

Aromatic Polybenzoxazoles Containing Ether–Sulfone Linkages

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ABSTRACT: A series of poly(*o*-hydroxy amide)s having both ether and sulfone linkages in the main chain were synthesized via the low-temperature solution polycondensation of 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]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-diamino-4-hydroxyphenyl)hexafluoropropane. Subsequent thermal cyclodehydration of the poly(*o*-hydroxy amide)s afforded polyethersulfone benzoxazoles. Most of the poly(*o*-hydroxy amide)s were soluble in polar organic solvents such as *N*-methyl-2-pyrrolidone; however, the polybenzoxazoles without the hexafluoroisopropylidene group were organic-insoluble. The polybenzoxazoles exhibited glass-transition temperatures (T_g) in the range of 219–282 °C by DSC and softening temperatures (T_s) of 242–320 °C by thermomechanical analysis. Thermogravimetric analyses indicated that most polybenzoxazoles were stable up to 450 °C in air or nitrogen. The 10% weight loss temperatures were recorded in the ranges of 474–593 °C in air and 478–643 °C in nitrogen. The methyl-substituted polybenzoxazoles had higher T_g 's but lower T_s 's and initial decomposition temperatures compared with the corresponding unsubstituted polybenzoxazoles. For a comparative purpose, the synthesis and characterization of a series of sulfonyl polybenzoxazoles without the ether group that derived from 4,4'-sulfonyldibenzoyl chloride and bis(*o*-aminophenol)s were also reported. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 2262–2270, 2001

Keywords: polyethersulfone benzoxazoles; poly(*o*-hydroxy amide)s; bis(*o*-aminophenol)s

INTRODUCTION

Aromatic polybenzoxazoles (PBO) are a class of aromatic heterocyclic polymers that have excellent thermal stability, high mechanical properties, and good chemical resistance.^{1,2} A few rigid-rod PBOs have attracted interest because they can be fabricated into high-strength and high-modulus fibers.^{3–5} PBO fiber has a superior ten-

sile strength and modulus compared with *p*-aramid fibers. The excellent thermal stability and high flame resistance of PBO make it the material of choice for high-temperature applications. However, analogous to aromatic polyimides, they are generally difficult to process because of their high melting and glass-transition temperatures (T_g 's) and poor solubility in organic solvents; consequently, versatile applications are limited. PBOs may be wet-spun from polyphosphoric acids or methanesulfonic acid lyotropic solutions to form molecularly oriented fibers or films. However, to allow for easier processing and fabricating, it is imperative that the melting temperatures or T_g 's

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of these rigid polymers be substantially depressed and their solubilities in common solvents be increased. Synthetic modification of the basic rigid-chain structure by the introduction of flexible linkages^{6–9} or bulky side groups^{10–12} along the polymer backbone is one of the most common strategies to improve the solubility and processing of PBOs.

In previous studies,¹³ we have shown that the incorporation of ether and sulfone groups into the polymer chain is able to give aromatic polyimides and polyamides with enhanced solubility, maintaining a moderately high T_g . In an attempt to improve the processability of PBOs through improved solubility and/or thermoplasticity, the present work deals with the synthesis of polyethersulfone benzoxazoles by the low-temperature solution polycondensation of ether–sulfone diacyl chlorides—4,4'-[sulfonylbis(1,4-phenylene)dioxy]dibenzoyl chloride (SODBC) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSO-DBC)—with three commercially available bis(*o*-aminophenols), followed by thermal cyclodehydration of the intermediate poly(*o*-hydroxy amide)s. The solubility, mechanical properties, crystallinity, and thermal properties of the poly(*o*-hydroxy amide)s and polybenzoxazoles are also described. For a comparative study, related sulfonyl polymers without ether linkages based on 4,4'-sulfonyldibenzoyl chloride (SDBC) and the same bis(*o*-aminophenols) are also prepared and characterized.

EXPERIMENTAL

Materials

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]dibenzoic acid (SODBA) (mp 291–292 °C) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoic acid (4MeSODBA) (mp 312–315 °C) were synthesized as previously reported.^{13a} The diacyl chloride monomers, SDBC (mp 160–161 °C), SODBC (mp 183–184 °C), and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dibenzoyl chloride (4MeSODBC) (mp 190–191 °C), were prepared by the reaction of the corresponding dicarboxylic acids, that is, 4,4'-sulfonyldibenzoic acid (SDBA) (New Japan Chemicals), SODBA, and 4MeSODBA, with thionyl chloride in the presence of a trace amount of *N,N*-dimethylformamide (DMF) as a catalyst. The bis(*o*-aminophenols), 4,4'-diamino-3,3'-dihydroxybiphenyl (4A3HBP) [Tokyo Chemical Industry (TCI), Japan], 3,3'-

diamino-4,4'-dihydroxybiphenyl (3A4HBP) (TCI), and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (BAHHFP) (TCI), were of high purity and used as received. *N*-Methyl-2-pyrrolidone (NMP), DMF, and pyridine were stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4-Å molecular sieves. Commercially obtained anhydrous lithium chloride (LiCl) was dried *in vacuo* at 180 °C for 8 h. Other reagents and solvents were obtained commercially and used as received.

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

A typical procedure for the synthesis of poly(*o*-hydroxy amide) **2b** is as follows. In a 50-mL flask, 1 mmol (0.2162 g) of bis(*o*-aminophenol) 3A4HBP was dissolved in 10 mL of NMP containing 0.4 g of dissolved lithium chloride, and the mixture was cooled in an external ice–acetone bath. To the stirred solution 1 mmol (0.5273 g) of diacyl chloride SODBC was added. The reaction was carried out at –10–0 °C in the initial 2 h and continued overnight at room temperature. The resulting viscous polymer solution was poured slowly into 300 mL of methanol with stirring. The pale brown fiberlike precipitate formed was washed repeatedly with methanol and hot water, collected by filtration, and dried. The yield was almost quantitative. The obtained poly(*o*-hydroxy amide) **2b** had an inherent viscosity of 0.48 dL/g, as measured in dimethylacetamide (DMAc)-5 wt % LiCl at a concentration 0.5 g/dL at 30 °C. The IR spectrum (film) exhibited absorptions at 3419 (N–H stretching), 3000–3400 (O–H stretching), 1645 (C=O stretching), and 1527 cm^{–1} (N–H bending).

Film Preparation and Cyclodehydration of the Poly(*o*-hydroxy amide)s

A polymer solution of about 10 wt % was made by dissolving the poly(*o*-hydroxy amide) sample in NMP or DMAc and poured into a glass culture dish of 9 cm diameter. Then, the liquid film was dried in a 90 °C oven for 12 h. The obtained semidried polymer film was lifted off the glass substrate and further dried *in vacuo* at 150 °C for 6 h. The thickness of the polymer films was controlled between 60 and 70 μm.

The conversion of the poly(*o*-hydroxy amide)s to the corresponding polybenzoxazoles was carried out by successive heating of the preceding fabricated polymer films at 150 °C for 1 h, 250 °C

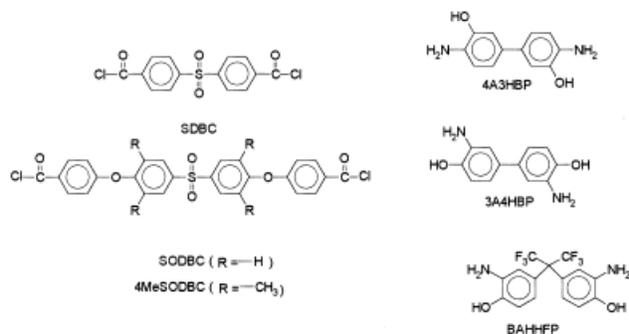
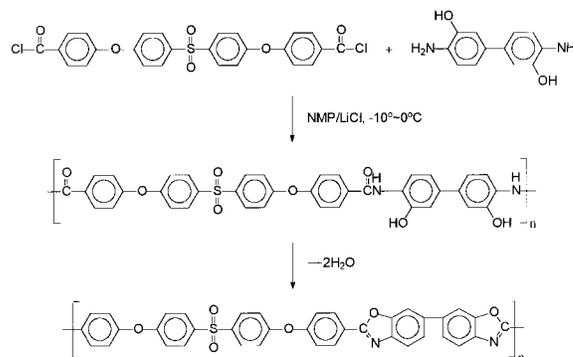


Figure 1. Structures and codes of monomers.

for 1 h, and finally at 320 °C for 1 h under nitrogen atmosphere.

Measurements

Inherent viscosities (η_{inh}) were measured for a polymer solution of 0.5 g/dL concentration in DMAc-5 wt % LiCl at 30 °C using a Cannon-Fenske viscometer. IR spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer on solution-cast films or potassium bromide (KBr) pellets. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer, operating in the 2θ range of 5–45° at the scan rate of 3°/min using nickel-filtered Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, operating at 40 kV and 20 mA). DSC was performed on a PerkinElmer DSC 7 instrument in flowing nitrogen with a heating rate of 20 °C/min. T_g 's were read at the middle of the change in the heat capacity. Thermomechanical analysis (TMA) experiments were performed on a PerkinElmer TMA 7 instrument at a heating rate 10 °C/min with a loaded penetration probe under an applied constant load of 10 mN. The experiments were carried out in duplicate from 40 to 300 °C. The softening temperatures (T_s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of intersection from the second TMA traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050 thermogravimetric analyzer. Experiments were carried out on 9–11-mg samples heated in flowing nitrogen or air (100 cm³/min) at a scan rate of 20 °C/min. The measurements were taken after a 350 °C/30-min drying step for the polybenzoxazole samples.



Scheme 1. A typical synthetic scheme for poly(*o*-hydroxy amide) **2a** and the corresponding polybenzoxazole **5a**.

RESULTS AND DISCUSSION

Polymer Synthesis

The PBOs in the present study were synthesized in a classical two-step process by the initial formation of soluble poly(*o*-hydroxy amide)s through solution polycondensation of aromatic diacid chlorides with bis(*o*-aminophenols) followed by thermal cyclodehydration.¹⁴ The structures and codes of the monomers used in the present study are shown in Figure 1, and a typical synthetic scheme is illustrated in Scheme 1. Thus, from various monomer combinations, nine poly(*o*-hydroxy amide)s as shown in Figure 2 and nine corresponding PBOs as depicted in Figure 3 were obtained.

The poly(*o*-hydroxy amide)s as PBO precursors were prepared by the low-temperature solution polycondensation of sulfonyl diacid chlorides such as SDBC, SODBC, and 4MeSODBC with bis(*o*-aminophenols) 4A3HBP, 3A4HBP, and BAHHFP in an NMP/LiCl solution. According to a recent

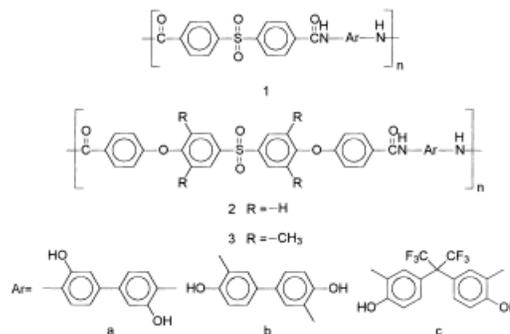


Figure 2. Structures and codes of poly(*o*-hydroxy amide)s.

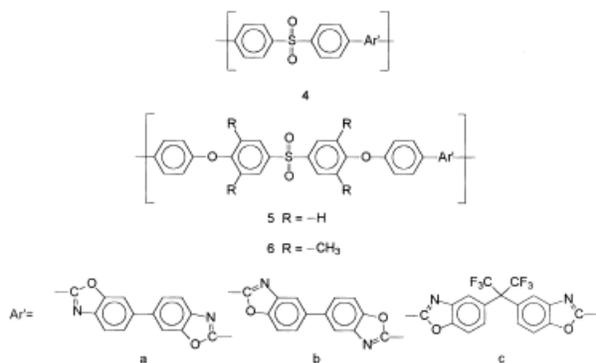
Table I. Synthesis Conditions, Inherent Viscosity, and Film Quality of Poly(*o*-hydroxy amide)s

Polymer Code	Combination of Monomers	Monomer Scale (mmol)	Amount of Reagents Used		η_{inh}^a (dL/g)	Film Quality ^b
			NMP (mL)	LiCl (g)		
1a	SDBC + 4A3HBP	2	10	0.4	0.74	Brittle
1b	SDBC + 3A4HBP	2	10	0.4	0.72	Brittle
1c	SDBC + BAHHFP	2	10	0.4	0.32	Brittle
2a	SODBC + 4A3HBP	1	10	0.4	0.50	Flexible
2b	SODBC + 3A4HBP	1	10	0.4	0.48	Flexible
2c	SODBC + BAHHFP	1	8	0.3	0.40	Brittle
3a	4MeSODBC + 4A3HBP	1	10	0.4	0.68	Flexible
3b	4MeSODBC + 3A4HBP	1	10	0.4	0.81	Flexible
3c	4MeSODBC + BAHHFP	1	5	0.2	0.32	Brittle

^a Measured in DMAc, 5 wt % LiCl at 30 °C on 0.5 g/dL.

^b Films were cast from slow evaporation of NMP or DMAc solutions and further dried at 150 °C under vacuum for 6 h.

report,¹⁵ the low-temperature reactions between the diacid chlorides and the bis(*o*-aminophenols) are believed to produce predominantly poly(*o*-hydroxy amide)s via a chemoselective polyamidation. By using the synthesis conditions listed in Table I, poly(*o*-hydroxy amide)s having inherent viscosities of 0.22–0.81 dL/g were obtained. The polymers derived from the hexafluoroisopropylidene (6F)-containing bis(*o*-aminophenol) BAHHFP 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 films made from the poly(*o*-hydroxy amide)s **1a** and **1b** were opaque and brittle, despite the fact that they exhibit a moderately higher inherent viscosity. The brittle nature of their cast films is probably attributable to the high rigidity and high packing density of their polymer chains.

**Figure 3.** Structures and codes of polybenzoxazoles.

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

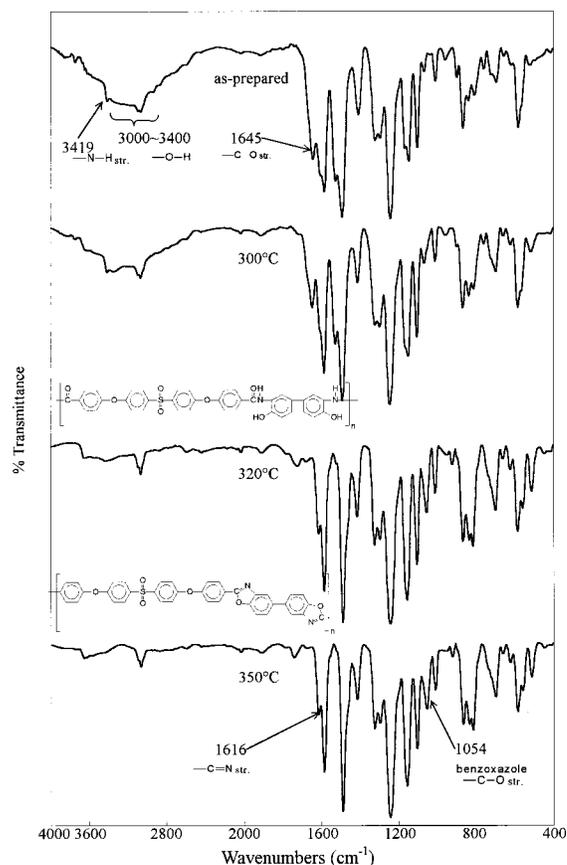
**Figure 4.** Fourier transform infrared spectra (thin films) of poly(*o*-hydroxy amide) **2b** after heating for 30 min under nitrogen at indicated temperatures.

Table II. Solubility Behavior of Poly(*o*-hydroxy amide)s

Polymer Code	Solvent ^a								
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	Chloroform	Acetone	Ethanol
1a	+	–	–	+	–	–	–	–	–
1b	+	–	–	+h	–	–	–	–	–
1c	+	+	+	+	+	+	–	–	–
2a	+	+h	+h	+h	–	–	–	–	–
2b	+h	+h	–	+	–	–	–	–	–
2c	+	+	+	+	+	+h	–	–	–
3a	+	+	+	+	–	+h	–	–	–
3b	+	+	+	+	–	+h	–	–	–
3c	+	+	+	+	+	+	–	–	–

^a +: Soluble at room temperature; +h: soluble on heating at 100 °C; –: insoluble even on heating. NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

150 °C for 1 h, 250 °C for 1 h, and 320 °C for 1 h under nitrogen. The conversion process could be confirmed by means of IR spectroscopy. Figure 4 demonstrates the IR spectra of a thin-film sample of poly(*o*-hydroxy amide) **2b** heated under nitrogen sequentially at 300, 320, and 350 °C each for 30 min. The as-prepared poly(*o*-hydroxy amide) film exhibited the characteristic absorption bands at 3419 cm^{–1} (N–H stretching), 3000–3400 cm^{–1} (O–H stretching), 1645 cm^{–1} (amide C=O stretching), and 1527 cm^{–1} (N–H bending). After heating at 320 °C for 30 min, the complete conversion of poly(*o*-hydroxy amide) to PBO was observed by the complete disappearance of the hydroxyl and amide absorptions at 3000–3500 and 1650 cm^{–1}, together with the appearance of char-

acteristic benzoxazole absorptions at 1054 cm^{–1} (C–O stretching) and 1616 cm^{–1} (C=N stretching).

Polymer Properties

The solubility behavior of poly(*o*-hydroxy amide)s is listed in Table II. All of the poly(*o*-hydroxy amide)s were soluble in polar solvents such as NMP and dimethyl sulfoxide. The poly(*o*-hydroxy amide)s **1a** and **1b** exhibited a lower solubility as a result of their crystalline nature, as observed by X-ray diffraction subsequently. The poly(*o*-hydroxy amide)s containing 6F groups such as **1c**, **2c**, and **3c** were also soluble in less polar *m*-cresol and tetrahydrofuran. The methyl substituents on the benzene rings leads to increased chain-pack-

Table III. Inherent Viscosities and Solubility of Polybenzoxazoles

Polymer Code	Combination of Monomers	η_{inh}^a	Solubility ^b		
			NMP	CH ₃ NO ₂ -10 wt % AlCl ₃	Concentrated H ₂ SO ₄
4a	SDBC + 4A3HBP	0.35	–	–	+
4b	SDBC + 3A4HBP	0.40	–	–	+
4c	SDBC + BAHHFP	0.12	+	+	+
5a	SODBC + 4A3HBP	0.21	–	–	+
5b	SODBC + 3A4HBP	0.24	–	–	+
5c	SODBC + BAHHFP	0.14	+	+	+
6a	4MeSODBC + 4A3HBP	0.32	–	–	+
6b	4MeSODBC + 3A4HBP	0.33	–	–	+
6c	4MeSODBC + BAHHFP	0.18	–	+	+

^a Measured in concentrated sulfuric acid at 30 °C on 0.5 g/dL.

^b +: Soluble at room temperature; +h: soluble on heating at 100 °C; –: insoluble even on heating.

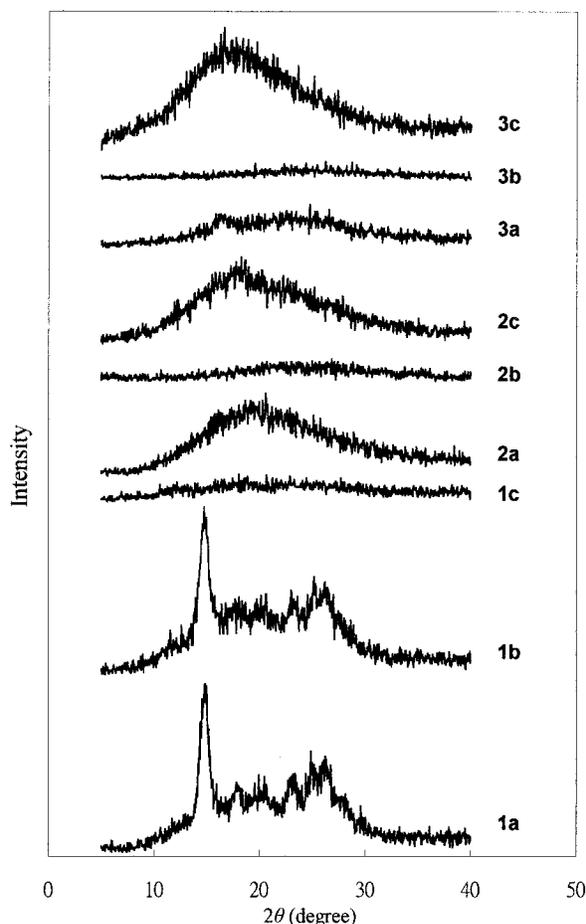


Figure 5. Wide-angle X-ray diffraction patterns of the poly(*o*-hydroxy amide)s.

ing distances and decreased interchain interactions such as hydrogen bonding; thus, the methyl-substituted polymers **3a–c** seemed to be more soluble than the corresponding polymers (**2a–c**) without methyl substituents.

Most of the PBOs, on the other hand, dissolved only in concentrated sulfuric acid. These results are listed in Table III. Despite the fact that most PBOs are amorphous, they were insoluble in organic solvents even in the nitromethane solution containing dissolved 10 wt % AlCl_3 , a solvent system described for aromatic heterocyclic rigid polymers.¹⁶ Only the 6F-containing PBOs were soluble in NMP or the nitromethane/Lewis acid solution.

The crystallinity of all polymers was measured by WAXD measurements. Figure 5 displays the WAXD patterns of the poly(*o*-hydroxy amide)s. Polymers **1a** and **1b** exhibited a moderate degree of crystallinity because of the rigid backbone, in agreement with the result of the solubility test.

Incorporation of ether or 6F linkages or simultaneously attaching methyl substituents led to a decrease in crystallinity. After cyclization, PBOs **4a** and **4b** showed a slightly different crystal structure as compared with their poly(*o*-hydroxy amide) prepolymers **1a** and **1b**. In addition to the strong diffraction peak around $2\theta = 15^\circ$, another strong diffraction peak appeared at around $2\theta = 25^\circ$, as shown in Figure 6. The other PBOs showed no increased ordering as indicated by the WAXD patterns, despite the presence of an oxazole ring.

The thermal behavior of the poly(*o*-hydroxy amide)s and PBOs was evaluated by DSC, TMA, and TGA, and the results are summarized in Table IV. Prior to the DSC experiment, all the poly(*o*-hydroxy amide)s were heated from 30 to 250 °C at 20 °C/min to remove the possible volatiles such as moisture and the residual solvent, followed by rapid cooling to 30 °C at -100 °C/min. A typical pair of the DSC traces of poly(*o*-hydroxy

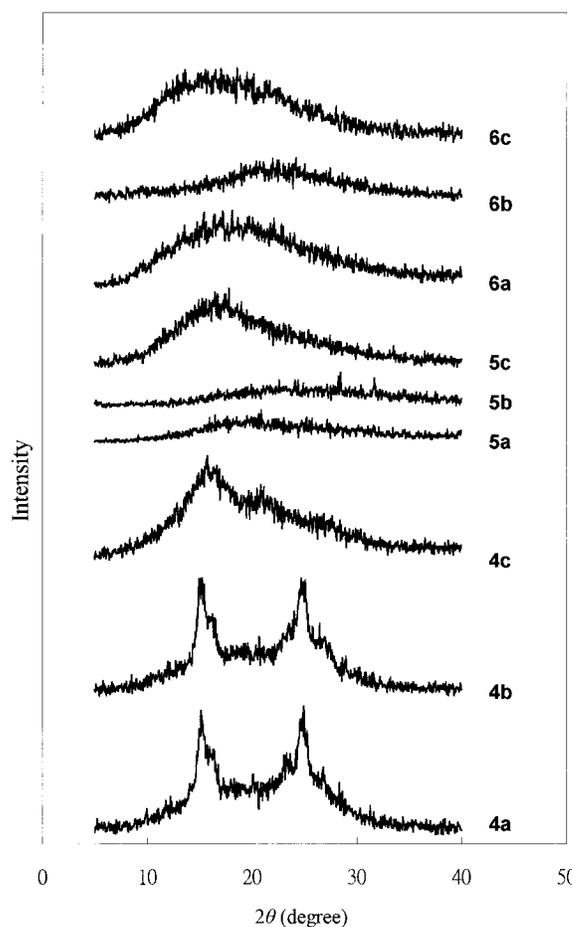


Figure 6. Wide-angle X-ray diffraction patterns of the polybenzoxazoles.

Table IV. Thermal Properties of Poly(*o*-hydroxy amide)s and Polybenzoxazoles

Poly(<i>o</i> -hydroxy amide)s			Polybenzoxazoles						
Polymer Code	T_g (°C) ^a	T_o (°C) ^b	T_p (°C) ^c	Polymer Code	T_s (°C) ^e	T_g (°C) ^f	T_d (°C) ^g		Char Yield (%) ^h
							In Air	In N ₂	
1a	—	—	—	4a	320	—	579	625	72
1b	—	—	—	4b	311	—	593	643	78
1c	172	250	301	4c	263	280	527	519	54
2a	—	274	307	5a	287	267	554	550	58
2b	—	248	304	5b	288	252	568	565	61
2c	165	244	310	5c	239	219	551	556	57
3a	—	252	303	6a	265	279	479	481	67
3b	219	267	305	6b	259	284	474	478	76
3c	176	250	319	6c	242	255	483	484	57

^a Temperature at the midpoint of baseline shift on the first DSC heating trace, with a heating rate of 20 °C/min in nitrogen.

^b Extrapolated onset temperature of the endothermic peak.

^c Endothermic peak temperature.

^d Specific heat of cyclodehydration.

^e 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 using an applied constant load of 10 mN with a heating rate of 10 °C/min.

^f Midpoint temperature of baseline shift on the second DSC heating trace of the sample after rapid cooling from 400 °C in nitrogen.

^g The temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

^h Residual weight percentage when heated to 800 °C in nitrogen.

amide) **3c** and the corresponding PBO **6c** are illustrated in Figure 7. Poly(*o*-hydroxy amide) **3c** showed a clear T_g at 176 °C and a broad endotherm between 250 and 400 °C, which was attrib-

uted to the evolution of water during the cyclization of poly(*o*-hydroxy amide) **3c** to PBO **6c**. After quenching from 400 °C, the PBO **6c** that formed *in situ* showed an increased T_g of around 255 °C

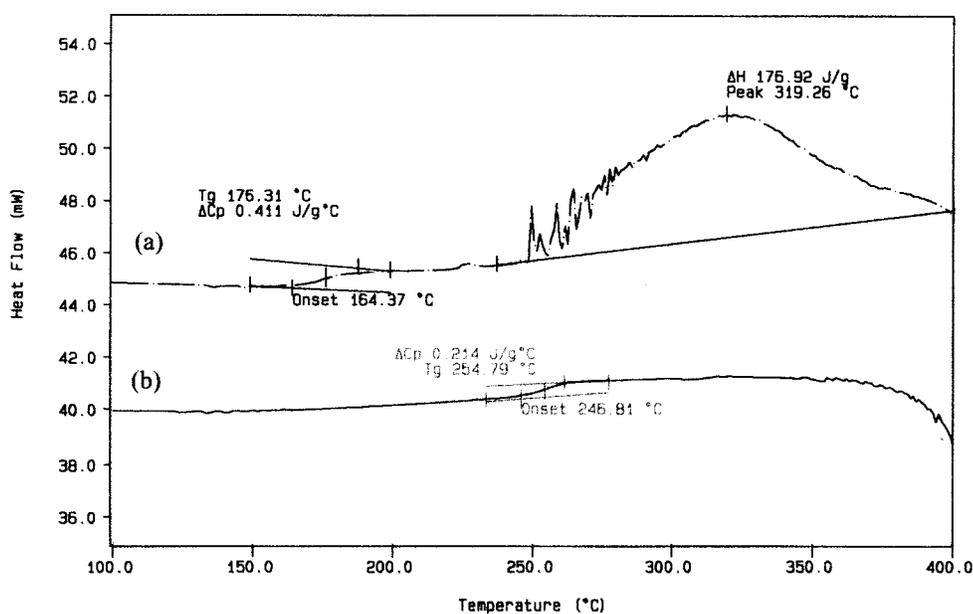


Figure 7. DSC curves of (a) poly(*o*-hydroxy amide) **3c** and (b) polybenzoxazole **6c** at a heating rate of 20 °C/min under nitrogen.

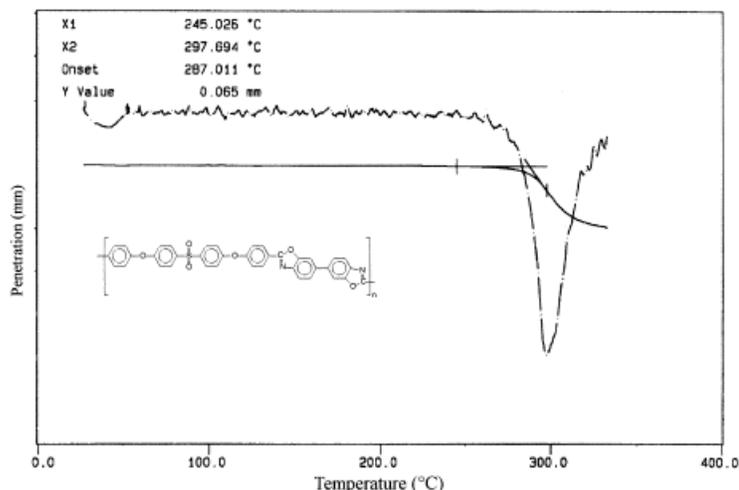


Figure 8. A typical TMA curve for polybenzoxazole **5a**, conducted with a penetration probe of 1.0 mm diameter using an applied constant load of 10 mN at a heating rate of 10 °C/min.

because of increased backbone stiffness. Some DSC data are presented in Table IV. Only four poly(*o*-hydroxy amide)s, that is, **1c**, **2c**, **3b**, and **3c**, showed discernible T_g 's on the DSC traces. However, except for the more rigid PBOs **4a** and **4b**, the other PBOs presented obvious baseline shifts on the DSC thermograms. The methyl-substituted PBOs (**6a–c**) exhibited higher T_g 's than the corresponding unsubstituted PBOs (**5a–c**) as a result of the hindrance effect of the chain rotation in the methyl-substituted polymers. The T_s values (may be referred as apparent T_g 's) of rigid **4a–c** together with other PBOs could be detected in the TMA experiments. A typical TMA trace for PBO **5a** is illustrated in Figure 8. As expected, the T_s values of PBOs **4a–c** were higher than those of the corresponding PBOs **5a–c** and **6a–c**, which contain the ether groups in the polymer backbones. In comparison with the T_s values measured by TMA, the methyl-substituted **6a–c** series PBOs showed a lower value than the corresponding unsubstituted **5a–c** series PBOs. The order in T_s values is contrary to that of the T_g values determined by DSC. This result may indicate that the PBOs containing methyl substituents exhibit a higher degree of plasticity near T_g than the analogues without methyl groups.

Dynamic TGA confirms the high thermal and thermooxidative stability of the prepared PBOs. Figure 9 shows a typical set of the TGA curves for the PBOs **4b**, **5b**, and **6b**. All the PBOs without methyl substituents were stable up to 450 °C in both air and nitrogen atmospheres. It is quite reasonable that the methyl-substituted PBOs be-

gan to decompose at lower temperatures compared with the unsubstituted polymers. All of the other PBOs showed a similar TGA behavior, and

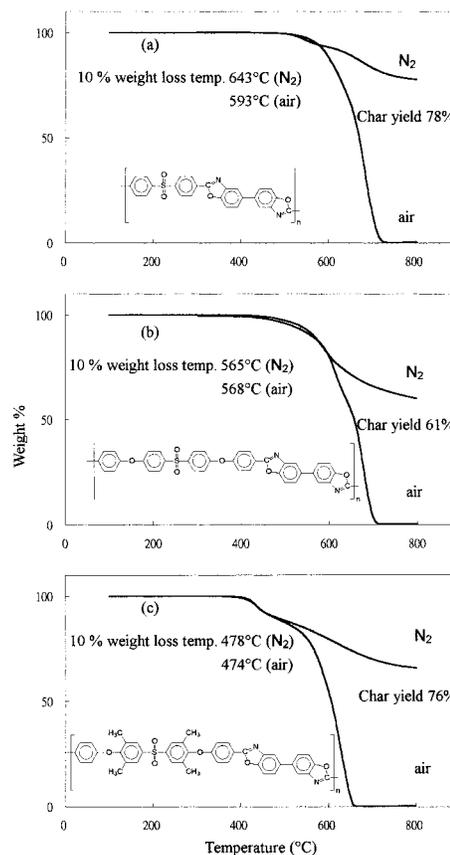


Figure 9. TGA curves of polybenzoxazoles (a) **4b**, (b) **5b**, and (c) **6b** with a heating rate of 20 °C/min.

their TGA data are also given in Table IV. Decomposition temperatures (T_d) corresponding to a 10% weight loss were recorded in the range of 474–593 °C in air and 478–643 °C in nitrogen, with 54–78% char residue remaining at 800 °C in nitrogen.

CONCLUSIONS

A series of novel poly(*o*-hydroxy amide)s, as the precursors of polybenzoxazoles, were successfully synthesized via the low-temperature solution polycondensation of the sulfonyl diacid chlorides SDBC, SODBC, and 4MeSODBC with bis(*o*-aminophenol)s in NMP/LiCl. The poly(*o*-hydroxy amide)s and polybenzoxazoles based on SDBC and diaminodihydroxybiphenyls were semicrystalline, and the other polymers were amorphous materials. Most of the poly(*o*-hydroxy amide)s were soluble in polar organic solvents; however, all the polybenzoxazoles except those with 6F groups were organic-insoluble. The thermally converted polybenzoxazoles showed increased T_g 's and greater solvent resistance than the poly(*o*-hydroxy amide) precursors. The introduction of ether and 6F groups in the polybenzoxazole main chain led to decreased T_g 's and T_s 's. The methyl-substituted polybenzoxazoles from 4MeSODBC revealed higher T_g 's but lower T_s 's and initial decomposition temperatures than the corresponding nonsubstituted ones from SODBC.

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