Synthesis and Properties of Novel Cardo Aromatic Poly(ether-benzoxazole)s

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ABSTRACT: Three new bis(ether-acyl chloride) monomers, 1,1-bis[4-(4-chloroformylphenoxy)phenyl]cyclohexane (**1a**), 5,5-bis[4-(4-chloroformylphenoxy)phenyl]-4,7-methanohexahydroindan (**1b**), and 9,9-bis[4-(4-chloroformylphenoxy)phenyl]fluorene (**1c**), were synthesized from readily available compounds. Aromatic polybenzoxazoles bearing ether and cardo groups were obtained by the low-temperature solution polycondensation of the bis(ether-acyl chloride)s with three bis(aminophenol)s and the subsequent thermal cyclodehydration of the resultant poly(o-hydroxy amide)s. The intermediate poly(o-hydroxy amide)s exhibited inherent viscosities in the range of 0.35–0.71 dL/g. All of the poly(o-hydroxy amide)s were amorphous and soluble in many organic polar solvents, and most of them could afford flexible and tough films by solvent casting. The poly(o-hydroxy amide)s exhibited glass-transition temperatures (T_g's) in the range of 141–169 °C and could be thermally converted into the corresponding polybenzoxazoles approximately in the region of 240–350 °C, as indicated by the DSC thermograms. Flexible and tough films of polybenzoxazoles could be obtained by thermal cyclodehydration of the poly(o-hydroxy amide) films. All the polybenzoxazoles were amorphous and showed an enhanced T_g but a dramatically decreased solubility as compared with their poly(o-hydroxy amide) precursors. They exhibited T_g's of 215–272 °C by DSC and showed insignificant weight loss before 500 °C in nitrogen or air. © 2001 John Wiley & Sons, Inc. J Polym Sci Part A: Polym Chem 39: 4014–4021, 2001

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INTRODUCTION

Aromatic polybenzoxazoles (PBOs) are a class of heterocyclic polymers with excellent thermal stability, high mechanical properties, and good chemical resistance.[1,2] Rigid-rod PBOs have become of interest because these polymers can be fabricated into high-strength and high-modulus fibers.[3,4] PBO fiber has a superior tensile strength and modulus as compared with p-aramid fibers. The properties of aromatic PBOs that make them attractive for many applications also lead to difficulties in synthesis and fabrication. In fact, PBOs have high transition temperatures and are soluble only in a strong acid medium[5] and through complexation-mediated solubilization in Lewis acid/organic solvent systems such as AlCl$_3$/nitromethane.[6] Therefore, many attempts have been made to improve their solubility or melt processability. Synthetic modification of the basic rigid-chain structures by introduction of flexibilizing linkages[7–11] into the backbone or attachment of bulky side groups[12–14] is one of the common strategies to improve the solubility and processing of PBOs.

An impressive series of high glass-transition temperature (T_g) soluble polymers, referred to as cardo polymers, was pioneered in the early 1960s and reviewed by Korshak et al.[15] Such polymers contain at least one element in the recurring unit that includes a cyclic side group such as 9,9-fluorenylidene that imparts a combination of enhanced thermal stability, high T_g, and improved solubility. It has been demonstrated in our previous articles[16−19] that incorporation of both the ether linkage and cardo units such as 1,1-cyclohexylidene, 4,7-methanohexahydroindane-5,5-diyl, 2,2-adamantylidene, and 9,9-fluorenylidene into the macromolecular backbone results in polyamides and polyimides with improved solubility that retains good thermal properties. In an attempt to improve the processability of PBOs through improved solubility and/or thermoplasticity, we carried out the synthesis of aromatic PBOs via the introduction of ether and cardo groups into the polymer backbone. Our strategy to achieve this goal was to first synthesize the poly(*o*-hydroxy amide)s from bis(ether-acyl chloride)s (**1a–c**) with bis(*o*-aminophenol)s, followed by thermal cyclodehydration. The solubility, thermal stability, and mechanical properties of the poly(*o*-hydroxy amide) prepolymers and the PBOs are subsequently described.

EXPERIMENTAL

Materials

The bis(ether-acyl chloride) monomers, 1,1-bis[4-(4-chloroformylphenoxy)phenyl]cyclohexane (**1a**) (mp 86–87 °C), 5,5-bis[4-(4-chloroformylphenoxy)-phenyl]-4,7-methanohexahydroindan (**1b**) (mp 70–72 °C), and 9,9-bis[4-(4-chloroformylphenoxy)-phenyl]fluorene (**1c**) (mp 256–258 °C), were prepared by chlorinating the corresponding bis(ether-carboxylic acid)s[16−18] with thionyl chloride in the presence of one drop of *N*,*N*-dimethylformamide (DMF) as a catalyst. Details of the synthesis and characterization data of these diacyl chlorides have been described in a separate article.[20] The aromatic bis(*o*-aminophenol) monomers including 4,4′-diamino-3,3′-dihydroxybiphenyl (**2**) [Tokyo Chemical Industry (TCI) Japan], 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. Lithium chloride (LiCl) was dried under vacuum at 180 °C for 10 h.

N-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

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

A typical procedure for the synthesis of poly(*o*-hydroxy amide) (**5c**) follows. In a 50-mL flask, a solution of 0.2162 g (1 mmol) of bis(*o*-aminophenol) **2** and 0.3 g of LiCl dissolved in 8 mL of NMP was cooled in an ice-acetone bath. To this solution, 0.5275 g (1 mmol) of solid diacyl chloride **1c** was added all at once. The reaction was carried out at −10–0 °C in the initial 2 h and continued at room temperature overnight. Pouring the solution into methanol (300 mL) with stirring precipitated the resulting polymer. After thorough washing with methanol and hot water and drying, a quantitative yield of **5c** was obtained. The inherent viscosity of the polymer was 0.53 dL/g, measured at a concentration of 0.5 g/dL in dimethylacetamide (DMAc) at 30 °C. The IR spectrum (film) showed absorptions at 3409 (N—H stretch), 1652 (C=O stretch), 2500–3500 (O—H stretch), 1597, and 1496 cm^{-1} (aromatic C=C stretch).

The other poly(*o*-hydroxy amide)s were prepared by a procedure similar to that described previously.

Film Preparation and Thermal Cyclodehydration to Polybenzoxazoles

A polymer solution was made by dissolving about 0.6 g of the poly(*o*-hydroxy amide) sample in 20 mL of DMAc. The solution was filtered through a paper filter into a flat glass culture disk of 9 cm diameter that was placed in a 90 °C oven for 12 h to remove the solvent. Then, the obtained semidried polymer film was stripped from the glass substrate and further dried *in vacuo* at 150 °C for 8 h. The thickness of the polymer films was controlled between 50 and 60 μm.

The conversion of poly(*o*-hydroxy amide)s to PBOs was carried out by heating the aforementioned fabricated polymer films at 250 °C for 30 min, 300 °C for 30 min, and 320 °C for 1 h under nitrogen atmosphere.

Measurements

Elemental analyses were run in a PerkinElmer model 2400 CHN analyzer. IR spectra were recorded on a Horiba FT-720 spectrometer. The in-

herent viscosities were measured with a Cannon-Fenske viscometer at a concentration of 0.5 g/dL at 30 °C. DSC was performed on a PerkinElmer DSC 7 differential scanning calorimeter equipped with a thermal analysis controller TAC 7/DX. The polymer samples were placed about 6–8 mg in aluminum sample pans and heated with a programmed rate of 20 °C/min under a nitrogen purge gas stream. T_g's were read at the middle of the change in the heat capacity. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 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. Apparent T_g's were taken as the onset temperature of probe displacement on the TMA traces. Thermogravimetic analysis (TGA) was performed using a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyst. Experiments were carried out on 9–11 mg samples under a nitrogen or air purge gas stream (50 mL/min) from 100 to 800 °C with a heating rate of 20 °C/min. Wide-angle X-ray diffraction measurements were performed at room temperature on a Siemens Kristalloflex D5000 X-ray diffractometer using nickel-filtered Cu $K\alpha$ radiation operating at 40 kV and 15 mA. The scanning rate was 2°/min over a range of $2\theta = 5-45°$. An Instron universal tester model 1130 with a load cell of 5 kg was used to examine the stress-strain behavior of the sample. 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 (6 cm long, 0.5 cm wide, and 50–60 μm thick). An average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Polymer Synthesis

Aromatic PBOs are commonly prepared by either of two methods. The first is a two-step process that involves the initial formation of poly(o-hydroxy amide)s from bis(o-aminophenol)s or their silylated derivatives with aromatic diacid chlorides followed by thermal cyclodehydration to PBOs in solid state or in solution.[7,10,21–24] The second is a one-step route directly producing PBOs by the melt polycondensation of bis(o-aminophenol)s with aromatic diacid diphenyl esters[25] and by the solution polycondensation with aromatic diacids,[14,26–29] poly(terephthalic acid anhydride),[30] or 1,4-bis(tri-

chloromethyl)benzene[31] in acidic media such as poly(phosphoric acid) and phosphorus pentoxide/methanesulfonic acid. Furthermore, another facile method has been reported for the preparation of PBOs, that is, the one-step polycondensation method from nitrile-bearing o-aminophenols[32] and from monomer pairs of bis(o-aminophenol)s and dinitriles.[33] Moreover, another synthetic route involves the reaction of aromatic bisphenols with bis-(fluorophenyl)benzoxazole monomers[8,9] or the self-polycondensation of fluorophenyl hydroxyphenyl benzoxazole monomer[34] by the nucleophilic displacement reaction to form PBOs. More recently, it has been reported that thermal conversion of hydroxy-containing polyimides is an alternative method for generating PBOs.[35,36]

In this study, the classical two-step procedure was used for the synthesis of these PBOs. The precursor poly(o-hydroxy amide)s were prepared by the low-temperature solution polycondensation of aromatic bis(ether-acyl chloride)s **1a–c** with bis(o-aminophenol)s **2–4** in an NMP/LiCl solution. According to a recent report,[37] the reactions between the diacid chlorides and the bis(o-aminophenol)s are believed to produce predominantly poly(o-hydroxy amide)s via a chemoselective polyamidation. Structures and codes of the monomers and poly(o-hydroxy amide)s are illustrated in Scheme 1. The results of the polymerizations are summarized in Table I. The inherent viscosities of the resulting poly(o-hydoxy amide)s were in the range of 0.30–0.69 dL/g, suggesting the formation of moderate to high molecular weights. The polymers derived from the hexafluoroisopropylidene (6F)-containing bis(o-aminophenol) **4** had relatively lower inherent viscosities than those derived from bis(o-aminophenol)s **2** and **3** that may be attributable to low nucleophilicity of the fluorine-containing monomer caused by the presence of electron-withdrawing 6F groups. The lower viscosities associated with the 6F-containing poly(o-hydroxy amide)s (**7a–c**) may also be due in part to their more flexible backbones. All of the poly(o-hydoxy amide)s were readily soluble in DMAc and could afford free-standing films by means of solution casting. However, the cast films of the **7a–c** series polymers cracked upon creasing, possibly because of insufficient molecular weights. All the other poly(o-hydroxy amdie)s afforded creasable and tough films. Polymer series **7a–c** are pale yellow, whereas polymers **5a–c** and **6a–c** are dark brown in color because of the high extent of conjugation in the backbone. In most cases, the thermal cy-
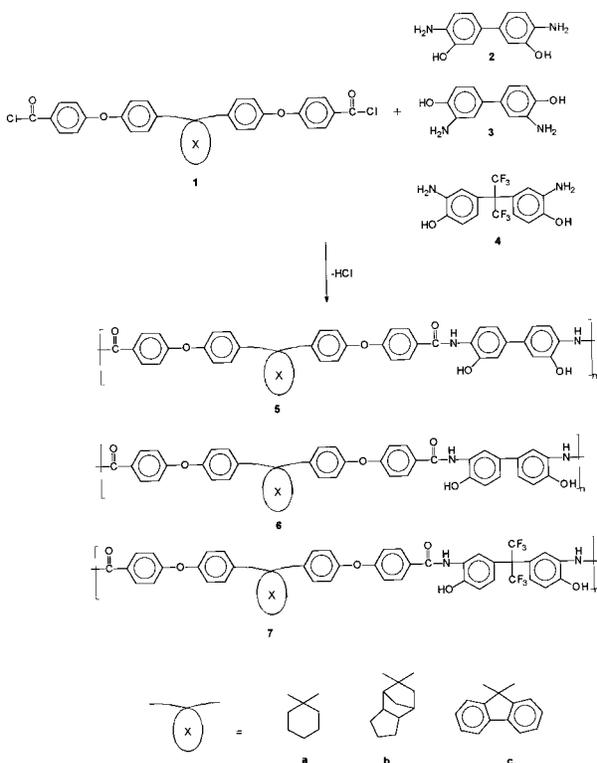
Scheme 1. Synthesis of poly(o-hydroxy amide)s.

clodehydration of the films of poly(o-hydroxy amide)s afforded pale yellow to dark brown, transparent, and tough PBO films. The thermally converted PBO films of **10b** and **10c** were flexible and tough, although their poly(o-hydroxy amide) precursors were a little brittle. This indicates that chain extension or crosslinking may occur during the cyclization process at elevated temperatures. The conversion process was monitored from the change in the IR spectra of the films. The complete conversion of o-hydroxy amide to the oxazole ring occurred at 300 °C as indicated by the disappearance of absorption as a result of hydroxyl and N—H groups at 3000–3500 cm^{-1} and an amide carbonyl peak at 1647 cm^{-1}, together with the appearance of characteristic benzoxazole absorptions at 1616 cm^{-1} (C=N) and 1053 cm^{-1} (C—O—C). This conversion also could be monitored by TGA and DSC analyses, which are discussed subsequently.

Polymer Characterization

As mentioned previously, the poly(o-hydroxy amide)s of the **5a–c** and **6a–c** series and all the PBOs except **10a** can afford flexible films. These

films were subjected to tensile testing, and the results are summarized in Table I. The tensile strengths, elongations to break, and initial moduli of these poly(o-hydroxy amide) films were in the range of 50–105 MPa, 9–18%, and 1.8–2.4 GPa, respectively. However, PBOs **8a–c** and **9a–c** showed lower tensile strengths and elongations 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.

All of the poly(o-hydroxy amide)s were soluble in NMP, DMAc, DMF, and cold or hot dimethyl sulfoxide. The introduction of the 6F group could hamper the close packing of chains and decrease interchain interactions; therefore, poly(o-hydroxy amide)s of the **7** series were also soluble in less polar m-cresol and tetrahydrofuran. On the other hand, the PBOs were insoluble in all the organic solvents tested and dissolved only in concentrated sulfuric acid. The poor solubility of the PBOs was probably caused by the rigid nature of their polymer chains.

The crystallinity of all poly(o-hydroxy amide)s and PBOs was examined by wide-angle X-ray diffraction in film samples over the 2θ range of 5–45°, and the results are illustrated in Figure 1. All the polymers, especially those containing the 6F groups, revealed essentially amorphous X-ray diffraction patterns as a result of the presence of flexible ether linkages and the packing-disruptive cardo groups.

The thermal properties of the poly(o-hydroxy amide)s and PBOs were investigated by using
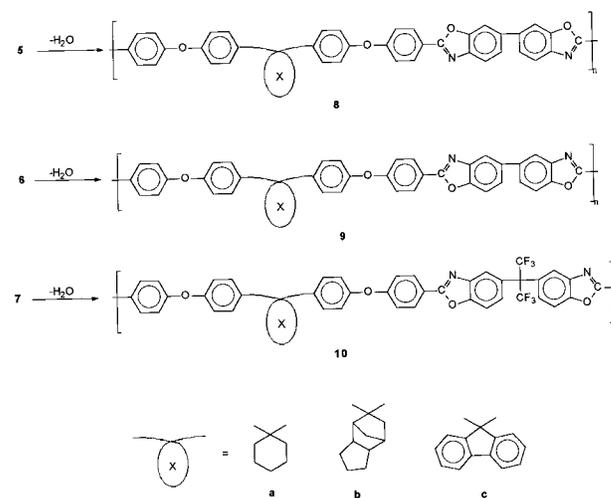
Scheme 2. Synthesis of polybenzoxazoles.

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

Polymer Code	ηinh[a] (dL/g)	Film Quality[b]	Tensile Properties of Polymer Films[b]		
			Strength to Break (MPa)	Elongation to Break (%)	Initial Modulus (GPa)
5a	0.64	Flexible, dark brown	95	12.0	1.8
6a	0.69	Flexible, dark brown	94	10.2	1.7
7a	0.44	Slightly brittle, pale yellow	—	—	—
5b	0.49	Flexible, dark brown	50	15.6	2.3
6b	0.43	Flexible, dark brown	57	18.1	1.8
7b	0.30	Slightly brittle, pale yellow	—	—	—
5c	0.53	Flexible, dark brown	105	15.9	2.0
6c	0.55	Flexible, dark brown	97	8.8	2.1
7c	0.39	Slightly brittle, pale yellow	—	—	—
8a		Flexible, dark brown	62	3.7	2.4
9a		Flexible, dark brown	67	6.5	1.8
10a		Slightly brittle, pale yellow	—	—	—
8b		Flexible, dark brown	30	2.5	2.2
9b		Flexible, dark brown	35	3.1	2.1
10b		Flexible, pale yellow	38	2.8	1.9
8c		Flexible, dark brown	52	3.2	2.1
9c		Flexible, dark brown	53	3.3	2.3
10c		Flexible, pale yellow	50	2.9	2.1

[a] Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.
[b] Films were cast from slow evaporation of the polymer solutions in DMAc and further dried *in vacuo* at 150 °C for 6 h. All the films are transparent.

TGA, DSC, and TMA. The relevant results are reported in Table II. Each sample was subjected to three subsequent DSC heating runs, the first run from 50 to 250 °C, after which the sample was cooled down with 100 °C/min to 50 °C followed by a second run from 50 to 400 °C. The sample was then cooled down again with 100 °C/min to 50 °C followed by a third run with an end temperature of 400 °C. All scans were recorded with a programmed rate of 20 °C/min under nitrogen atmosphere. The first run was aimed at eliminating any possible volatiles such as the absorbed mois-
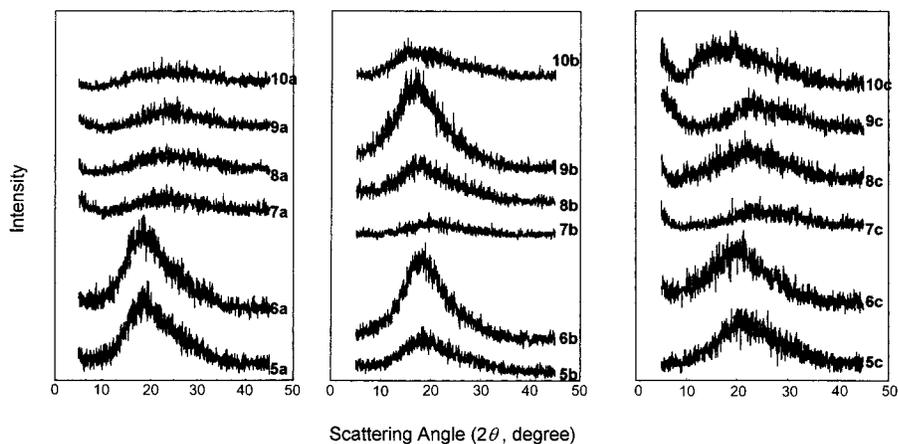

Figure 1. Wide-angle X-ray diffractograms of poly(*o*-hydroxy amide)s and polybenzoxazoles.

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

					Polybenzoxazoles				
Poly(*o*-hydroxy amide)s[a]					T_g (°C)		T_d (°C)[d]		Char Yield
Polymer Code	T_g (°C)	T_o (°C)	T_p (°C)	Polymer Code	DSC[b]	TMA[c]	In N$_2$	In Air	(%)[e]
5a	—	254	310	**8a**	231	243	545	540	50
6a	—	266	315	**9a**	227	239	541	537	54
7a	145	246	302	**10a**	215	229	527	543	52
5b	168	251	298	**8b**	266	303	539	529	62
6b	166	262	299	**9b**	261	305	538	535	65
7b	141	240	275	**10b**	247	269	520	531	66
5c	169	251	299	**8c**	272	310	598	558	61
6c	165	252	301	**9c**	272	307	578	545	61
7c	154	245	306	**10c**	246	271	565	528	48

[a] DSC data from the first DSC heating trace at 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 400 °C.
[c] 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.
[d] The temperature at which 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.
[e] Residual weight percentage at 800 °C in nitrogen.

ture and residual solvent in the samples. The second run yielded the T_g and endothermal peak as a result of cyclodehydration of the poly(*o*-hydroxy amide) sample. After rapid cooling from the elevated temperature, the PBOs formed *in situ* in the DSC cell were predominantly amorphous. Thus, in the third run, all the PBOs exhibited a clear baseline shift. A typical pair of DSC curves of poly(*o*-hydroxy amide) **5b** and PBO **8b** are shown in Figure 2 (only the second and third heating runs are shown). On the second heating trace that was recorded from 50 to 400 °C with a heating rate of 20 °C/min, poly(*o*-hydroxy amide) **6c** showed a discernible glass transition at 168 °C
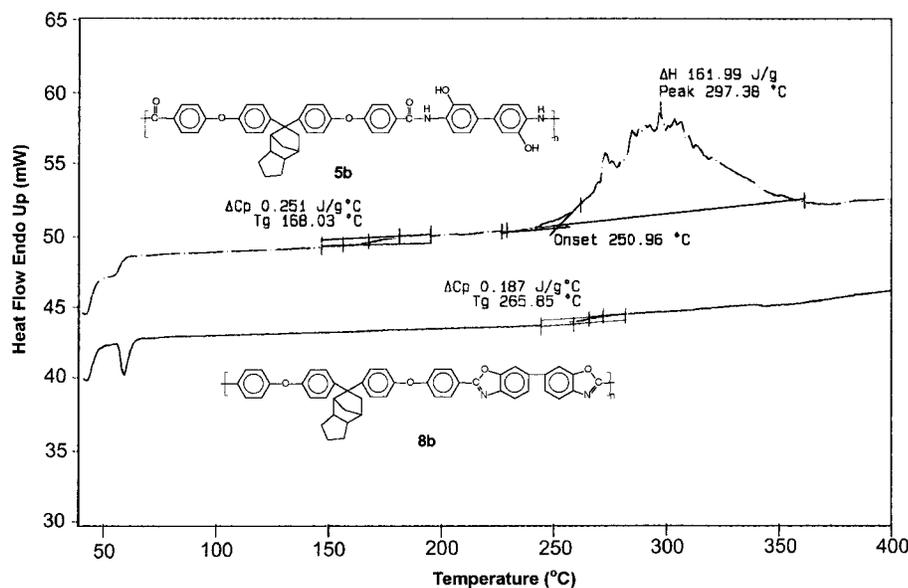

Figure 2.   DSC curves of poly(*o*-hydroxy amide) **5b** and the corresponding polybenzoxazole **8b** with a heating rate of 20 °C/min in nitrogen.
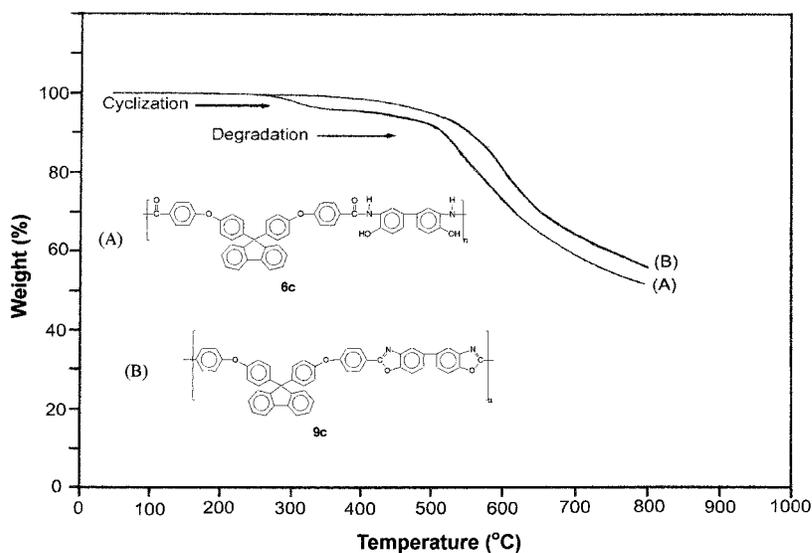
Figure 3. TGA curves of (A) poly(*o*-hydroxy amide) **6c** and (B) polybenzoxazole **9c** with a heating rate of 20 °C/min in nitrogen.

and a strong endothermic peak between 250 and 350 °C that was attributed to loss of water during the conversion of **5b** to **8b**. After quenching from 400 °C, the **8b** formed *in situ* during the second heating scan revealed an obvious T_g at 266 °C in the subsequent scan. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Table II. Except for **5a** and **6a**, all the other poly(*o*-hydroxy amide)s displayed discernible glass transitions between 141 and 169 °C in the DSC traces and strong endothermic peaks between 250 and 400 °C. As can be seen from the DSC thermograms, all the poly(*o*-hydroxy amide)s were almost completely converted to the corresponding PBOs when heated to 350–400 °C at a scan rate of 20 °C/min in nitrogen. The thermally converted PBOs had T_g's in the range of 231–272 °C that are higher than those of the corresponding poly(*o*-hydroxy amide)s by 92–107 °C because of increased chain rigidity. The T_g's of PBOs were also determined by TMA. As listed in Table II, these PBOs exhibited T_g's in the range of 229–310 °C by TMA. 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 because of more flexible backbones. All the T_g's detected by TMA were higher than those from DSC. These differences may be ascribed to the different thermal history of the samples and mainly to the distinct nature of the testing methods (mechanical vs calorimetric). On the other hand, the polymers bearing bulky fluorene or hexahydromethanoindan cardo groups revealed a higher T_g than the corresponding counterparts with the cyclohexane group. This is reasonable because the cyclohexane structure has a smaller effect on steric hindrance and more conformational flexibility in comparison with the other two bulkier cardo groups.

Figure 3 illustrates typical TGA curves for poly(*o*-hydroxy amide) **6c** and PBO **9c** in nitrogen. The TGA curve of **6c** revealed an initial weight loss between 250 and 350 °C. The weight loss is due to thermal cyclodehydration of the poly(*o*-hydroxy amide), which also agrees well with the strong endotherm on the DSC curve. The second break in the TGA curve that occurred at around 500 °C corresponded to the decomposition of the PBO formed *in situ*. All the other PBOs showed a similar thermal behavior as that of **9c**, and their TGA data are also summarized in Table II. All the PBOs did not show a significant weight loss up to 500 °C in air or nitrogen, and the temperatures at 10% weight loss were in the range of 520–598 °C in nitrogen and 529–558 °C in air, with more than 50 wt % residue remaining at 800 °C in nitrogen.

CONCLUSIONS

A series of poly(*o*-hydroxy amide)s were successfully prepared from **1a**, **1b**, and **1c** with bis(*o*-aminophenol)s such as 4,4′-diamino-3,3′-dihydroxybiphenyl,

3,3′-diamino-4,4′-dihydroxybiphenyl, and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane via the low-temperature solution polycondensation in NMP/LiCl. All of these poly(o-hydroxy amide)s were amorphous in nature and soluble in various organic solvents such as NMP, DMF, DMAc, and DMSO, and most of them could be solution cast into flexible and tough films. The poly(o-hydroxy amide)s exhibited T_g's in the 141–169 °C range and could be thermally cyclodehydrated in the solid state into the PBOs approximately in the region of 240–350 °C, as seen by the DSC thermograms. All of the thermally converted PBO films were also flexible and creasable. Although these PBOs were noncrystalline, they showed a dramatically decreased solubility as compared with the poly(o-hydroxy amide) precursors and dissolved only in concentrated sulfuric acid. The T_g's of the prepared PBOs were recorded in the range of 239–310 °C by TMA and 215–272 °C by DSC. The polymers bearing bulky fluorene or methanohexahydroindan cardo groups revealed a higher T_g than those with the cyclohexane group. The PBOs showed good thermal stability; they did not show significant weight loss before 500 °C. Although the PBOs were organically insoluble, the large window between the T_g and the decomposition temperature could be advantageous in the melt processing of these polymers.

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