

Synthesis and properties of hydroxy-containing *ortho*-linked poly(ether-imide)s

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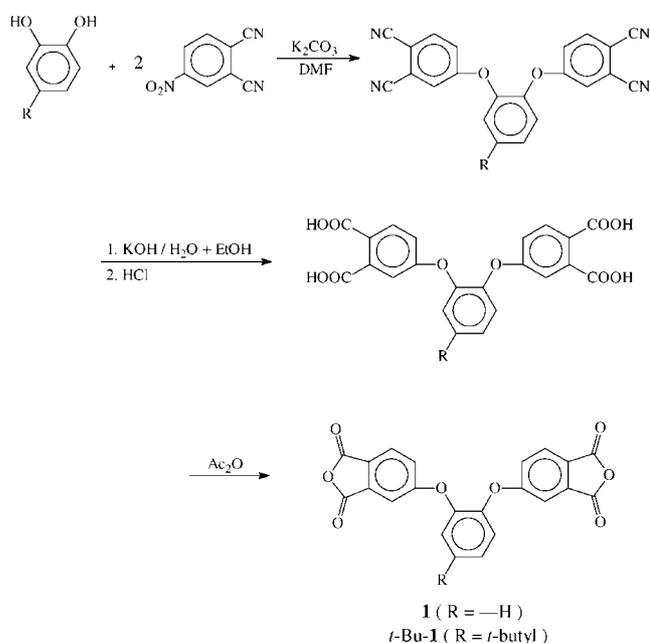
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Abstract. A series of hydroxy-containing poly(ether-imide)s having *ortho*-linked, main chain aromatic units were prepared via the solution polycondensation of bis(ether anhydride)s such as 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride and 1,2-bis(3,4-dicarboxyphenoxy)-4-*tert*-butylbenzene dianhydride with bis(*o*-aminophenol)s such as 3,3'-dihydroxybenzidine, 3,3'-diamino-4,4'-dihydroxybiphenyl and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane. All the poly(ether-imide)s were amorphous, as evidenced by x-ray diffraction analysis, soluble in various polar solvents such as *N,N*-dimethylacetamide, and most of them afforded transparent and flexible films by solution casting. These hydroxy-containing poly(ether-imide)s had glass transition temperatures in the range from 241 to 277 °C and underwent thermal conversion to poly(ether-benzoxazole)s upon heating between 420 and 550 °C under nitrogen. The thermally converted benzoxazole polymers did not show significant weight loss up to 500 °C in nitrogen.

1. Introduction

Soluble hydroxy-containing polyimides have been demonstrated as potential high glass transition temperature (T_g), thermally stable polymers for photoresist [1–4] and nonlinear optical (NLO) applications [5, 6]. The hydroxy-containing polyimides can be prepared from aromatic dianhydrides with aromatic bis(*o*-aminophenol)s [1–3] or hydroxy-containing aromatic diamines [4, 7] by synthetic routes similar to the synthesis of conventional polyimides. The pendant hydroxyl groups on the backbones of the imidized polyimides were important to ensure the solubility and the reactive sites for subsequent condensation reactions (such as the covalent bonding of NLO chromophores) [8]. The hydroxy-containing side-chain polyimides can be further used as reactive polyimides and cross-linked with polyurethane prepolymers or epoxy resins to improve the mechanical properties, solvent resistance, and thermal stability of the materials [9, 10]. Recently, Tullos *et al* [11, 12] reported that aromatic polyimides containing hydroxyl groups *ortho* to the imide nitrogens could undergo thermal conversion to polybenzoxazoles upon heating between 350 and 500 °C under nitrogen or vacuum. The thermal conversion was accompanied by loss of carbon dioxide. Thus, this versatility may lead to the potential use of the hydroxy-containing polyimides in a wide variety of applications.

It has been reported that poly(ether-imide)s having *ortho*-linked aromatic units in the main chain exhibit a good combination of properties including processability, either by solution or melt processing [13–15]. 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 [16] and polyimides [17]. The present study deals with the synthesis of novel hydroxy-containing *ortho*-linked poly(ether-imide)s by the polymerization of bis(ether



Scheme 1. Synthesis of bis(ether anhydride)s.

anhydride)s such as 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride and 1,2-bis(3,4-dicarboxyphenoxy)-4-*tert*-butylbenzene dianhydride with aromatic bis(*o*-aminophenols). The preliminary characteristics such as solubility and thermal properties of the obtained poly(ether-imide)s and their thermal conversion to poly(ether-benzoxazole)s are investigated. Effects of the introduction of the *tert*-butyl group on the properties of these polymers are also discussed.

2. Experiment

2.1. Materials

According to a well developed procedure [13–15], the *ortho*-linked bis(ether anhydride)s, 1,2-bis(3,4-dicarboxyphenoxy)benzene dianhydride (**1**) (mp 187–188 °C) and 1,2-bis(3,4-dicarboxyphenoxy)-4-*tert*-butylbenzene dianhydride (*t*-Bu-**1**) (mp 188–190 °C), were prepared from catechol, 4-*tert*-butylcatechol, and 4-nitrophenyl dicyanide via three main steps, as shown in scheme 1: (a) nucleophilic nitrodisplacement of 4-nitrophenyl dicyanide with the potassium salts of catechol and 4-*tert*-butylcatechol to obtain the tetranitrile compounds; (b) alkaline hydrolysis of tetranitriles to their corresponding tetraacids; and (c) cyclodehydration to yield the final bis(ether anhydride)s. Three bis(*o*-aminophenols) including 4,4'-diamino-3,3'-dihydroxybiphenyl (**2**) (mp 299–300 °C) (TCI), 3,3'-diamino-4,4'-dihydroxybiphenyl (**3**) (mp 301–302 °C) (TCI) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (**4**) (mp 252–253 °C) (Wako) were used as received. Other reagents and solvents were obtained commercially and used without further purification.

2.2. Polymer synthesis

The synthesis of *t*-Bu-**5** is used as an example to illustrate the general synthetic route used to produce the hydroxy-containing poly(ether-imide)s. An equimolar amount of the dianhydride

Table 1. Inherent viscosities and film quality of hydroxy-containing poly(ether-imide)s.

Polymer code	η_{inh}^a (dl g ⁻¹)	Film quality ^b
5	0.36	Slightly brittle
6	0.44	Slightly brittle
7	0.54	Flexible
<i>t</i> -Bu-5	0.59	Flexible
<i>t</i> -Bu-6	0.61	Flexible
<i>t</i> -Bu-7	0.58	Flexible

^a Measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30 °C.

^b Films were cast by slow evaporation of polymer solutions in DMAc.

t-Bu-1 (0.6795 g, 1.48 mmol) and bis(*o*-aminophenol) **2** (0.3205 g, 1.48 mmol) and *m*-cresol (9 ml) were added in a 50 ml flask. The mixture was heated slowly to 90 °C. After stirring for 1 h, the solution was then heated to reflux (ca 210 °C) and held there for 2 h. After being cooled to room temperature, the solution was slowly added to 300 ml of methanol with stirring, giving a light brown fibre-like precipitate. The precipitated polymer was collected by filtration, washed several times with methanol, and dried. The polymer *t*-Bu-5 was obtained from this process in near quantitative yield. The inherent viscosity of this polymer in DMAc was 0.61 dl g⁻¹, measured at a concentration of 0.5 g dl⁻¹ at 30 °C.

IR spectrum of *t*-Bu-5 (thin film): 3200–3600 (broad, O–H str.), 2964 (ali. C–H str.), 1778 (asym. C=O str.), 1718 (sym. C=O str.), 1388 (C–N str.) and 1284 cm⁻¹ (C–O–C str.).

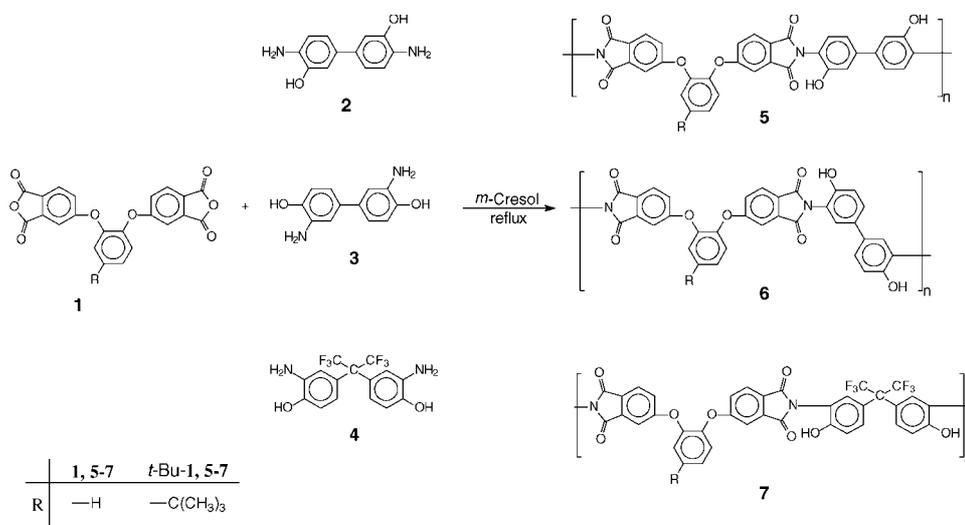
2.3. Measurements

All melting points of low molecular weight materials were determined by differential scanning calorimetry (DSC) at a scan rate of 10 °C min⁻¹ in nitrogen. The inherent viscosities were measured with an Ubbelohde viscometer at 30 °C at a concentration of 0.5 g dl⁻¹. IR spectra were recorded on a Horiba FT-720 Fourier-transform infrared spectrometer. DSC analyses of the polymer samples were performed on a Perkin-Elmer DSC 7 coupled to a Perkin-Elmer thermal analysis controller TAC 7/DX at a scan rate of 20 °C min⁻¹ in flowing nitrogen (30 cm³ min⁻¹). Glass transition temperatures (T_g) were read at the middle of the transition in the heat capacity and were taken from the second heating scan after quick cooling from 400 °C. Thermomechanical analysis (TMA) was conducted at a scan rate of 10 °C min⁻¹ with a Perkin-Elmer TMA 7 instrument using a penetration probe 1.0 mm in diameter under an applied constant load of 30 mN. Thin-film specimens, about 60 μm thick, were used and were heated to 300 °C for 30 min prior to the test. Apparent T_g measurements were taken as the onset temperature of probe displacement on the TMA traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2950. Experiments were carried out on 9–11 mg film samples heated in flowing nitrogen or air (flow rate 100 cm³ min⁻¹) at a heating rate of 20 °C min⁻¹. Wide-angle x-ray diffraction measurements were performed at room temperature (about 25 °C) with film specimens of about 60 μm thick on a Siemens Kristalloflex D 5000 x-ray diffractometer, using nickel-filtered copper K_α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 15 mA). The scanning rate was 2° min⁻¹ over a range of $2\theta = 5\text{--}45^\circ$.

3. Results and discussion

3.1. Polymer synthesis

A series of novel hydroxy-containing *ortho*-linked poly(ether-imide)s **5** to **7** and *t*-Bu-5 to **7** were prepared via a one-step method from bis(ether anhydride)s **1** and *t*-Bu-1 with bis(*o*-



Scheme 2. Synthesis of *ortho*-linked hydroxy-containing poly(ether-imide)s.

aminophenols **2** to **4** in refluxing *m*-cresol (scheme 2). As shown in table 1, the inherent viscosities of the poly(ether-imide)s are in the range 0.36–0.61 dl g⁻¹. All of the poly(ether-imide)s had sufficient molecular weight to allow the casting of free-standing films. The cast films of poly(ether-imide)s **5** and **6** were semi-transparent and embrittled upon ‘fingernail’ creasing, whereas the other films were transparent, flexible and creasable. Introduction of a hexafluoroisopropylidene (6F) group between aromatic rings is capable of disrupting conjugation. Hence, the films obtained from polymers **7** and *t*-Bu-**7** appeared light yellow. However, the other films were pale brown in colour. The brittleness and semi-transparency of the films from poly(ether-imide)s **5** and **6** may be a result of the rigid nature of the main chain and better chain packing, even though they showed amorphous x-ray diffraction patterns. Introduction of the bulky pendant *t*-butyl group destroys the backbone symmetry and regularity and interferes with the tight packing of the polymer chains; therefore, the films of poly(ether-imide)s *t*-Bu-**5** and *t*-Bu-**6** were transparent and flexible.

Key structural features of the poly(ether-imide)s were confirmed by IR and ¹H NMR spectroscopy. A typical set of IR and ¹H NMR spectra of polymer *t*-Bu-**7** are illustrated in figure 1. The IR spectrum shows characteristic absorptions at about 1780 and 1720 cm⁻¹ due to the asymmetric and symmetric vibrations of the cyclic imide carbonyl. Furthermore, the characteristic broad absorption of O–H stretching is observed in the region of 3200–3600 cm⁻¹. The strong absorption at 1200–1300 cm⁻¹ is assigned to the aryl ether stretching. The ¹H NMR spectrum of *t*-Bu-**7** shows a completely imidized polyimide structure with the aromatic hydroxy resonance at 10.49 ppm. The multiple sets of resonance peaks between 6.56 and 7.86 ppm are assigned to the aromatic protons. The strong singlet at 1.35 ppm is attributed to the *t*-butyl groups.

3.2. Properties of poly(ether-imide)s

The solubility of the poly(ether-imide)s was studied qualitatively, and the results are listed in table 2. All poly(ether-imide)s revealed good solubility in highly polar aprotic solvents such as NMP, DMAc, DMF and DMSO. Except for polymers **5** and **6**, all the other polymers

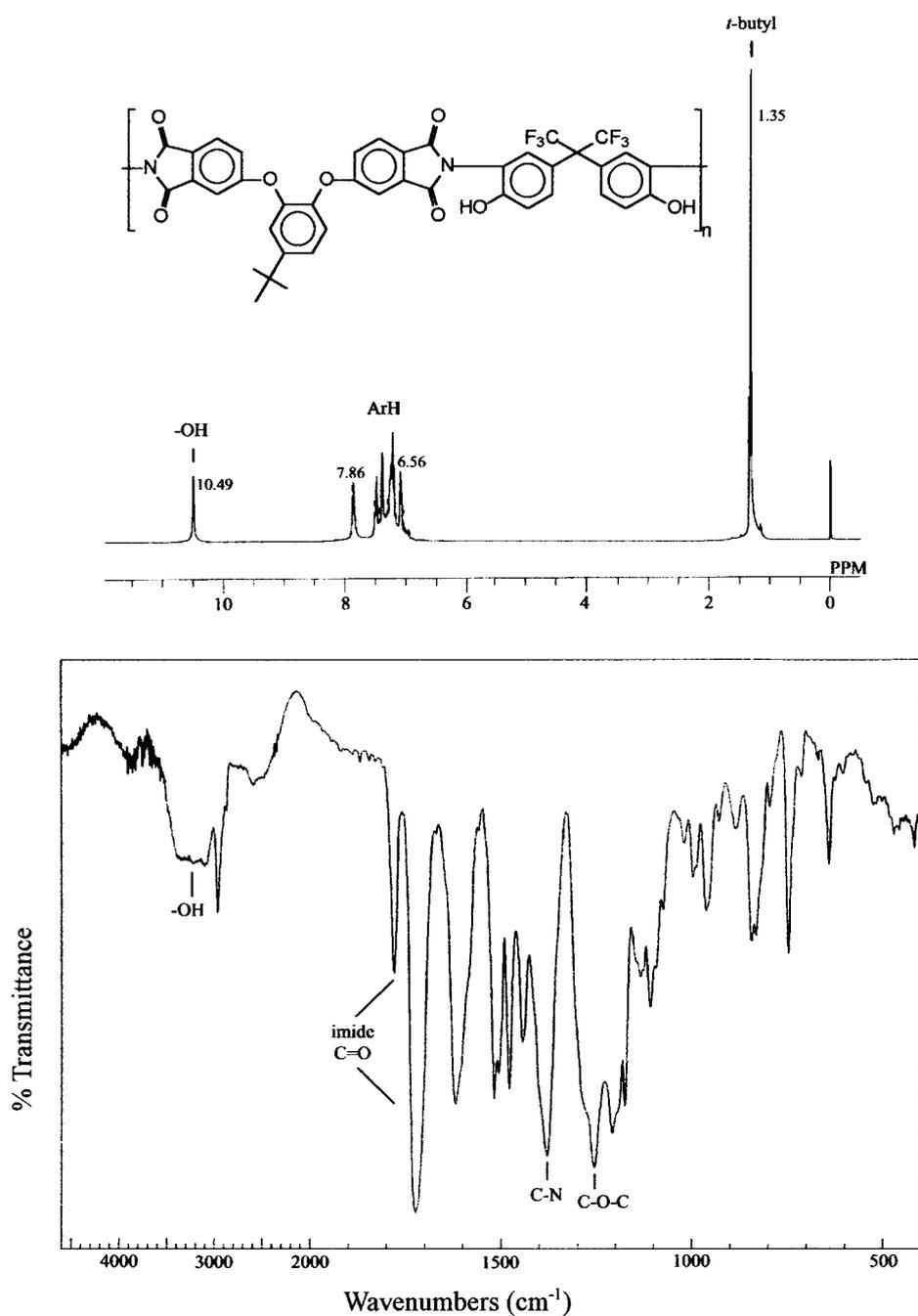


Figure 1. Typical ¹H NMR and IR spectra of the representative hydroxy-containing poly(ether-imide) *t*-Bu-7.

also dissolved in *m*-cresol and THF. The high solubility of these polymers was apparently due in part to the presence of flexible *ortho*-linked bis(phenoxy)benzene units in the main chain. Another factor contributing to the enhanced solubility is the introduction of pendant hydroxyl

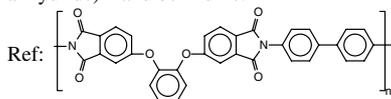
Table 2. Solubility behaviour of hydroxy-containing poly(ether-imide)s^a.

Polymer	Solvent ^b							1 M NaOH (aq)
	NMP	DMAc	DMF	DMSO	<i>m</i> -cresol	THF	CHCl ₃	
5	+	+	+	+	–	–	–	+
6	+	+	+	+	–	–	–	+
7	+	+	+	+	+	+	–	+
<i>t</i> -Bu- 5	+	+	+	+	+	+	–	–
<i>t</i> -Bu- 6	+	+	+	+	+	+	–	–
<i>t</i> -Bu- 7	+	+	+	+	+	+	–	+
Ref ^c	–	–	–	–	–	–	–	–

^a Qualitative solubility was tested with 10 mg of sample in 1 ml of solvent. +: soluble at room temperature; –: insoluble even on heating.

^b NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

^c A poly(ether-imide) with an analogous structure as polymer **5**, synthesized from bis(ether anhydride) **1** and benzidine.



groups, which increase the affinity between the polymer chain and the solvent molecule. As can be seen from table 2, the hydroxy-containing poly(ether-imide) **5** showed a dramatically enhanced solubility compared with the reference poly(ether-imide) prepared from bis(ether anhydride) **1** and benzidine [15]. When comparing the solubility behaviour of the polymer pairs **5**/*t*-Bu-**5** and **6**/*t*-Bu-**6** in *m*-cresol and THF, it can be found that the introduction of the *t*-butyl group onto the backbone further enhanced the solubility of these poly(ether-imide)s. Furthermore, most of these poly(ether-imide)s were soluble not only in organic solvents but also in sodium hydroxide aqueous solution. This result implies that these polymers might be developed as a matrix for a novel alkaline-developable photosensitive polyimide system.

The crystallinity of the poly(ether-imide)s was measured by wide-angle x-ray diffraction analysis. The diffraction patterns shown in figure 2 indicate that all poly(ether-imide)s are completely amorphous, in good agreement with their high solubility in organic solvents. In contrast, the reference poly(ether-imide), as shown in the footnote of table 2, showed a highly crystalline diffraction pattern, as described in a previous publication [15].

TGA, DSC, and TMA techniques evaluated thermal properties of all polymers. A typical TGA curve in nitrogen for the poly(ether-imide) **5** is illustrated in figure 3. An initial weight loss comprising 15.1% of the sample weight was observed between 380 and 484 °C. Calculations showed that the expulsion of two molecules of carbon dioxide per repeat unit would exactly account for this weight loss. Tullos and Mathias [11, 12] recently noted this phenomenon. They proposed and proved the reaction sequence shown in scheme 3, where the hydroxy-imide underwent thermal conversion to the benzoxazole via a carboxy-benzoxazole intermediate followed by decarboxylation at 350 °C. Heating of the poly(ether-imide) **5** for 1 h under nitrogen at 500 °C gave a black, opaque and embrittled film. The observed brittleness is likely to be caused by chain shrinkage and/or degradation during benzoxazole formation. TGA testing of this film under nitrogen showed that the temperature for 10% weight loss increased to 606 °C (curve B in figure 3). A general reaction sequence for the thermal conversion of the hydroxy-containing poly(ether-imide)s to the poly(ether-benzoxazole)s is shown in scheme 4. Some TGA data of the poly(ether-imide)s and their corresponding polybenzoxazoles in air

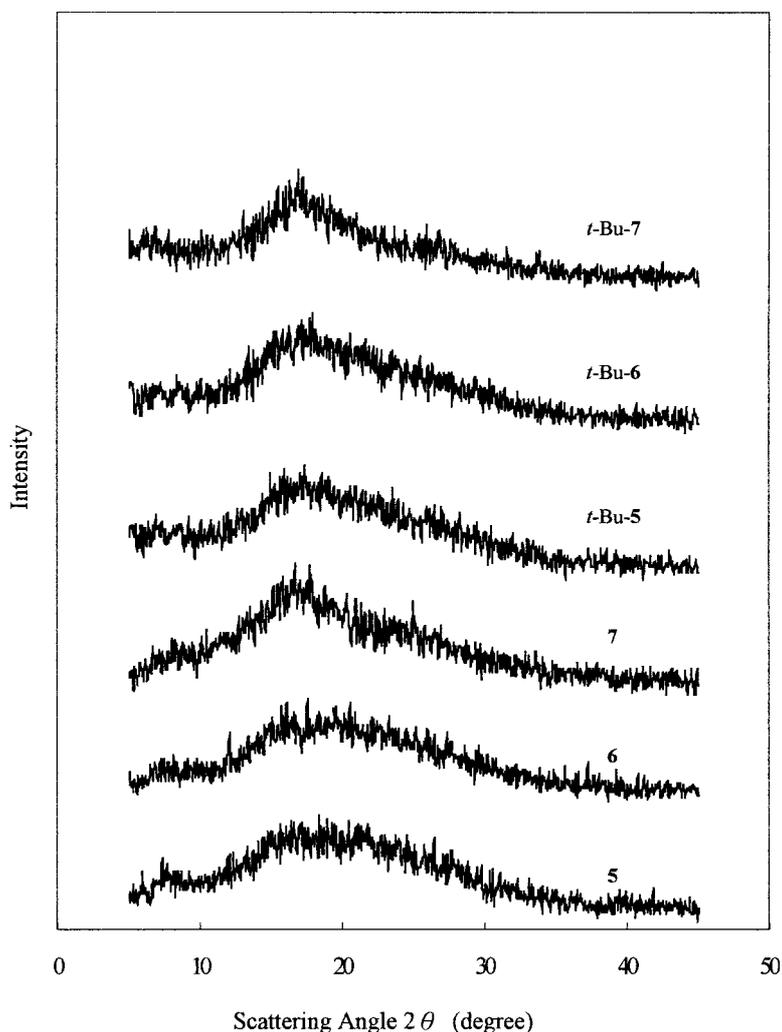


Figure 2. Wide-angle x-ray diffraction patterns of poly(hydroxy-imide)s 5 to 7 and *t*-Bu-5 to 7.

and nitrogen are given in table 3. The initial decomposition temperatures in air ranged from 399 to 432 °C, and those in nitrogen were from 401 to 429 °C. Similar thermal stabilities in both air and nitrogen revealed that the onset of the thermal conversion reaction of the hydroxy-imide occurred at around 400 °C. The data reported in table 3 show that the 10% weight loss temperatures of the thermally converted polybenzoxazoles were recorded in the range of 473–511 °C in air and 576–606 °C in nitrogen. Char yields at 800 °C in nitrogen of the polybenzoxazoles stayed in the range 58–62%. Lower decomposition temperatures of the polybenzoxazoles in air may imply a lower thermo-oxidative stability. The degradation starts from the decarboxylation of the poly(ether-imide)s and, hence, the introduction of *t*-butyl groups onto the backbone does not seem to significantly influence the thermal stability.

Only the 6F-containing poly(ether-imide)s 7 and *t*-Bu-7 revealed discernible glass transitions on the DSC traces, and their T_g values were recorded at 255 and 257 °C, respectively. The poly(ether-imide)s containing a rigid biphenylene structure showed no discernible glass

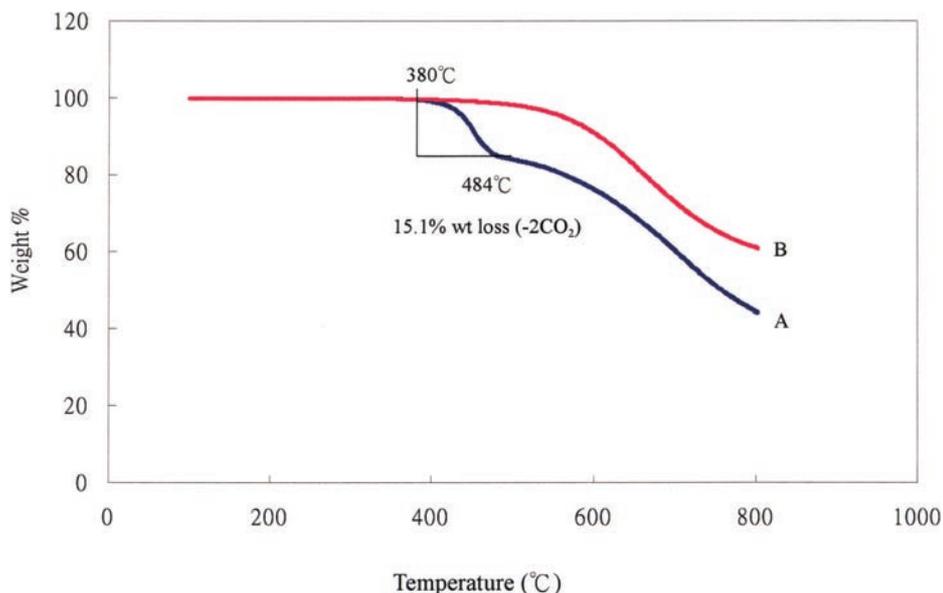


Figure 3. Thermogravimetric analysis in nitrogen (heating rate $20^{\circ}\text{C min}^{-1}$) of hydroxy-containing poly(ether-imide) **5** (curve A) and the same polymer after heating isothermally at 500°C for 1 h under nitrogen (curve B).

Table 3. Thermal properties of hydroxy-containing poly(ether-imide)s.

Polymer	T_g ($^{\circ}\text{C}$)		TGA initial wt loss ($^{\circ}\text{C}$) ^c		TGA data for the polybenzoxazoles ^d		
					10% wt loss temperature ($^{\circ}\text{C}$)		Char yield at 800°C in N_2 (%)
	DSC ^a	TMA ^b	Air	N_2	Air	N_2	
5	–	270	432	429	503	606	61
6	–	276	429	428	478	582	58
7	255	241	399	402	511	576	58
<i>t</i> -Bu- 5	–	283	407	427	473	590	61
<i>t</i> -Bu- 6	–	277	404	426	480	585	60
<i>t</i> -Bu- 7	257	237	400	401	493	576	62

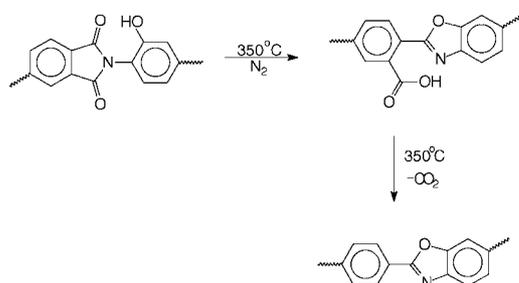
^a The sample was heated to 350°C at a heating rate of $20^{\circ}\text{C min}^{-1}$ and then was cooled down to 30°C at $-100^{\circ}\text{C min}^{-1}$. T_g was defined as the midpoint temperature of baseline shift on the subsequent DSC heating trace at $20^{\circ}\text{C min}^{-1}$.

^b The film specimen was heated to 300°C for 30 min prior to test. TMA was determined by a penetration method with a load of 30 mN at a heating rate of $10^{\circ}\text{C min}^{-1}$.

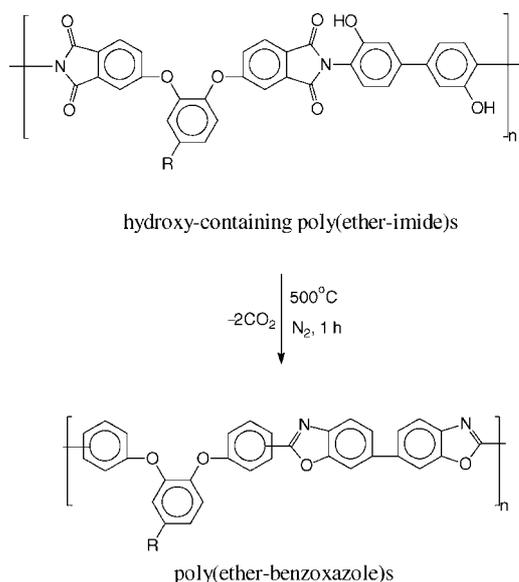
^c TGA was carried out at a heating rate of $20^{\circ}\text{C min}^{-1}$.

^d From the thermal conversion of the hydroxy-containing poly(ether-imide)s at 500°C for 1 h under nitrogen.

transitions on the DSC curves. However, the T_g of these more rigid polymers could be readily determined using TMA. The T_g of **7** and *t*-Bu-**7** have also been measured in TMA. As shown in table 3, the T_g measured by TMA were in the range 237 – 283°C . The polymers containing the 6F groups in the main chain, such as **7** and *t*-Bu-**7**, exhibited lower T_g , due to a more flexible backbone. The slight differences in T_g values determined by DSC and TMA experiments may be attributed to the distinctive nature of the testing techniques and different heating history of



Scheme 3. Proposed reaction for thermal conversion of hydroxy-imides to benzoxazoles [11, 12].



Scheme 4. Thermal conversion of hydroxy-containing poly(ether-imide)s to poly(ether-benzoxazole)s at 500 °C under nitrogen.

the samples. The attachment of *t*-butyl groups causes only small changes in T_g . Thus, the effect of asymmetry and irregularity introduced with the pendant groups, which should decrease T_g , is overcome by the steric hindrance effect caused by the great volume of the substituents.

4. Summary

Novel hydroxy-containing *ortho*-linked poly(ether-imide)s were successfully prepared from bis(ether anhydride)s with bis(*o*-aminophenol)s in refluxing *m*-cresol. They had inherent viscosities in the range of 0.36–0.61 dl g⁻¹. All of the poly(ether-imide)s dissolved readily in polar solvents such as DMAc, DMF, DMSO and NMP and even in less efficient *m*-cresol and THF for those containing 6F and/or pendant *tert*-butyl groups in the main chain. In addition, most of these polymers were also soluble in aqueous alkaline solutions. Only the poly(ether-imide)s containing the flexible 6F groups exhibited clear glass transitions on their DSC traces. TMA experiments indicated that these polymers had T_g values in the range 237–283 °C. All polymers were stable up to approximately 400 °C in nitrogen or air atmosphere. They could be

converted to polybenzoxazoles upon heating in the region of 400–500 °C under nitrogen. These poly(ether-imide)s containing pendant hydroxyl groups demonstrate a good combination of properties and may be considered as new candidates for the processable high-performance polymeric matrix used for photoresists and NLO materials.

References

- [1] Omote T, Koseki K and Yamaoka T 1990 *Macromolecules* **23** 4788
- [2] Yu H S, Yamashita T and Horie K 1996 *Macromolecules* **29** 1114
- [3] Ueda M and Nakayama T 1996 *Macromolecules* **29** 6427
- [4] Akimoto S, Jikei M and Kakimoto M 2000 *High Perform. Polym.* **12** 177
- [5] Chen T-A, Jen A K-Y and Cai Y 1996 *Macromolecules* **29** 535
- [6] Kim E-H, Moon I K, Kim H K, Lee M-H, Han S-G, Yi M H and Choi K-Y 1999 *Polymer* **40** 6157
- [7] Akimoto S, Jikei M and Kakimoto M 2000 *High Perform. Polym.* **12** 197
- [8] Chen T-A, Jen A K-Y and Cai Y 1995 *J. Am. Chem. Soc.* **117** 7295
- [9] Zuo M and Takeichi T 1999 *Polymer* **40** 5153
- [10] Agag T and Takeichi T 1999 *Polymer* **40** 6557
- [11] Tullos G L and Mathias L J 1999 *Polymer* **40** 3463
- [12] Tullos G L, Powers J M, Jeskey S J and Mathias L J 1999 *Macromolecules* **32** 3598
- [13] Eastmond G C and Paprotny J 1995 *Macromolecules* **28** 2140
- [14] Eastmond G C, Paprotny J and Irwin R S 1996 *Macromolecules* **29** 1382
- [15] Hsiao S-H, Yang C-P and Chu K-Y 1997 *Macromolecules* **30** 165
- [16] Hsiao S-H, Yang C-P and Chen S-H 2000 *Polymer* **41** 6537
- [17] Hsiao S-H, Yang C-P and Chen S-H 2000 *J. Polym. Sci. A* **38** 1551