o*-hydroxy amide) **5** after sequential heating at indicated temperatures and time.

Table 2  
Solubility behavior of poly(*o*-hydroxy amide)s and polybenzoxazoles

Polymer code	Solvent <sup>a</sup>								
	NMP	DMAc	DMSO	DMF	<i>m</i> -Cresol	Sulfolane	THF	Chloroform	<i>o</i> -DCB
<b>5</b>	+	+	+	+	–	–	–	–	–
<b>6</b>	+	+	+	+	–	–	–	–	–
<b>7</b>	+	+	+	+	+	+h	+h	–	–
<i>t</i> -Bu-5	+	+	+	+	–	–	–	–	–
<i>t</i> -Bu-6	+	+	+	+	–	–	–	–	–
<i>t</i> -Bu-7	+	+	+	+	+	+h	+	–	+h
<b>8</b>	–	–	–	–	–	–	–	–	–
<b>9</b>	–	–	–	–	–	–	–	–	–
<b>10</b>	+	+	+	–	+	–	+	+	–
<i>t</i> -Bu-8	–	–	–	–	–	–	–	–	–
<i>t</i> -Bu-9	–	–	–	–	–	–	–	–	–
<i>t</i> -Bu-10	+	+	+	+h	+	–	+	–	+h

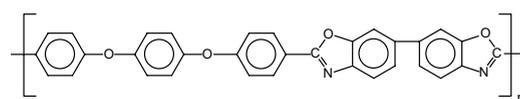
+: soluble at room temperature; +h: soluble on heating; –: insoluble even on heating; NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; *o*-DCB: 1,2-dichlorobenzene.

<sup>a</sup>Qualitative solubility was tested with 10 mg sample in 1 ml solvent.

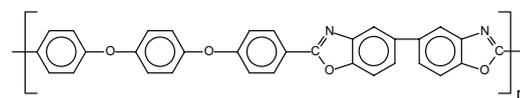
close chain packing. The poly(*o*-hydroxy amide)s and PBOs that could be fabricated into flexible, creasable thin films were subjected to tensile test. The tensile properties of these flexible films are summarized in Table 3. These films exhibited tensile strengths of 65–108 MPa, elongations to break of 6–13%, and tensile moduli of 1.5–2.1 GPa. In general, PBOs showed a lower tensile strength and elongation to break as compared with their corresponding poly(*o*-hydroxy amide) precursors. The deteriorating effect on the mechanical properties of PBO films may be attributed to stress buildup and chain shrinkage upon thermal cyclodehydration. As reported previously [10], the PBOs (Ref 1 and Ref 2) derived from 4,4'-(1,4-phenylenedioxy)dibenzoyl chloride and bis(*o*-aminophenols) **2** and **3** were semicrystalline and afforded highly brittle films. In contrast, the *ortho*-catenated counterparts PBOs **8** and **9** were amorphous in nature and gave flexible and tough films. Thus, the incorporation of *ortho*-substituted units resulted in a significant decrease in crystallinity and an enhanced film quality.

Table 3  
Thin-film tensile properties of poly(*o*-hydroxy amide)s and polybenzoxazoles

Polymer code	Strength to break (MPa)	Elongation to break (%)	Initial modulus (GPa)
<b>5</b>	108	12	2.1
<b>6</b>	99	13	1.5
<i>t</i> -Bu-5	65	6	1.7
<i>t</i> -Bu-6	94	9	2.0
<b>8</b>	98	10	2.2
<b>9</b>	88	11	2.0
<i>t</i> -Bu-8	52	4	2.3
<i>t</i> -Bu-9	77	8	2.0



Ref 1



Ref 2

The thermal properties of the poly(*o*-hydroxy amide)s and PBOs were evaluated by DSC, TMA and TGA techniques. The relevant results are reported in Table 4. A typical pair of DSC curves of poly(*o*-hydroxy amide) *t*-Bu-5 and the corresponding PBO *t*-Bu-8 are illustrated in Fig. 2. When heated from 50 to 400 °C at 20 °C/min in nitrogen, poly(*o*-hydroxy amide) *t*-Bu-5 showed a discernible glass transition at 182 °C and a strong endothermic peak around 250–350 °C that was attributed to loss of water during the formation of oxazole ring. After quenching from 400 °C, the PBO *t*-Bu-8 formed in situ during the first heating scan revealed an obvious  $T_g$  at 232 °C in the subsequent DSC heating scan. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Table 4. Except for **5** and **6**, all the other poly(*o*-hydroxy amide)s displayed discernible glass transitions between 129 and 190 °C in the DSC traces. All the poly(*o*-hydroxy amide)s exhibited strong endothermic peaks in the region of 250–350 °C. As can be seen from the DSC thermograms, all the poly(*o*-hydroxy amide)s were almost completely converted to the corresponding PBOs

Table 4  
Thermal properties of poly(*o*-hydroxy amide)s and polybenzoxazoles

Poly( <i>o</i> -hydroxy amide)s			Polybenzoxazoles				Char yield <sup>g</sup> (%)		
Code	$T_g^a$ (°C)	$T_o^b$ (°C)	$T_p^c$ (°C)	Code	$T_g^d$ (°C)	$T_s^e$ (°C)		$T_d^f$ (°C)	
							In air	In N <sub>2</sub>	
<b>5</b>	–	239	300	<b>8</b>	224	250	606	620	71
<b>6</b>	–	236	300	<b>9</b>	228	250	579	631	69
<b>7</b>	129	242	295	<b>10</b>	200	–	577	596	61
<i>t</i> -Bu- <b>5</b>	182	242	279	<i>t</i> -Bu- <b>8</b>	232	256	559	581	57
<i>t</i> -Bu- <b>6</b>	190	243	296	<i>t</i> -Bu- <b>9</b>	232	253	549	586	60
<i>t</i> -Bu- <b>7</b>	150	246	306	<i>t</i> -Bu- <b>10</b>	215	–	546	574	55

<sup>a</sup> Temperature at the middle point of baseline shift on the first DSC heating trace, with a heating rate of 20 °C/min in nitrogen.

<sup>b</sup> Extrapolated onset temperature of the endothermic peak.

<sup>c</sup> Endothermic peak temperature.

<sup>d</sup> Midpoint temperature of baseline shift on the second DSC heating trace of the sample after rapid cooling from 400 °C in nitrogen.

<sup>e</sup> Onset temperature of probe displacement on the TMA trace, in which the TMA experiments were conducted with a penetration probe of 1.0 mm diameter and using an applied constant load of 10 mN with a heating rate of 10 °C/min.

<sup>f</sup> The temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

<sup>g</sup> Residual weight % when the samples were heated to 800 °C in nitrogen.

when heated to 350–400 °C at a scan rate of 20 °C/min in nitrogen. All the PBOs showed enhanced  $T_g$  values (200–232 °C) in comparison with the corresponding precursor poly(*o*-hydroxy amide)s because of the increased chain stiffness. Both the poly(*o*-hydroxy amide)s and PBOs containing the 6F group in the backbone showed relatively lower  $T_g$ 's than the corresponding analogues derived from bis(*o*-aminophenols) **2** and **3** because of more flexible backbones and less interchain interactions caused by the bulky 6F groups. The softening temperatures ( $T_s$ ) (may be referred as apparent  $T_g$ ) of the PBO films were determined by the TMA method using a

loaded penetration probe. They were read from the onset temperature of the probe displacement on the TMA trace. A typical TMA thermogram for PBO *t*-Bu-**8** is illustrated in Fig. 3, and this polymer had  $T_s$  of 256 °C according to the above definition. The softening temperature ( $T_s$ ) values measured by TMA are also listed in Table 4. As can be seen, in most cases the  $T_s$  values obtained by TMA are slightly higher than the  $T_g$  values measured by the DSC experiments. These differences may be attributed to the different heating story of the samples and the distinct nature of these two testing methods.

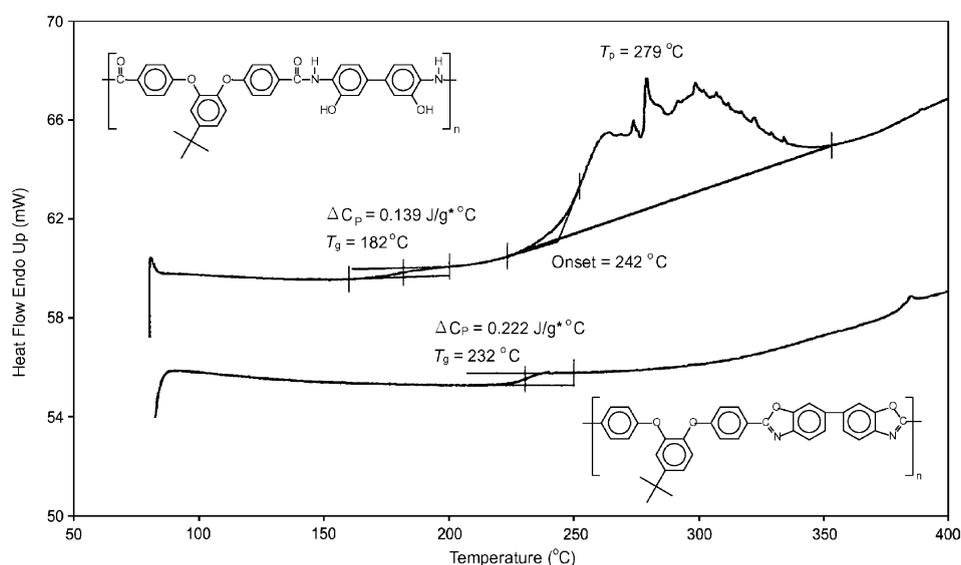


Fig. 2. DSC thermograms of poly(*o*-hydroxy amide) *t*-Bu-**5** and polybenzoxazole *t*-Bu-**8** at heating of 20 °C/min in nitrogen.

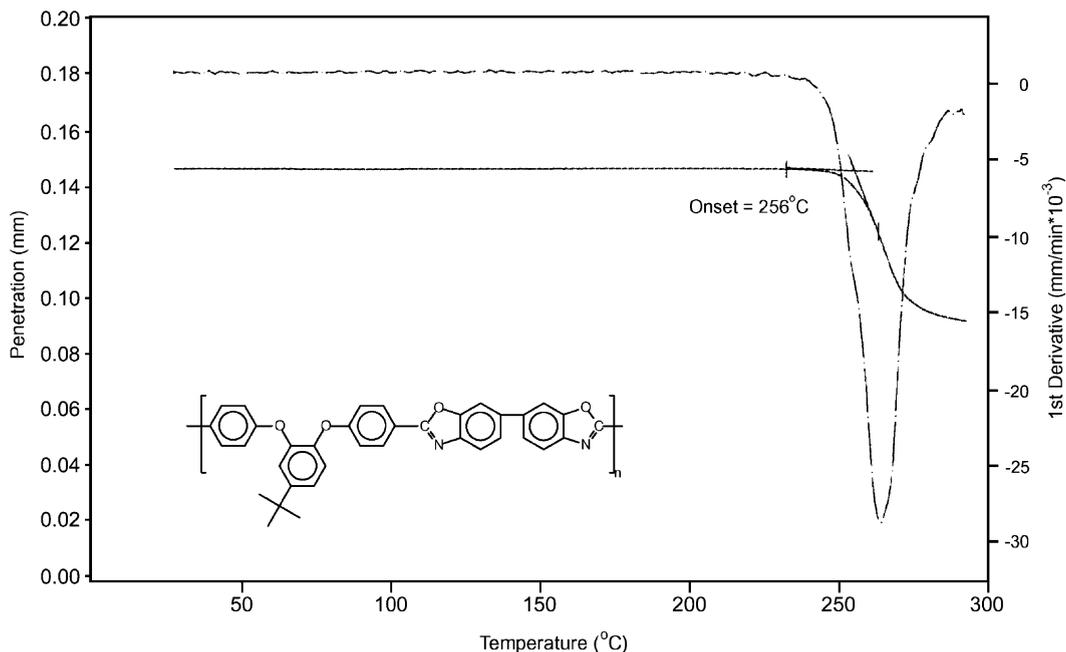


Fig. 3. The TMA curve of polybenzoxazole *t*-Bu-8.

The cyclodehydration of precursor poly(*o*-hydroxy amide)s were also monitored by dynamic TGA. The TGA thermograms of all poly(*o*-hydroxy amide)s revealed an initial weight loss in the approximate temperature range of 250–350 °C (Fig. 4). The weight loss is due to thermal cyclodehydration of the poly(*o*-hydroxy amide), which also agrees well with the strong endo-

thermic peak on the DSC trace. Fig. 5 illustrates two typical sets of the TGA curves for the PBOs **8** and *t*-Bu-**8** in both air and nitrogen atmospheres. These PBOs all possessed excellent thermal stability in nitrogen, since in no case they begin to breakdown before 500 °C. In air, the gradual decomposition of these polymers occurred from about 400 °C. The earlier decomposition in air

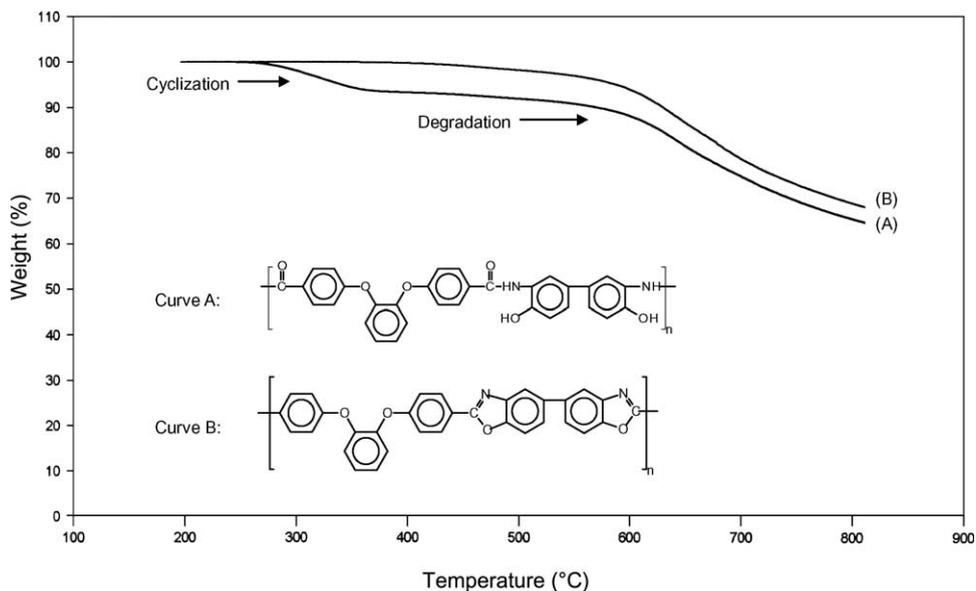


Fig. 4. TGA curves of poly(*o*-hydroxy amide) **6** (A) and polybenzoxazole **9** (B) with a heating rate of 20 °C/min.

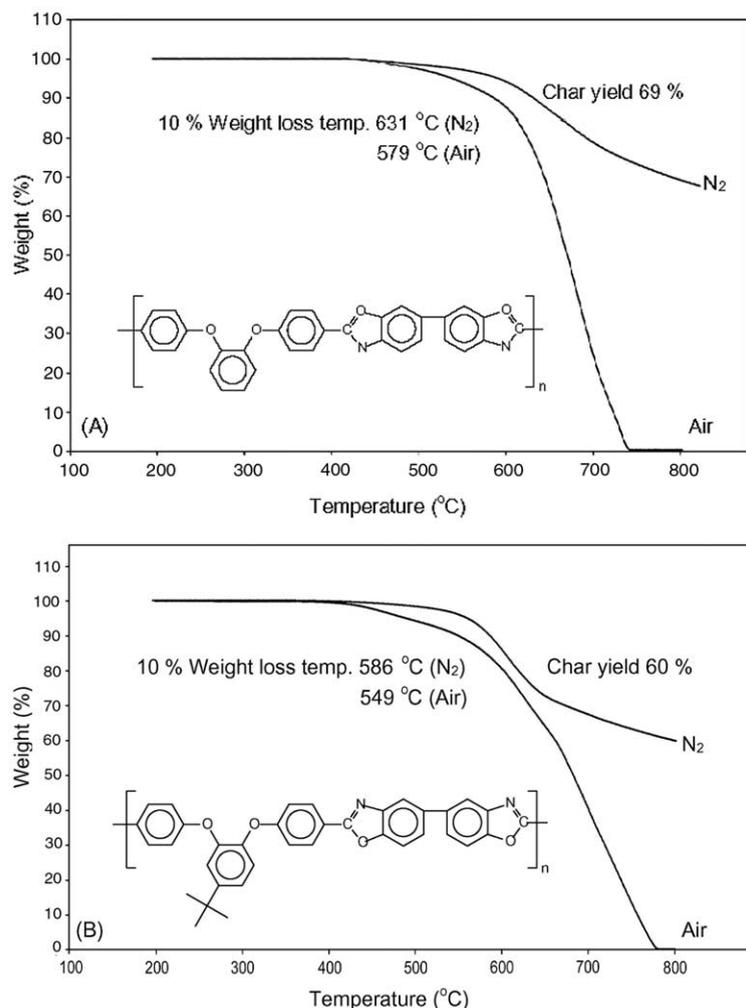


Fig. 5. TGA curves of polybenzoxazoles **8** (A) and *t*-Bu-**8** (B) with a heating rate of 20 °C/min.

indicated that these PBOs exhibited a slightly lower oxidative stability. This result is similar to that reported in literature [5,9]. As shown in Table 4, these PBOs showed decomposition temperatures ( $T_d$ ) at which a 10% weight loss was recorded in the ranges of 574–631 °C in nitrogen and 546–606 °C in air, with more than 55% residue remaining when they were heated to 800 °C in nitrogen. All the *t*-Bu-**8** to **10** series PBOs exhibited a lower  $T_d$  value as compared to their corresponding counterparts without the *t*-butyl group. This is reasonable when considering the less stable aliphatic segments.

#### 4. Conclusions

A series of poly(*o*-hydroxy amide)s were successfully prepared from 4,4'-(1,2-phenylenedioxy)dibenzoyl chlo-

ride (**1**) and 4,4'-(4-*tert*-butyl-1,2-phenylenedioxy)dibenzoyl chloride (*t*-Bu-**1**), respectively, with bis(*o*-aminophenols) such as 4,4'-diamino-3,3'-dihydroxybiphenyl (**2**), 3,3'-diamino-4,4'-dihydroxybiphenyl (**3**), and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (**4**) by the low-temperature solution polycondensation in NMP/PO. These poly(*o*-hydroxy amide)s were easily soluble in a variety of organic solvents. The poly(*o*-hydroxy amide)s derived from bis(*o*-aminophenols) **2** and **3** could be solution cast into flexible and tough films, and their thermally converted PBO films were also flexible and creasable. All of the poly(*o*-hydroxy amide)s and PBOs were amorphous materials as evidenced by WAXD patterns. The prepared PBOs had  $T_g$ 's in the range of 200–232 °C and were generally stable up to 500 °C. The large window between  $T_g$  and decomposition temperature makes these *ortho*-linked PBOs interesting for bulk processing.

### Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for financial support of this work.

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