

Syntheses and Properties of New Aromatic Polybenzoxazoles Bearing Ether and Phenylethylidene or 1-Phenyl-2,2,2-trifluoroethylidene Linkages

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ABSTRACT: Two new bis(ether acyl chloride)s, 1,1-bis[4-(4-chloroformylphenoxy)phenyl]-1-phenylethane and 1,1-bis[4-(4-chloroformylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane, were prepared from readily available reagents. Aromatic polybenzoxazoles with both ether and phenylethylidene or 1-phenyl-2,2,2-trifluoroethylidene linkages between phenylene units were obtained by a conventional two-step procedure including the low-temperature solution polycondensation of the bis(ether acyl chloride)s with three bis(*o*-aminophenol)s, yielding poly(*o*-hydroxyamide) precursors, and subsequent thermal cyclodehydration. The intermediate poly(*o*-hydroxyamide)s exhibited inherent viscosities of 0.39–0.98 dL/g. All of the poly(*o*-hydroxyamide)s were amorphous and soluble in polar organic solvents such as *N,N*-dimethylacetamide, and most of them could afford flexible and tough films via solvent casting. The poly(*o*-hydroxyamide)s exhibited glass-transition temperatures (T_g 's) of 129–194 °C and could be thermally converted into corresponding polybenzoxazoles in the solid state at temperatures higher than 300 °C. All the polybenzoxazoles were amorphous and showed an enhanced T_g but a dramatically decreased solubility with respect to their poly(*o*-hydroxyamide) precursors. They exhibited T_g 's of 216–236 °C through differential scanning calorimetry and were stable up to 500 °C in nitrogen or air, with 10% weight-loss temperatures being recorded between 538 and 562 °C in nitrogen or air.

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INTRODUCTION

Aromatic polybenzoxazoles (PBOs) are a class of heterocyclic polymers that exhibit outstanding thermooxidative stability, high tensile modulus and strength, and superior chemical resistance.^{1,2} High-modulus fibers can be produced by the spinning of liquid-crystalline solutions of rodlike PBOs in sulfuric acid or poly(phosphoric acid).^{2–4}

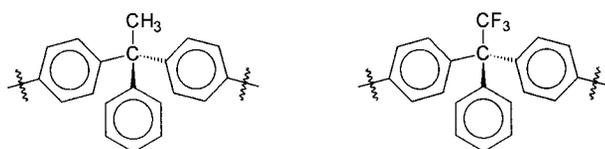
However, similar to polyimides, most PBOs have high thermal transitions and are generally only soluble in strong acids, and so their applicability may be narrow. To overcome such difficulties, researchers have made many attempts to modify the backbone structure and improve their processability.^{5–15} One successful approach is to introduce flexible linkages into the PBO backbone to increase processability. For example, the incorporation of hexafluoroisopropylidene (6F) groups into the polymer backbone enhances the solubility of PBOs and preserves thermooxidative stability to some extent.^{5–8} In some cases, the 6F groups are combined with other flexible linkages

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such as aryl ether to lower the glass-transition temperature (T_g).^{8,9} Similarly, some other poly(ether benzoxazole)s have been generated, and they display properties intermediate between those of the two homopolymers.^{10–14} Desired properties resulting from these materials include thermoplasticity, excellent tensile properties, and enhanced toughness.

We have proved that the incorporation of ether and isopropylidene or 6F linkages between phenylene units in the PBO backbone leads to improved tractability with retention of high thermal stability.⁸ This work is also along those lines, but it emphasizes the preparation of a series of new PBOs containing both ether and phenylethyli-dene or 1-phenyl-2,2,2-trifluoroethylidene (3F) units. Our strategy to achieve this goal was first to synthesize multiring, flexible diacyl chlorides {1,1-bis[4-(4-chloroformylphenoxy)phenyl]-1-phenylethane (**1**) and 1,1-bis[4-(4-chloroformylphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (**2**)}, which were subsequently reacted with bis(*o*-aminophenol) monomers; this was followed by thermal cyclodehydration of the intermediate poly(*o*-hydroxyamide)s to PBOs. The obtained PBOs had the following packing-disruptive, kinked 1,1,1-triphenylethane or 1,1,1-triphenyl-2,2,2-trifluoroethane segments:



It was expected that the incorporation of these hindered segments would sterically inhibit significant chain–chain interactions and disturb the coplanarity of aromatic units, reducing packing efficiency and crystallinity. In addition, the presence of flexible ether linkages was expected to reduce chain rigidity. As a result, we anticipated that the resultant PBOs would exhibit enhanced solubility or melt processability. An emphasis was also placed on investigating the influence of the chemical structure of PBOs on their acid resistance, their solubility in organic solvents, their T_g 's, and their thermal and thermooxidative stability.

EXPERIMENTAL

Materials

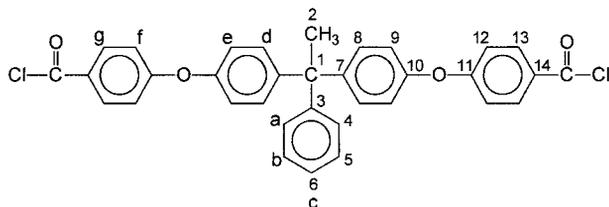
The aromatic bis(*o*-aminophenol) monomers, including 3,3'-diamino-4,4'-dihydroxybiphenyl

(**3**; TCI), 4,4'-diamino-3,3'-dihydroxybiphenyl (**4**; TCI), and 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (**5**; TCI) were of high purity and were 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. Propylene oxide was used as received.

Synthesis of Diacyl Chloride Monomers

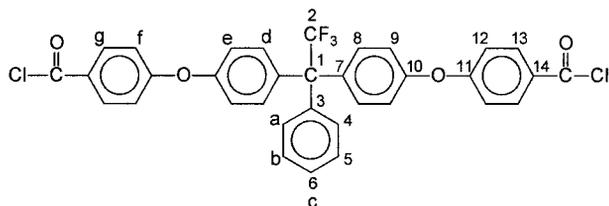
According to well-established synthetic procedures,¹⁶ the multiring flexible bis(ether carboxylic acid)s, 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane [mp = 269 °C; by differential scanning calorimetry (DSC)] and 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane (mp = 294 °C; by DSC), were prepared from the fluorodisplacement of *p*-fluorobenzonitrile with the potassium phenoxides of the corresponding bisphenols, that is, 1,1-bis(4-hydroxyphenyl)-1-phenylethane and 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane, followed by the alkaline hydrolysis of the bis(ether nitrile) intermediates. The synthetic details and characterization data of these two diacids have been reported in our previous publications.^{17,18} The diacyl chloride monomers were prepared by chlorination of the corresponding bis(ether carboxylic acid)s with thionyl chloride. A typical synthetic procedure for **1** was as follows: 10.6 g (0.02 mol) of 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenylethane was suspended in a mixture of 30 mL of thionyl chloride and 30 mL of dichloromethane in the presence of two to three drops of *N,N*-dimethylformamide (DMF) as the catalyst. After the mixture was heated at 60 °C for about 2 h, the suspension solution turned into a clear solution. The solution was kept at 60 °C for another 4 h so that a complete reaction was ensured. Dichloromethane and an excess of thionyl chloride were removed by distillation. The residual solid was dried *in vacuo* to give an almost quantitative yield of diacyl chloride **1**.

mp: 54 °C. IR (KBr): 1770 (C=O stretching), 1250 cm^{-1} (C—O stretching). ¹H NMR (CDCl₃, δ , ppm): 8.07 (d, H_g, 4H), 7.32 (m, H_b, 2H), 7.25 (m, H_c, 1H), 7.16 (two overlapped AB doublets, H_a + H_d, 6H), 7.02 (two overlapped AB doublets, H_e + H_f, 8H), 2.23 (s, —CH₃, 3H). ¹³C NMR (CDCl₃, δ , ppm): 169.2 (C=O), 166.1 (C¹¹), 154.8 (C¹⁰), 150.3 (C³), 147.7 (C⁷), 135.6 (C¹³), 132.4 (C⁸), 130.1 (C⁴), 129.8 (C⁵), 128.7 (C⁶), 128.0 (C¹⁴), 121.4 (C¹²), 118.7 (C⁹), 52.6 (C¹), 31.1 (C²).



2 (mp = 134 °C), the other diacyl chloride, was synthesized in a similar procedure from 1,1-bis[4-(4-carboxyphenoxy)phenyl]-1-phenyl-2,2,2-trifluoroethane.

IR (KBr): 1770 (C=O stretching), 1255 cm^{-1} (C—O stretching). ^1H NMR (CDCl_3 , δ , ppm): 8.09 (d, H_g , 4H), 7.38 (m, H_b , 2H), 7.36 (m, H_c , 1H), 7.22 (two overlapped AB doublets, $\text{H}_a + \text{H}_d$, 6H), 7.07 (two overlapped AB doublets, $\text{H}_e + \text{H}_f$, 8H). ^{13}C NMR (CDCl_3 , δ , ppm): 169.2 (C=O), 165.4 (C^{11}), 156.4 (C^{10}), 141.4 (C^3), 138.4 (C^7), 135.7 (C^{13}), 133.5 (C^8), 131.4 (C^4), 130.1 (C^5), 130.0 (C^{14}), 129.4 (q, $^1J_{\text{C-F}} = 286$ Hz, C^2), 129.2 (C^6), 121.3 (C^{12}), 119.2 (C^9), 65.3 (q, $^2J_{\text{C-F}} = 24$ Hz, C^1).



General Synthetic Procedure for Poly(*o*-hydroxyamide)s and PBOs

The low-temperature solution polycondensation technique was employed for the preparation of the poly(*o*-hydroxyamide)s from diacyl chlorides **1** and **2** with bis(*o*-aminophenol)s **3–5**. In a 50-mL, round-bottom flask, 1 mmol of a bis(*o*-aminophenol) was dissolved in 5 mL of NMP and maintained at -10 to 0 °C in an ice–acetone bath. To the solution, 0.3 mL of propylene oxide was added, and then 1 mmol of diacyl chloride was added at once. The reaction was carried out at -10 to 0 °C in the initial 2 h and continued at room temperature overnight (ca. 10 h). As the polycondensation proceeded, the reaction mixture gradually became viscous. The resulting polymer solution was diluted with 5 mL of NMP and filtered into a 11-cm-diameter glass culture dish, which was placed in a 90 °C oven for 12 h for the removal of the solvent. Then, the obtained semi-dried polymer film was stripped from the glass substrate and further dried *in vacuo* at 160 °C for 8 h.

The conversion of poly(*o*-hydroxyamide)s into PBOs was carried out through the heating of the

aforementioned fabricated polymer films at 250 °C for 30 min, at 275 °C for 30 min, and at 300 °C for 1 h under a nitrogen atmosphere.

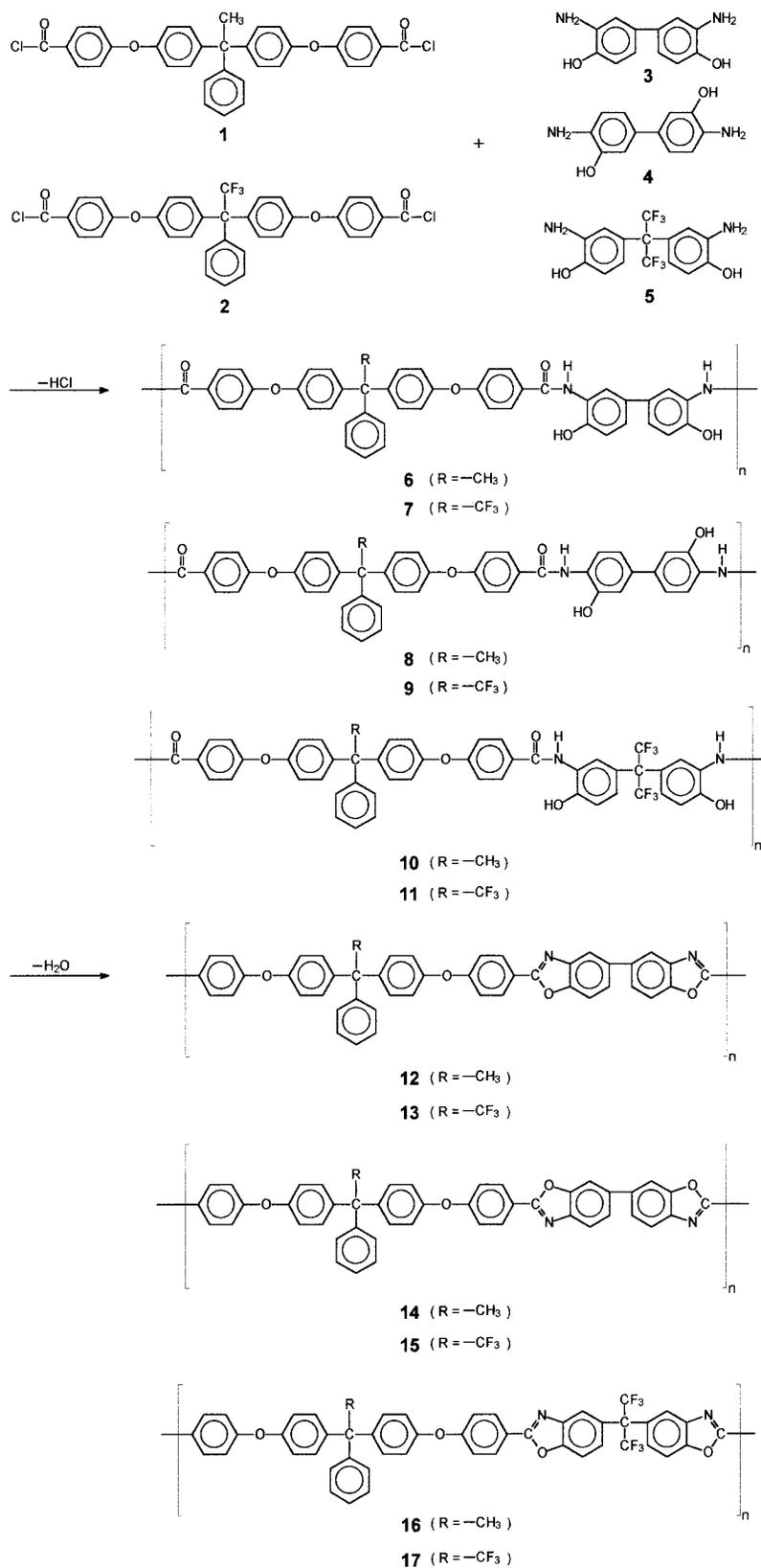
Measurements

IR spectra were recorded on a Horiba FT-720 Fourier transform infrared spectrometer. An elemental analysis was performed with a PerkinElmer 2400 CHN analyzer. ^1H and ^{13}C NMR spectra were measured on a JEOL EX 400 spectrometer at 399.65- and 99.00-MHz frequencies, respectively. The inherent viscosities of the polyamides were determined with a Cannon-Fenske viscometer at 30 °C. An Instron model 1130 universal tester with a load cell of 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 mm/min were used for this study. The measurements were performed at room temperature with film specimens (0.5 cm wide, 6 cm long, and ca. 0.08 mm thick), and an average of at least five individual determinations was used. Wide-angle X-ray diffraction measurements were performed at room temperature (ca. 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer (operating at 40 kV and 20 mA) with nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418$ Å). The scanning rate was $3^\circ/\text{min}$ over a range of $2\theta = 5$ – 45° . Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 4–6 mg of samples in flowing nitrogen (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a heating rate of 20 °C/min under nitrogen. T_g 's 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 at a cooling rate of 200 °C/min. Thermomechanical analysis (TMA) was conducted with a PerkinElmer TMA 7 instrument. The TMA experiments were conducted from 40 to 300 °C at a scanning rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s 's) were taken as the onset temperatures of probe displacement on the TMA traces.

RESULTS AND DISCUSSION

Polymer Synthesis

The aromatic PBOs in this study were synthesized in a classical two-step process by the initial forma-



Scheme 1. Synthesis of poly(*o*-hydroxyamide)s and PBOs.

Table 1. Inherent Viscosities (η_{inh}) of Poly(*o*-hydroxyamide)s and PBOs

Monomers	Poly(<i>o</i> -hydroxyamide) ^a		PBO ^b	
	Code	η_{inh} (dL/g) ^a	Code	η_{inh} (dL/g) ^d
1 + 3	6	0.93	12	0.08
2 + 3	7	0.98	13	0.66
1 + 4	8	0.72	14	0.15
2 + 4	9	0.62	15	0.54
1 + 5	10	0.56	16	0.12
2 + 5	11	0.39	17	0.29

^a Polymerizations were carried out with 1 mmol of each monomer in 5 mL of NMP and 0.3 mL of propylene oxide at $-10-0$ °C for 2 h and then at room temperature overnight.

^b The conversion of the poly(*o*-hydroxyamide)s to benzoxazoles was carried out via heating at 300 °C for 1 h.

^c Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

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

tion of soluble poly(*o*-hydroxyamide)s through the solution polycondensation of aromatic diacyl chlorides with bis(*o*-aminophenol)s followed by thermal cyclodehydration.¹⁹ The structures and codes of the monomers and polymers are illustrated in Scheme 1.

The poly(*o*-hydroxyamide)s as PBO precursors were prepared by low-temperature solution polycondensation of diacyl chloride **1** or **2** with three structurally different bis(*o*-aminophenol)s (**3–5**) in an NMP solution in the presence of propylene oxide as the acid acceptor. The inherent viscosities of the resulting poly(*o*-hydroxyamide)s were 0.39–0.98 dL/g (Table 1). The poly(*o*-hydroxyamide)s derived from the 6F-containing bis(*o*-aminophenol) **5** had relatively lower inherent viscosities, which may be attributable to the low nucleophilicity of the fluorine-containing monomer caused by the presence of electron-withdrawing 6F groups. All of the poly(*o*-hydroxyamide)s were readily soluble in amide-type solvents such as NMP and *N,N*-dimethylacetamide (DMAc) and could afford freestanding films by means of solution casting. However, the cast films of the poly(*o*-hydroxyamide) **11** cracked upon creasing, possibly because of low molecular weights. All the other poly(*o*-hydroxyamide)s afforded creasable and tough films. Polymers **10** and **11** were pale yellow, whereas polymers **6–9** were pale brown because of the high extent of conjugation in the backbone.

All of the poly(*o*-hydroxyamide)s could be thermally converted into the corresponding PBOs by the fabricated films being heated to 300 °C and held there for 1 h under a nitrogen atmosphere. The conversion process could be confirmed by means of IR spectroscopy. The poly(*o*-hydroxyamide) films exhibited the characteristic absorption bands at 3414 (N—H stretching), 3000–3400 (O—H stretching), 1650 (amide C=O stretching), and 1520 cm^{-1} (N—H bending). After 1 h of heating at 300 °C, the complete conversion of poly(*o*-hydroxyamide) to PBO was observed by the complete disappearance of the hydroxyl and amide absorptions at 3000–3400 and 1650 cm^{-1} , together with the appearance of characteristic benzoxazole absorptions at 1058 (C—O stretching) and 1616 cm^{-1} (C=N stretching). This conversion was also monitored by the DSC analysis and TGA discussed subsequently. The PBOs obtained, except for **17**, were insoluble in most organic solvents but were soluble in cold concentrated sulfuric acid. The PBOs based on diacyl chloride **1** were decomposed simultaneously during the dissolution process, as indicated by very low inherent viscosity values (0.08–0.15 dL/g). The PBOs derived from diacyl chloride **2** had inherent viscosities of 0.29–0.66 dL/g in concentrated sulfuric acid, and this indicated that less degradation leading to molecular chain scission occurred during the dissolution and viscosity determination. This also indicated that the 3F linkage had a better acid resistance.

Polymer Properties

The solubility of all the poly(*o*-hydroxyamide)s and PBOs were tested qualitatively in various organic solvents. All of the poly(*o*-hydroxyamide)s were soluble in NMP, DMAc, DMF, and dimethyl sulfoxide. The introduction of 6F-bis(*o*-aminophenol) **5** could further hamper the close packing of the chains and interchain interactions; therefore, poly(*o*-hydroxyamide)s **10** and **11** were also soluble in less polar *m*-cresol and tetrahydrofuran. The PBOs, however, dissolved only in concentrated sulfuric acid, with the exception of 6F-containing polymers **16** and **17**. The poor solubility of PBOs **12–15** could be attributed to the rigid nature of their polymer chains caused by the bi(*p*-phenylenebenzoxazole) segments.

As mentioned earlier, the poly(*o*-hydroxyamide)s **6–10** and the PBOs **12–15** could afford flexible films. These films were subjected to tensile testing, and the results are summarized in

Table 2. Tensile Properties of the Poly(*o*-hydroxyamide) and PBO Films

Polymer Code	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
6	102	11	2.5
7	88	18	2.1
8	104	12	2.3
9	82	18	2.3
10	50	4	2.0
12	80	6	1.9
13	81	7	2.2
14	84	8	1.8
15	99	9	2.2

Table 2. The tensile strengths, elongations to break, and tensile moduli of these poly(*o*-hydroxyamide) films were 50–104 MPa, 4–18%, and 2.0–2.5 GPa, respectively. The PBOs **12–15** showed tensile strengths of 80–99 MPa, elongations to break of 6–9%, and tensile moduli of 1.8–2.2 GPa. However, the poly(*o*-hydroxyamide) **11** and the thermally converted PBO films of **16** and **17** were so brittle that they cracked with fingernail creasing. Their mechanical properties were not evaluated. In general, the PBOs showed lower tensile strengths and elongations to break than their cor-

responding poly(*o*-hydroxyamide) precursors. The deterioration effect on the mechanical properties of PBO films may be attributed to stress buildup and chain shrinkage upon thermal cyclodehydration.

The crystallinity of all the poly(*o*-hydroxyamide)s and PBOs was examined by wide-angle X-ray diffraction in film or powder samples. All the poly(*o*-hydroxyamide) and PBO films revealed essentially amorphous X-ray diffraction patterns resulting from the presence of the flexible ether linkages and the packing-disruptive 1-phenylethylidene or 3F groups in the polymer backbones.

The thermal properties of the poly(*o*-hydroxyamide)s and PBOs were studied with DSC, TMA, and TGA. The relevant results are reported in Table 3. In the DSC experiments, each sample was subjected to three subsequent heating runs at a scanning rate of 20 °C/min in nitrogen. The first run was from 40 to 250 °C, after which the sample was cooled down with a programmed rate of 200 °C/min to 40 °C, followed by a second run from 40 to 400 °C. The sample was then cooled down again at 200 °C/min to 40 °C, and this was followed by a third run with an end temperature of 400 °C. The first run was aimed at eliminating any possible volatiles such as the residual solvent and the absorbed moisture in the samples. The second run yielded the T_g and endothermal peak

Table 3. Thermal Behavior Data of Poly(*o*-hydroxyamide)s and PBOs

Poly(<i>o</i> -hydroxyamide)				PBO				
Code	DSC			Code	DSC	TMA	TGA	
	T_g (°C) ^a	T_o (°C) ^b	T_p (°C) ^c		T_g (°C) ^d	T_s (°C) ^e	T_d (°C) ^f	Char Yield (%) ^g
6	194	258	303	12	233	248	557 (552)	70
7	137	248	299	13	231	240	561 (539)	67
8	189	255	292	14	231	245	554 (542)	61
9	130	245	280	15	236	245	562 (549)	68
10	181	259	289	16	216	214	549 (538)	63
11	129	234	296	17	222	211	556 (542)	63

^a Temperature at the middle point of the 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 Endotherm peak temperature.

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

^e Softening temperature measured by TMA (penetration method) with a constant applied load of 10 mN at a heating rate of 10 °C/min.

^f 10% weight-loss temperature at a heating rate of 20 °C/min in nitrogen. The values in parentheses are those observed in air.

^g Residual weight percentage when it was heated to 800 °C in nitrogen.

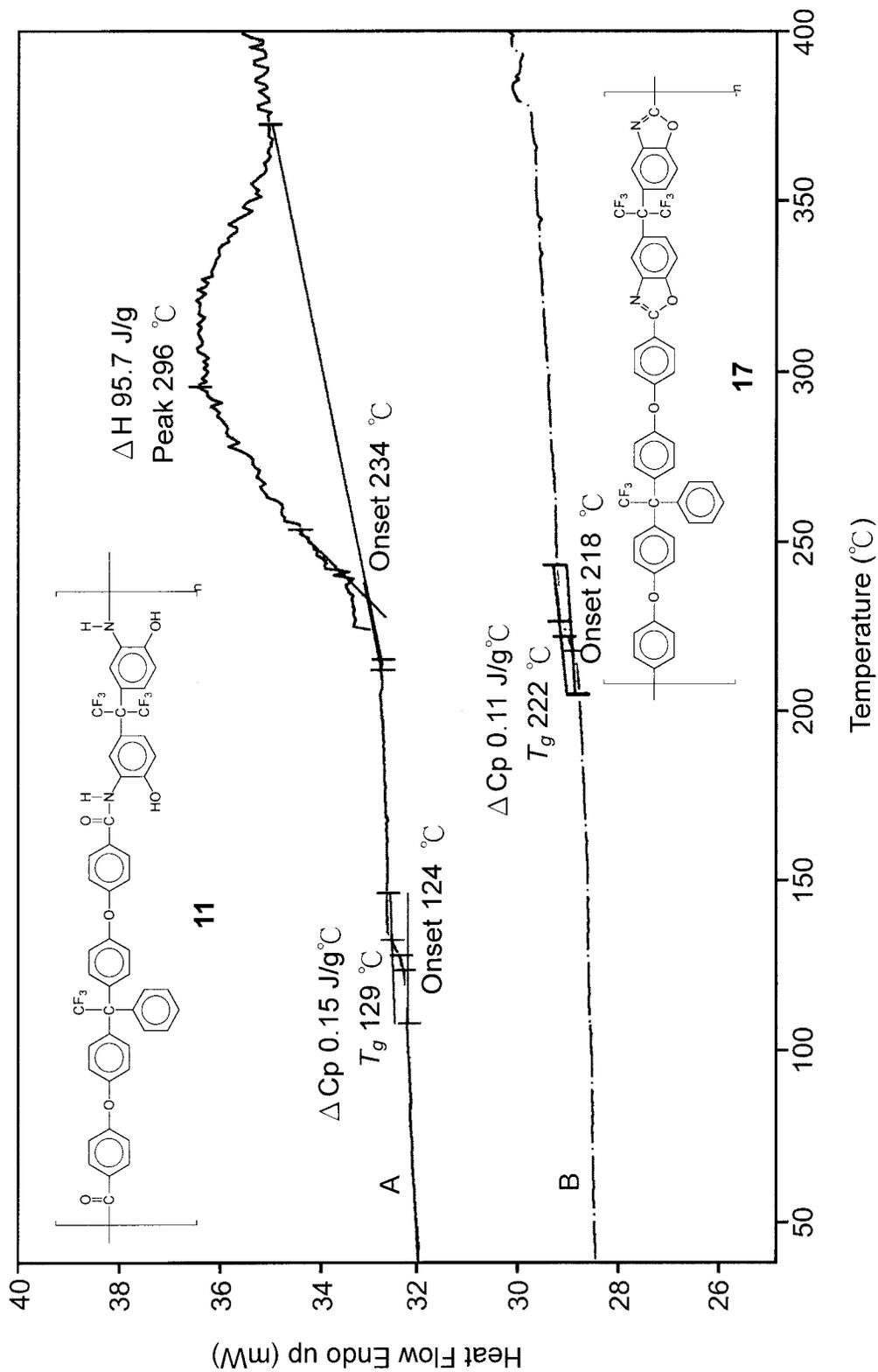


Figure 1. DSC thermograms of (A) poly(o-hydroxyamide) **11** and (B) the corresponding PBO **17** at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ in nitrogen.

because of the cyclodehydration of the poly(*o*-hydroxyamide) sample. After rapid cooling from the elevated temperature, the PBOs formed *in situ* in the DSC cell were predominately amorphous. Therefore, in the third run, all the PBOs revealed a clear baseline shift peculiar to the glass transition. A typical pair of DSC traces of poly(*o*-hydroxyamide) **11** and the corresponding PBO **17** are illustrated in Figure 1 (only the second and third heating runs are shown). Poly(*o*-hydroxyamide) **11** showed a clear T_g at 129 °C and a broad endotherm between 230 and 370 °C, which was attributed to the loss of water during the conversion of poly(*o*-hydroxyamide) **11** to PBO **17**. After quenching from 400 °C, the PBO **17** that formed *in situ* showed an increased T_g of around 222 °C because of increased backbone stiffness. All the other polymers displayed similar DSC traces, and some of the DSC data are given in Table 3. The T_s values (which may be called apparent T_g 's) of the PBOs were determined by TMA with the penetration method. As listed in Table 3, these PBOs exhibited T_s values of 211–248 °C. Both the poly(*o*-hydroxyamide)s and PBOs containing 6F groups in the backbone showed relatively lower T_g 's and T_s 's than the corresponding analogues because of more flexible backbones. The TGA curves of the poly(*o*-hydroxyamide)s revealed an initial loss between 250 and 400 °C. The weight loss was due to thermal cyclodehydration of the poly(*o*-hydroxyamide) and agreed well with the strong endotherm on the DSC curves. None of the PBOs showed a significant weight loss up to 500 °C in nitrogen or air, and the temperatures at 10% weight losses were 549–562 °C in nitrogen and 538–552 °C in air, with more than 60 wt % residue remaining at 800 °C in nitrogen. Therefore, these PBOs may be potential candidates for melt-processable, thermally stable polymers.

CONCLUSIONS

Six poly(*o*-hydroxyamide)s with moderate to high molecular weights were prepared from multiring, flexible, ether-bridged diacyl chlorides **1** and **2** with bis(*o*-aminophenols) by low-temperature solution polycondensation. Most of the poly(*o*-hydroxyamide)s were easily soluble in variety of organic solvents and could be cast into flexible, tough films from their polymer solutions. They could be transformed into the corresponding PBOs at elevated temperatures in the solid state. The PBOs revealed a dramatically decreased sol-

ubility but higher T_g values than their corresponding poly(*o*-hydroxyamide) prepolymers. The PBOs derived from 6F-containing bis(*o*-aminophenol) components were soluble in polar organic solvents. All the PBOs showed excellent thermal stability. There was a large window between T_g or T_s and the decomposition temperature of each PBO, and this could be advantageous in the processing of these polymers by a thermoforming technique. Therefore, the prepared PBOs are promising candidates for new high-performance polymeric materials.

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