Synthesis and Properties of Novel Aromatic Poly(*o*-hydroxy amide)s and Polybenzoxazoles Based on the Bis(ether benzoyl chloride)s from Hydroquinone and Its Methyl-, *tert*-Butyl-, and Phenyl-Substituted Derivatives

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ABSTRACT: Four series of poly(*o*-hydroxy amide)s were prepared by the low-temperature solution polycondensation of the bis(ether benzoyl chloride)s extended from hydroquinone and its methyl-, *tert*-butyl-, or phenyl-substituted derivatives with three bis(*o*-aminophenol)s. Most of the poly(*o*-hydroxy amide)s displayed an amorphous nature, were readily soluble in various polar solvents such as *N,N*-dimethylacetamide (DMAc), and could be solution-cast into flexible and tough films. These poly(*o*-hydroxy amide)s had glass transition temperatures (T_g) in the range of 152–185°C and could be thermally cyclodehydrated into the corresponding polybenzoxazoles approximately in the region of 200–400°C, as evidenced by the DSC thermograms. The thermally converted benzoxazole polymers exhibited T_gs in the range of 215–247°C and did not show significant weight loss before 500°C either in nitrogen or in air. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 2129–2136, 1999

Keywords: hydroquinone; methylhydroquinone; *tert*-butylhydroquinone; phenyl-hydroquinone; bis(ether benzoyl chloride)s; poly(*o*-hydroxy amide)s; polybenzoxazoles

INTRODUCTION

Aromatic polybenzoxazoles belong to the class of rigid-rod aromatic heterocyclic polymers capable of being processed into fibers and films which exhibit high modulus and strength and high thermal stability.[1] However, rigidity of the backbone and charge transfer complex formation results in insolubility in most organic solvents and high softening temperatures. These properties make them generally difficult or too expensive to process, thus restricting their applications. Therefore, many attempts have been tried to prepare polybenzoxazoles which are soluble in common organic solvents and, in some cases, thermoplastic in nature. For example, by the incorporation of fluorinated linking groups into the polymer backbone solubility was enhanced, while good thermooxidative stability and high glass transition temperatures were retained.[2–8] Similarly, soluble poly(aryl ether benzoxazole)s have been prepared and display properties intermediate between the two homopolymers.[9–11] Desirable properties resulting from these materials include thermoplasticity, good tensile properties and enhanced toughness.

In an attempt to improve the processability of these polymers through improved solubility and thermoplasticity, we carried out the synthesis of aromatic poly(ether benzoxazole)s via the introduction of diphenoxybenzene units into the polymer backbone by using the bis(ether benzoyl chloride)s of hydroquinones as the monomers. Preliminary characterization of the poly(*o*-hydroxy

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amide) prepolymers and the polybenzoxazoles are described below. The effect caused by the attachment of pendent groups on the properties of polymers is also discussed.

EXPERIMENTAL

Materials

The diacyl chloride monomers, 4,4′-(1,4-phenylenedioxy)dibenzoyl chloride (**1**) (mp 207–209°C), 4,4′-(2,5-tolylenedioxy)dibenzoyl chloride (Me-**1**) (mp 165–167°C), 4,4′-(2-*tert*-butyl-1,4-phenylenedioxy)dibenzoyl chloride (*t*-Bu-**1**) (mp 126–128°C), and 4,4′-(2,5-bipheneylenedioxy)dibenzoyl chloride (Ph-**1**) (mp 118–121°C), were prepared by chlorinating the precursor dicarboxylic acids[12,13] with thionyl chloride and two drops of *N*,*N*-dimethylfomamide (DMF). The aromatic bis(*o*-aminophenol) monomers that included 3,3′-dihydroxybenzidine (**2**) (TCI), 3,3′-diamino-4,4′-dihydroxybiphenyl (**3**) (TCI) and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (**4**) (TCI) were of high purity and used as received. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Commercially obtained anhydrous lithium chloride was dried under vacuum at 180°C for 8 h.

Synthesis of Poly(*o*-hydroxy amide)s

The low-temperature solution polycondensation technique was adopted in this investigation. A typical procedure of preparing poly(*o*-hydroxy amide)s is as follows. In a 50 mL flask, 1 mmol of a bis(*o*-aminophenol) was dissolved in 5 mL of NMP containing 0.2 g of LiCl and cooled in an ice-acetone bath. To the solution 1 mmol of a diacyl chloride was added, and the reaction was carried out at −10°C to 0°C for about 1 h and then at room temperature overnight. The reaction solution became homogeneously transparent gradually, leading to a clear, highly viscous polymer solution. The resulting polymer solution was poured slowly into 300 mL of methanol with stirring. The white fiber-like precipitate formed was washed repeatedly with methanol and hot water, collected by filtration, and dried. The yields were usually quantitative.

Preparation of Poly(*o*-hydroxy amide) Films 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 to remove the solvent. Then, the obtained semidried polymer film was lifted off the glass substrate and further dried *in vacuo* at 150°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, and 300°C for 3 h under a nitrogen atmosphere.

Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. The inherent viscosities were measured with an Ubbelohde viscometer at 30°C. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. Scans were run at 20°C /min. Glass transition temperatures (T_gs) were read at the middle of the transition in the heat capacity. Dynamic thermogravimetry (TG) was performed using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyst. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K_α radiation (40 kV, 15 mA). The scanning rate was 2°C/min over a range of $2\theta = 5–40°$. An Instron universal tester model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples. A gauge length of 2 cm and a crosshead speed of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 cm wide, and about 0.05 mm thick).

RESULTS AND DISCUSSION

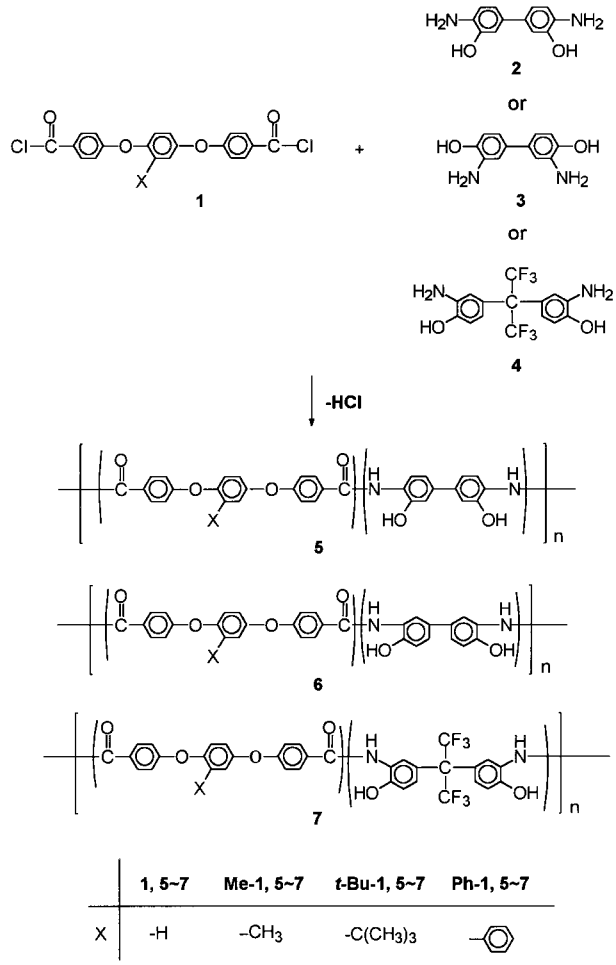
Polymer Synthesis

Aromatic polybenzoxazoles might be synthesized easily in one-step procedure from aromatic bis(*o*-aminophenol)s with aromatic diacid derivatives using poly(phosphoric acid) (PPA),[14] phosphorus pentoxide/methanesulfonic acid (MSA),[15] or tri-

methylsilyl phosphate[16] as the condensing medium. High molecular weight aromatic polybenzoxazoles also could be obtained by reacting bis(*o*-aminophenol)s with poly(terephthalic acid anhydride) or 1,4-bis(trichloromethyl)benzene in PPA or a mixture of PPA and MSA.[17,18] Imai and coworkers[19,20] have developed a facile one-step method for the synthesis of aliphatic polybenzoxazoles from bis(*o*-aminophenol)s and aliphatic dinitriles. Isolation and thermal cyclodehydration of soluble poly(*o*-hydroxy amide), derived from the polycondensation of diacid derivatives and bis(*o*-aminophenol)s in polar solvents, is a conventional method for the production of polybenzoxazole films and fibers.[21]

In this study, poly(*o*-hydroxy amide)s **5**~**7**, Me-**5**~**7**, *t*-Bu-**5**~**7**, and Ph-**5**~**7** were prepared by a low-temperature solution polycondensation technique from diacyl chloride **1**, Me-**1**, *t*-Bu-**1**, and Ph-**1** with three structurally different bis(*o*-aminophenol)s, **2**, **3**, and **4** in an NMP solution dissolved LiCl at −10°C to 0°C for 1 h and at room temperature for another 10 h. Structures and codes of the monomers and poly(*o*-hydroxy amide)s are shown in Scheme 1. The results of the polymerizations are summarized in Table I. The inherent viscosities of the resulting poly(*o*-hydroxy amide)s stayed in the range of 0.31–1.74 dL/g. The polymers derived from the hexafluoroisopropylidene (6F)-containing bis(*o*-aminophenol) **4** had relatively lower inherent viscosities, which may be attributable to low nucleophilicity of the fluorine-containing monomer caused by the presence of electron-withdrawing 6F groups. However, the molecular weights of most the **7** series polymers are sufficiently high to permit the casting of flexible and tough films. All the poly(*o*-hydroxy amide)s were readily soluble in amide-type solvents such as NMP and DMAc and could afford free-standing films by means of solution casting. Expect for polymers **5**, Me-**5**, Me-**6** and *t*-Bu-**7**, all the other films were transparent, smooth, and creasable. Polymers **7** series are pale yellow, while polymers **5** and **6** series are pale to dark brown in color.

The formation of poly(*o*-hydroxy amide)s was confirmed by means of IR spectroscopy. The polymers exhibited the broad absorption bands in the region of 2500–3500 cm^{-1} (O—H and N—H str.) and 1650 cm^{-1} (amide C═O str.). The conversion of poly(*o*-hydroxy amide)s to polybenzoxazoles (shown in Scheme 2) was carried out by heating the above fabricated polymer films at 200°C for 30 min, 250°C for 30 min, and 300°C for 3 h under a



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

nitrogen atmosphere. The conversion process to polybenzoxazoles could be followed by the change in the IR spectra of the films. Figure 1 shows typical IR spectra of the representative pair of poly(*o*-hydroxy amide) Ph-**5** and its corresponding polybenzoxazole Ph-**8**. The complete disappearance of the absorption bands around 3000 and 1650 cm^{-1} indicates the completion of the cyclodehydration process, together with the appearance of an absorption at 1613 cm^{-1} characteristic of the benzoxazole ring, almost overlapping with one of the absorption bands of aromatic C═C str. This conversion also could be monitered by the thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis, which will be discussed subsequently.

Polymer Characterization

Tensile Properties

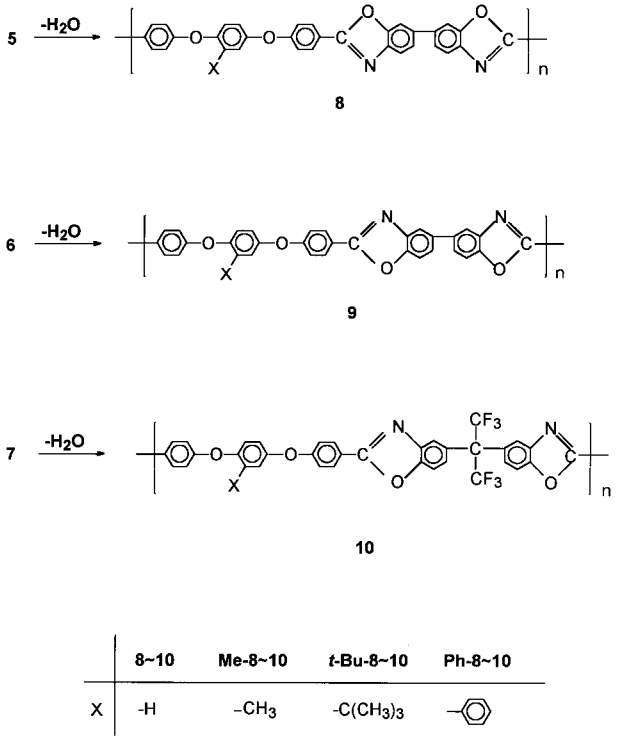
As mentioned above, most of the poly(*o*-hydroxy amide)s could be solution-cast into smooth, flexi-

Table I. Inherent Viscosities, Film Quality, and Tensile Properties of Poly(*o*-hydroxy amide)s[a]

Polymer Code	η_{inh}[b] (dL/g)	Film Quality[c]	Tensile Properties of Polymer Films[c]		
			Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
5	1.72	Shrunk, brittle, pale brown	—	—	—
6	1.74	Flexible, pale brown	146	8	3.98
7	0.42	Flexible, pale yellow	80	5	2.45
Me-5	0.97	Shrunk, flexible, pale brown	—	—	—
Me-6	0.92	Shrunk, brittle, pale brown	—	—	—
Me-7	0.47	Flexible, pale yellow	99	6	2.40
***t*-Bu-5**	0.75	Flexible, dark brown	92	13	2.18
***t*-Bu-6**	0.73	Flexible, pale brown	112	7	2.99
***t*-Bu-7**	0.43	Brittle, pale yellow	—	—	—
Ph-5	0.89	Flexible, dark brown	137	20	3.06
Ph-6	0.94	Flexible, pale brown	123	11	3.06
Ph-7	0.31	Flexible, pale yellow	95	6	2.32

[a] Monomer scale = 1 mmol, NMP = 5 mL, LiCl = 0.2 g.
[b] Measured at a concentration of 0.5 g/dL in DMAc at 30°C.
[c] Films were cast from slow evaporation of the polymers in DMAc and further dried *in vacuo* at 150°C for about 6 h. All the films are transparent.

ble, and tough films. These films were subjected to tensile testing, and the results are given in Table I. The tensile strengths, and elongations at



Scheme 2. Synthesis of polybenzoxazoles.

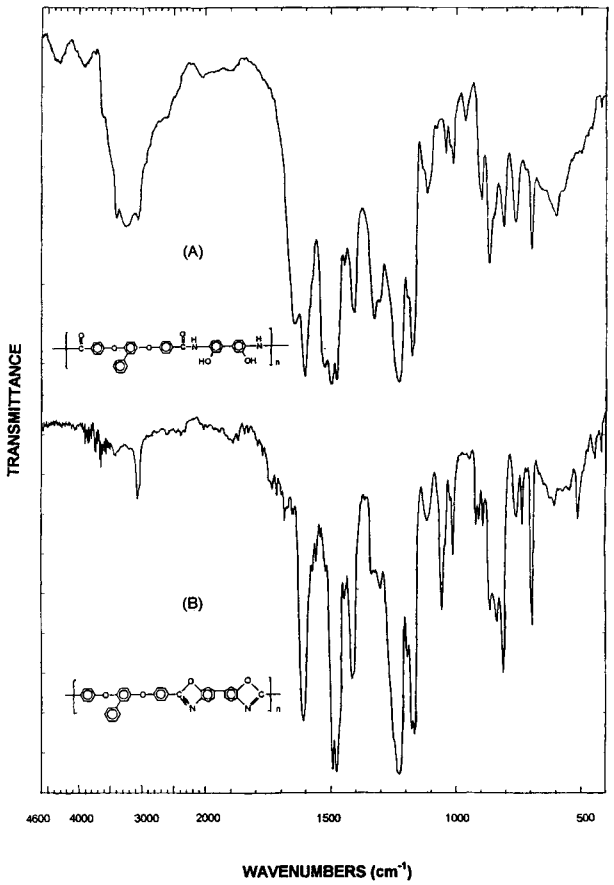


Figure 1. IR spectra of (A) poly(*o*-hydroxy amide) Ph-**5** and (B) polybenzoxazole Ph-**8**.

Table II. Solubility Behavior[a] of Poly(*o*-hydroxy amide)s and Polybenzoxazoles

	Solvent[b]								
Polymer	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF	Chloroform	Acetone	Ethanol
5	+	+	−	−	−	−	−	−	−
6	+	+	+	−	−	−	−	−	−
7	+	+	+	+	+h	+	−	+	−
Me-5	+	+	−	+h	−	−	−	−	−
Me-6	+	+	−	+h	−	−	−	−	−
Me-7	+	+	+	+	+h	+	−	+	−
***t*-Bu-5**	+	+	−	−	−	−	−	−	−
***t*-Bu-6**	+	+	+	+	−	−	−	−	−
***t*-Bu-7**	+	+	+	+	+h	+	−	+	−
Ph-5	+	+	−	−	−	−	−	−	−
Ph-6	+	+	+	+	−	−	−	−	−
Ph-7	+	+	+	+	+h	+	−	+	−
Ph-10[c]	+	−	−	−	−	−	−	−	−

[a] +: soluble at room temperature; +h: soluble on heating; −: insoluble even on heating.
[b] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.
[c] All other polybenzoxazoles are insoluble in all the tested solvents.

break, and initial moduli of these films were in the range of 80–146 MPa, 6–20%, and 2.18–3.98 GPa, respectively. Most of thermally converted polybenzoxazole films are also flexible and tough. However, most of the films shrank or bubbled during the cyclization process; therefore, their tensile properties were not evaluated.

Solubility

Solubility of the poly(*o*-hydroxy amide)s and polybenzoxazoles was determined for the film samples in excess solvents, and the results are listed in Table II. All poly(*o*-hydroxy amide)s were readily soluble in DMAc and NMP, and most of them were also soluble in DMF and DMSO. When the **5** series are compared with the **6** series, it seems that the former displayed a lower solubility. The slight solubility difference between the **5** and **6** series are believed to be related to the molecular symmetry in 3,3′-dihydroxybenzidine (**2**) which allows better packing, stronger intermolecular interactions and therefore lower solubility for the **5** series. Poly(*o*-hydroxy amide)s derived from 6F bis(*o*-aminophenol) **4** were soluble in THF, acetone, and *m*-cresol (with heating), probably due to their nonplanar structures and low cohesive energies caused by the —CF_3 group.

The polybenzoxazoles, on the other hand, dissolved only in cold sulfuric acid. Despite the fact that most polybenzoxazoles are amorphous, they were quite insoluble in organic solvents, with the exception of Ph-**10**, which contains bulky 6F group in the bis(*o*-aminophenol) moiety and bulky pendent phenyl group in the diacid moiety along the polymer backbone.

Crystallinity

An attempt was made to estimate the crystallinity of polymers by means of X-ray diffraction measurement. Figure 2 presents the wide-angle X-ray diffractograms of poly(*o*-hydroxy amide)s **5**–**7** with films. Polymer **5** displayed a moderately high crystallinity due to the presence of symmetric, rod-like benzidine moiety. Changing the component of 3,3′-dihydroxybenzidine to 3,3′-diamino-4,4′-dihydroxybiphenyl, for example, polymer **6**, reduced the polymer crystallinity drastically. A broad amorphous halo of polymer **7** indicated the absence of crystallinity, which could be attributed to the steric hindrance of the bulky 6F groups. Figure 3 illustrates the X-ray diffraction patterns of the **5** series poly(*o*-hydroxy amide)s with different pendent groups. The effect of asymmetry, irregularity, and steric hindrance introduced with the pendent group resulted in a significant decrease in crystallinity.

After cyclodehydration, the polybenzoxazoles generally revealed a decreased crystallinity, probably due to the lack of hydrogen bonding. Figure 4 shows typical X-ray diffractograms of polyben-

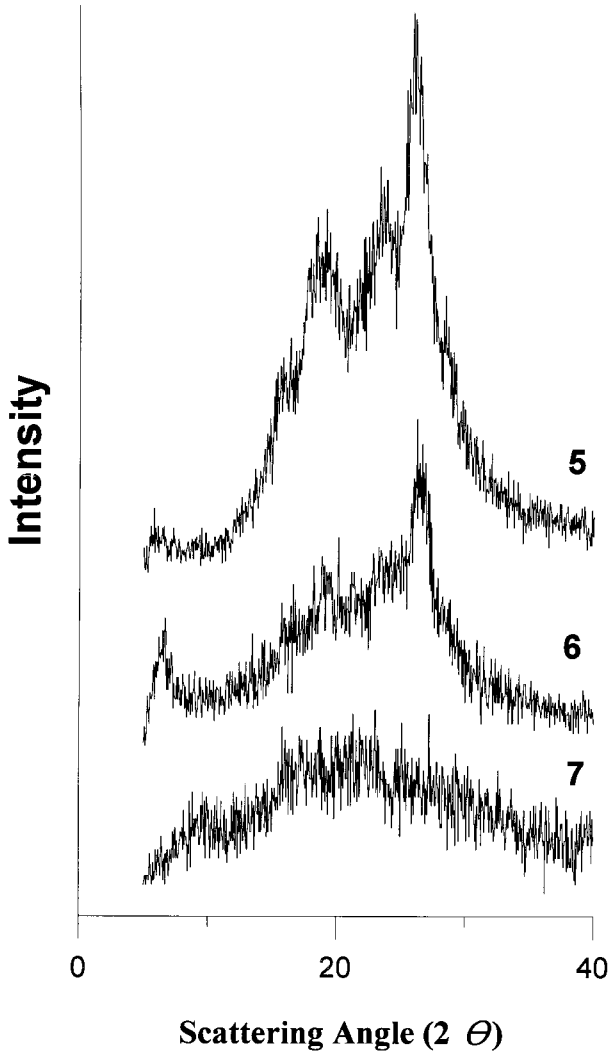


Figure 2. Wide-angle X-ray diffractograms of poly(*o*-hydroxy amide)s.

zoxazoles **8–10**. All other polybenzoxazoles with the pendent group showed amorphous patterns as that of polybenzoxazole **10** shown in Figure 4.

Thermal Properties

Thermal properties of the poly(*o*-hydroxy amide)s and polybenzoxazoles were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC), and their thermal behavior data are summarized in Table III. Except for **7**, Me-**7** and *t*-Bu-**7**, all the other poly(*o*-hydroxy amide)s displayed discernible glass transitions between 150–185°C in the DSC traces. All the poly(*o*-hydroxy amide)s exhibited strong endothermic peaks between 200–400°C, centered around 285–307°C, which are attributed to loss of water during the conversion of poly(*o*-hydroxy amide) to polybenzoxazole. The T_gs of the polybenzoxazoles formed *in situ* were recorded in the 215–247°C range, which were higher than the corresponding poly(*o*-hydroxy amide) prepolymers due to an increased chain stiffness. The T_gs of the polymers did not show any clear dependence on the structure of the diacyl chloride or the bis(*o*-aminophenol).

Figure 5 shows typical TG curves for poly(*o*-hydroxy amide) **5** and polybenzoxazole **8**. The TG trace of poly(*o*-hydroxy amide) **5** revealed that the weight loss started at around 250°C and came to an end at about 350°C. The weight loss was due to the thermal cyclodehydration of the poly(*o*-hydroxy amide), which was also evidenced from the DSC curve. Polybenzoxazole **8** started to lose weight at around 500°C and left 68% residual char at 800°C in nitrogen. All the other polybenzoxazoles showed similar thermal behavior, and

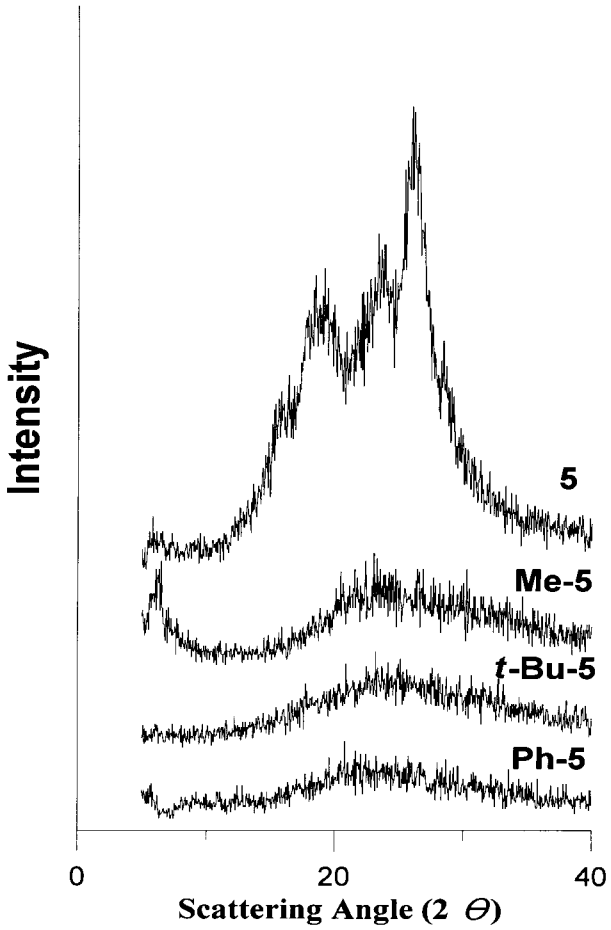


Figure 3. Wide-angle X-ray diffractograms of poly(*o*-hydroxy amide)s.

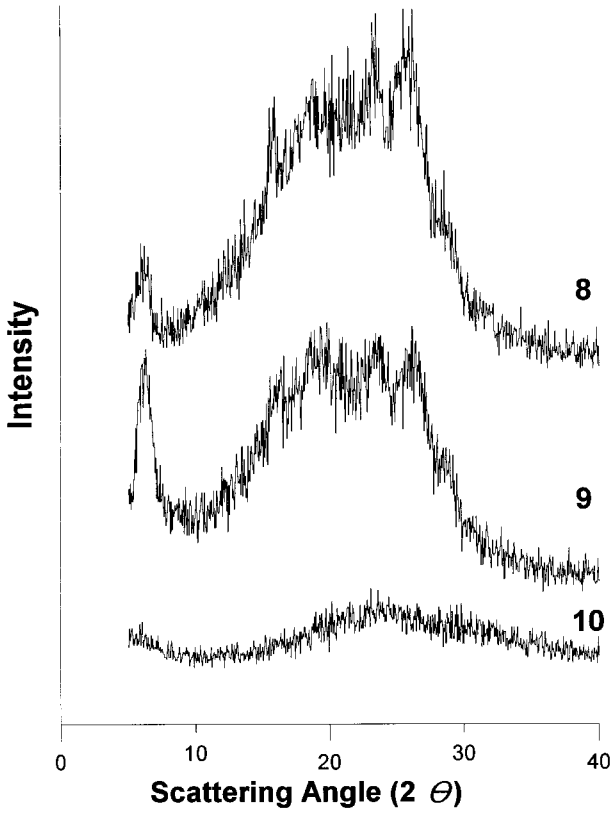


Figure 4. Wide-angle X-ray diffractograms of polybenzoxazoles.

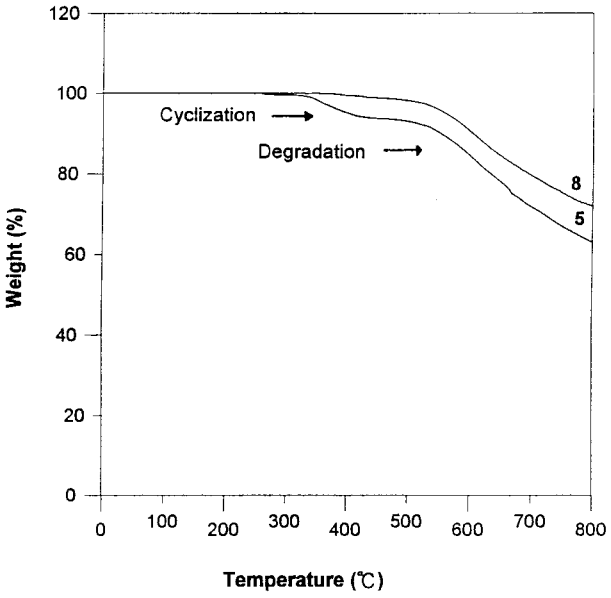


Figure 5. TG curves of poly(*o*-hydroxy amide) **5** and polybenzoxazole **8** with a heating rate of 20°C/min in nitrogen.

some of their TG data are summarized in Table III. All the polybenzoxazoles did not lose weight up to 500°C in air or nitrogen, and the temperatures at which 10% weight loss was recorded were

Table III. Thermal Behavior Data of Poly(*o*-hydroxy amide)s and Polybenzoxazoles

Poly(*o*-hydroxy amide)s[a]				Polybenzoxazoles			
Code	T_g (°C)	T_o (°C)	T_p (°C)	Code	T_g[b] (°C)	T_d[c] (°C)	Char Yield[d] (%)
5	184	231	307	**8**	—[e]	594	68
Me-5	175	202	285	**Me-8**	226	516	72
***t*-Bu-5**	185	231	296	***t*-Bu-8**	247	537	60
Ph-5	150	235	287	**Ph-8**	227	604	73
6	178	230	300	**9**	—	594 (580)	67
Me-6	175	210	290	**Me-9**	228	513	69
***t*-Bu-6**	162	212	288	***t*-Bu-9**	230	534	58
Ph-6	170	235	290	**Ph-9**	227	600	72
7	—[e]	238	285	**10**	215	575	65
Me-7	—	240	290	**Me-10**	225	534	61
***t*-Bu-7**	—	232	286	***t*-Bu-10**	230	543	58
Ph-7	152	238	287	**Ph-10**	218	579	65

[a] DSC data obtained from the first DSC heating trace with a heating rate of 20°C/min. T_g: midpoint of baseline shift on the DSC curve. T_o: extrapolated onset temperature of the endotherm peak. T_p: endotherm peak temperature.
[b] Midpoint temperature of baseline shift on the second DSC heating trace of the sample after quenching from 450°C.
[c] The temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min in nitrogen. The value indicated in parentheses was that observed in air.
[d] Residual weight % when heated to 800°C in nitrogen.
[e] Difficult to judge.

in the ranges of 513–604°C, with more than 58 wt % residue remaining at 800°C in nitrogen. The polymers with methyl or *t*-butyl groups were less thermally stable than the corresponding ones without alkyl substituents.

CONCLUSIONS

High-molecular-weight poly(*o*-hydroxy amide)s were prepared from the bis(ether benzoyl chloride)s of hydroquinone and its derivatives with bis(*o*-aminophenol)s by the low-temperature solution polycondensation in NMP/LiCl. The inherent viscosities of the polymers were in the range of 0.31–1.74 dL/g, most of the polymers could be solution-cast into flexible and tough films. The poly(*o*-hydroxy amide)s had T_gs in the range of 150–185°C and could be thermally cyclodehydrated into the corresponding polybenzoxazoles approximately in the region of 200–400°C. The T_gs of these thermally converted polybenzoxazoles were recorded in the range of 215–247°C. The polybenzoxazoles showed good thermal stability, with 10% weight loss temperature being recorded above 500°C in air or nitrogen atmosphere.

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