Aromatic polybenzoxazoles bearing ether and isopropylidene or hexafluoroisopropylidene units in the main chain

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SUMMARY: A series of poly(*o*-hydroxyamide)s having high molecular weights were synthesized by means of low-temperature solution polycondensation of 4,4′-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**1**) and 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**2**) with three bis(*o*-aminophenol)s. Subsequent thermal cyclodehydration of the poly(*o*-hydroxyamide)s afforded polybenzoxazoles. All poly(*o*-hydroxyamide)s are readily soluble in a variety of solvents, whereas the polybenzoxazoles are insoluble with one exception. The polybenzoxazoles exhibit glass transition temperatures in the range of 218–231 °C and are stable up to 500 °C in air or nitrogen, with the 10% weight loss temperatures being recorded between 553–607 °C in nitrogen.

Introduction

Aromatic polybenzoxazoles are a class of heterocyclic polymers that exhibit outstanding thermo-oxidative stability, high tensile modulus and strength, and superior chemical resistance[1, 2]. A few rigid-rod polybenzoxazoles have been reported to have potential for fabrication into high-modulus, high-strength fiber[3, 4]. However, analogous to aromatic polyimides they are generally difficult to process because of their non-melting behavior and poor solubility in conventional organic solvents and, consequently, potential applications are limited. Therefore, many attempts have been tried to modify and improve their processibility[5–11]. One successful approach is to introduce flexible linkages into the polybenzoxazole backbone so as to increase the overall flexibility. Fluorinated monomers appear to be the key to soluble, high performance materials in most of these synthetic efforts. For example, by incorporation of the hexafluoroisopropylidene (6F) group into the polybenzoxazole backbone solubility was enhanced, while favorable thermo-oxidative stability and high glass transition temperatures were retained[5, 8–11]. The 6F group has also been reported as a component in a variety of other thermally stable polymeric systems[12–18]. Similarly, soluble poly(ether benzoxazole)s have been generated and display properties intermediate between the two homopolymers[19, 20]. Desired properties resulting from these materials include thermoplasticity, excellent tensile properties, and enhanced toughness.

As part of an effort to develop high performance, high temperature resistant polymers, the present article deals with the synthesis and basic characterization of flexible aromatic polybenzoxazoles bearing both ether and 6F groups from 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**2**) and bis(*o*-amino-phenol)s by low-temperature solution polycondensation. The analogous polybenzoxazoles having no fluorine atom were also prepared and characterized for comparison.

Experimental part

Materials

According to reported procedures[16, 21], 4,4′-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (m. p. 276 °C) and 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoic acid (m. p. 318 °C) were synthesized in high purity and high yields via two steps from commercially available reagents. Details of the synthesis were described in a previous paper[22]. The diacyl choride monomers, 4,4′-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**1**) (m. p. 140 °C) and 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**2**) (m. p. 160–161 °C), were prepared by chlorinating the precursor dicarboxylic acid with thionyl chloride and tow drops of *N,N*-dimethylformamide (DMF). The aromatic bis(*o*-aminophenol) monomers that included 3,3′-diamino-4,4′-dihydroxybiphenyl (**3**), 3,3′-dihydroxybenzidine (**4**) and hexafluoroisopropylidenebis(3-amino-4-hydroxyphenyl) (**5**) 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-hydroxyamide)s

The low-temperature solution polycondensation technique was employed in this investigation. A typical procedure of preparing poly(*o*-hydroxyamide)s is as follows. First, 1 mmol of a bis(*o*-aminophenol) was dissolved in 5 mL of NMP containing 0.2 g of LiCl and maintained at −10 °C to

0 °C in an ice/acetone bath. To the solution 1 mmol of a dia-cyl 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 (for about 10 h). As the polycondensation pro-ceeded, the reaction mixture became gradually viscous. The resulting polymer solution was slowly poured into 300 mL of methanol giving rise to a fiber-like precipitate which was washed thoroughly with methanol and hot water, collected by filtration and dried. The yields were usually quantitative and the inherent viscosity of the poly(o-hydroxyamide)s was measured in N,N-dimethylacetamide (DMAc) at a concentra-tion of 0.5 g/dL at 30 °C.

Preparation of poly(o-hydroxyamide) films and thermal conversion to polybenzoxazoles

A polymer solution for preparing the film was made by dis-solving about 0.6 g of the poly(o-hydroxyamide) sample in 6 mL of DMAc. The solution was poured into a 9 cm dia-meter glass culture dish, which 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.

Polybenzoxazoles were obtained from the thermal cyclo-dehydration of poly(o-hydroxyamide)s at 300 °C *in vacuo* for 8 h. The conversion was proceeded in form of films and the inherent viscosities of the polybenzoxazoles thus obtained were measured in concentrated sulfuric acid at a concentra-tion of 0.5 g/dL at 30 °C.

Measurements

IR spectra were recorded on a Jasco IR-700 infrared spectro-meter. Elemental analyses were run on a Perkin-Elmer Model 2400 C, H, N analyzer at the National Taiwan Univer-sity (Taipei). The inherent viscosities were measured at 0.5 g/dL with a Cannon-Fenske viscometer thermostated at 30 °C. A Sinku Riko DSC-7000 differential scanning calori-meter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions; the heating rate was 20 °C/min. Glass transition temperatures (T_g's) were read at the middle of the change in the heat capacity. Ther-mogravimetry (TG) was analyzed using a DuPont 951 ther-mogravimetric analyzer. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20 °C/min. Wide-angle X-ray dif-fraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray dif-fractometer, using Ni-filtered Cu K_a radiation (40 kV, 15 mA). The scanning rate was 2 °/min over a range of $2\theta = 5$–40 °. Tensile properties of solution cast films were deter-mined using an Instron universal tester, model HT-9102 (Hung Ta Instrument Co., Taiwan), with a load cell of 100 kg. A gauge 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 0.1 mm thick). An average of at least five individual determinations was used.

Results and discussion

Polymer synthesis

Polybenzoxazoles can be synthesized easily in one-step procedure using poly(phosphoric acid)[3], phosphorus pentoxide/methanesulfonic acid[23], or trimethylsilyl phos-phate[24] as the condensing medium. Isolation and thermal cyclodehydration of soluble poly(o-hydroxyamide), derived from the polycondensation of diacid derivatives and bis(o-aminophenol)s in polar solvents, is an alterna-tive method for the production of polybenzoxazole films and fibers[25]. Because one of the diacyl chloride mono-mers exhibits the isopropylidene group, an acid-sensitive group, the latter two-stage synthetic procedure is employed in the synthesis of polybenzoxazoles. Six poly(o-hydroxyamide)s **6**–**11** were prepared by a low-temperature solution polycondensation technique from the diacyl chlorides **1** and **2** with three structurally differ-ent bis(o-aminophenol)s **3**, **4**, and **5** in an NMP solution containing 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-hydroxyamide)s are illu-strated in Fig. 1 and 2, respectively. The results of the
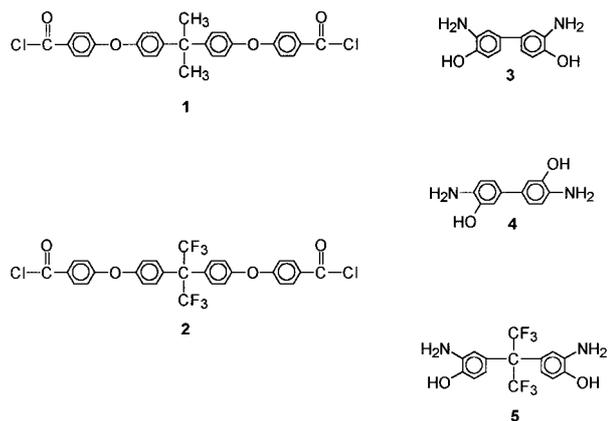

Fig. 1. Structures and codes of monomers

polymerizations are summarized in Tab. 1. The inherent viscosities η_{inh} of the resulting poly(o-hydroxyamide)s stay in the range of 0.60–0.93 dL/g. It is worth mention-ing that the 6F-containing bis(o-aminophenol) (**5**)-derived poly(o-hydroxyamide)s **10** and **11** were attained with moderately high molecular weights, as evidenced by the inherent viscosity value around 0.6 dL/g. It seems that the silylation of bis(o-aminophenol) (**5**) reported by Mar-uyama et al.[5] is not a necessary step to attain high molar mass poly(o-hydroxyamide)s in the low-temperature solution polycondensation reaction. All these poly(o-hydroxyamide)s are readily soluble in amide-type sol-vents such as NMP and DMAc and can afford free-stand-ing films by means of solution casting. The films obtained are all flexible and tough. Polymers **6**–**9** are
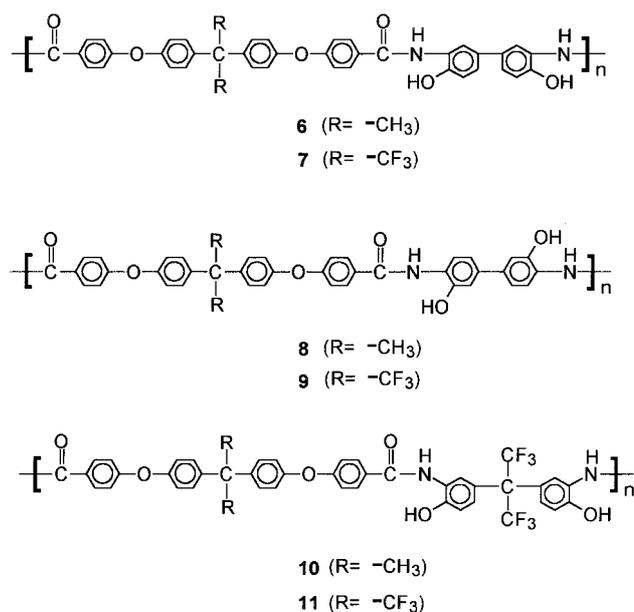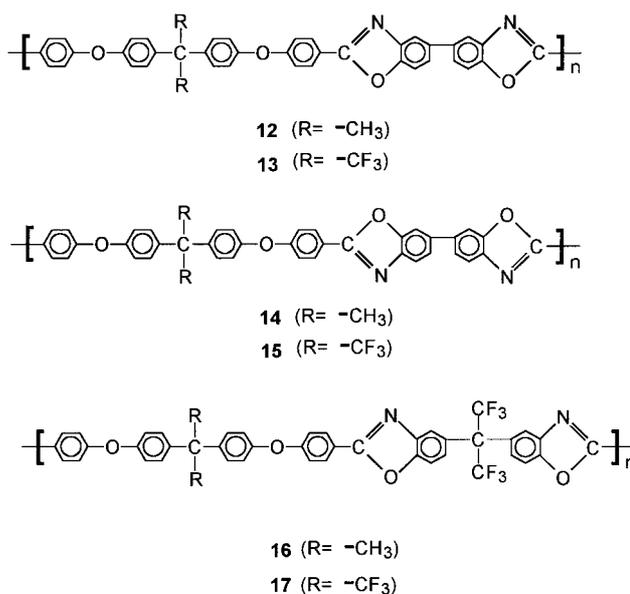
6 (R= −CH$_3$)

7 (R= −CF$_3$)

8 (R= −CH$_3$)

9 (R= −CF$_3$)

10 (R= −CH$_3$)

11 (R= −CF$_3$)

Fig. 2 .   Structures and codes of poly(*o*-hydroxyamide)s

12 (R= −CH$_3$)

13 (R= −CF$_3$)

14 (R= −CH$_3$)

15 (R= −CF$_3$)

16 (R= −CH$_3$)

17 (R= −CF$_3$)

Fig. 3.   Structures and codes of polybenzoxazoles

Tab. 1. Inherent viscosities of poly(*o*-hydroxyamide)s and polybenzoxazoles

Monomers	Poly(*o*-hydroxyamide)[a]		Polybenzoxazole[b]	
	Code	η_{inh} [c] dL/g	Code	η_{inh} [d] dL/g
1 + 3	**6**	0.64	**12**	Dec.[e]
2 + 3	**7**	0.93	**13**	0.53
1 + 4	**8**	0.60	**14**	Dec.
2 + 4	**9**	0.92	**15**	1.03
1 + 5	**10**	0.62	**16**	Dec.
2 + 5	**11**	0.63	**17**	0.53 (0.45)[c]

[a] Polymerizations carried out with 1 mmol of each monomer in 5 mL NMP in the presence of 0.2 g LiCl at −10 °C to 0 °C for 1 h and at room temperature for another 10 h.

[b] Conversion of the poly(*o*-hydroxyamide)s to polybenzoxazoles was carried out by heating at 300 °C for 8 h *in vacuo*.

[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, unless otherwise indicated.

[e] Decomposed.

brownish, while polymers **10** and **11** are colorless to light yellow.

The formation of poly(*o*-hydroxyamide)s was confirmed by means of IR spectroscopy and elemental analysis. The polymers exhibit broad absorption bands in the region of 2 500–3 500 cm^{-1} (O—H and N—H str.) and 1 650 cm^{-1} (amide C=O str.). The elemental analysis values are in good agreement with the calculated values of the proposed structures of the polymers. In all cases, however, the carbon percentages were found to be slightly lower than the calculated ones for the proposed

structures. This is probably caused by the hygroscopic nature of the amide groups of these polymers.

In the second stage, the poly(*o*-hydroxyamide)s thus obtained were subjected to thermal cyclodehydration. The conversion to polybenzoxazoles (Fig. 3) was carried out in the form of films at 300 °C *in vacuo* for about 8 h, and the conversion process was followed by changes in the IR spectra of the films. Fig. 4 shows typical IR spectra of the representative pair of poly(*o*-hydroxyamide) **11** and its corresponding polybenzoxazole **17**. The complete disappearance of the absorption bands around 3 000 and 1 650 cm^{-1} indicates the completion of the cyclization process, together with the appearance of an absorption at 1 602 cm^{-1} characteristic of the benzoxazole ring, almost overlapping with one of the absorption bands of aromatic C=C str. The elemental analysis values of the transformed polymers agree well with the values calculated for the polymers with benzoxazole structures. There is sufficient difference in oxygen content between the poly(*o*-hydroxyamide) and the resulting polybenzoxazole to make possible a determination of the extent of reaction. This conversion could also be monitered by means of thermogravimetry (TG) and differential scanning calorimetry (DSC), which will be discussed subsequently. The polybenzoxazoles thus obtained, except for **17**, are insoluble in most organic solvents, while they are soluble in cold concentrated sulfuric acid. The isopropylidene group-containing polybenzoxazoles were decomposed simultaneously during the dissolution process, as indicated by the very low inherent viscosity values (near zero). The polybenzoxazoles derived from diacyl chloride **2** have inherent viscosities of 0.53–1.03 dL/g in concentrated sulfuric acid, indicating that no thermal degrada-
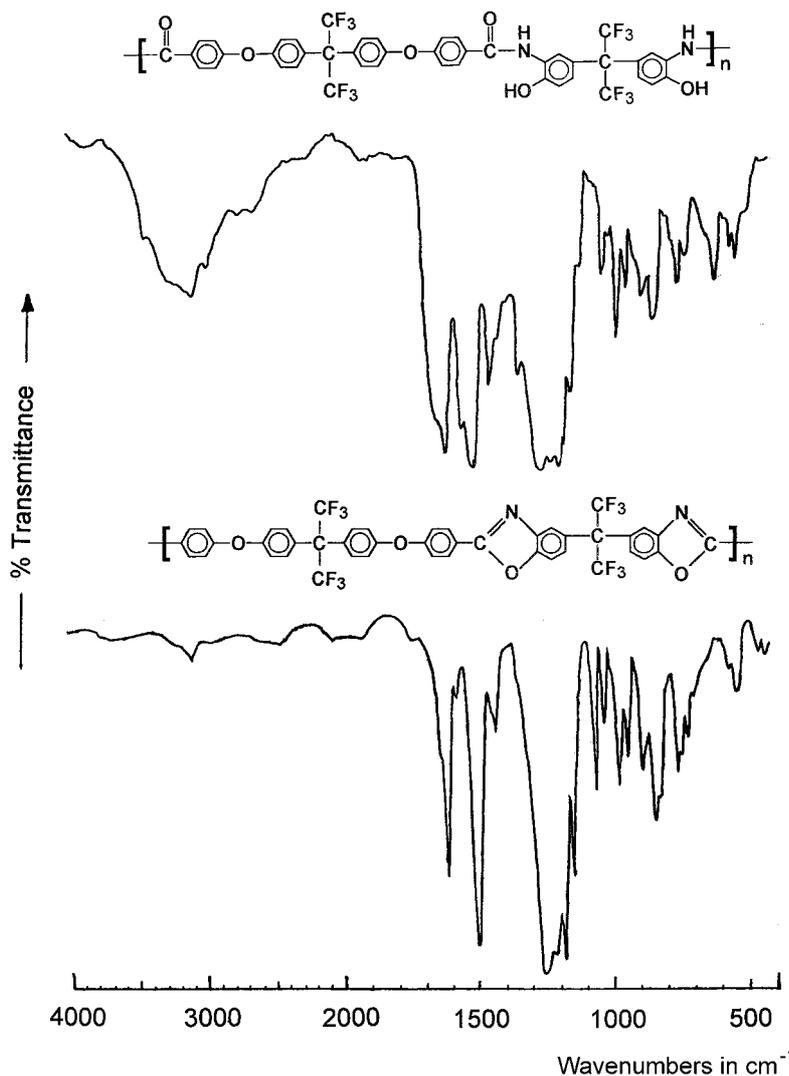
Fig. 4. IR spectra of poly(*o*-hydroxyamide) **11** (top) and polybenzoxazole **17** (bottom)

tion leading to molecular chain scission occurred during the conversion process and during the viscosity determination. This also indicates that the 6F linkage has a good acid-resistance.

Properties of the polymers

The solubility of the polymers was evaluated qualitatively and the results are presented in Tab. 2. All poly(*o*-hydroxyamide)s are easily soluble in polar aprotic solvents such as NMP, DMAc, DMSO, and DMF at room temperature. Nevertheless, they still exhibit excellent resistance to less polar solvents such as *m*-cresol, THF, chloroform, acetone, and ethanol. The poly(*o*-hydroxy-amide)s **10** and **11** derived from 6F bis(*o*-aminophenol) **5** reveal an enhanced solubility. In addition to highly polar solvents, they are also soluble in cold or hot *m*-cresol,

THF, and acetone. This may be due to the existence of the bulky flexible hexafluoroisopropylidene groups that loose the chain packing and allow the solvent molecules to diffuse into the polymer chains more easily.

The polybenzoxazoles, on the other hand, dissolved only in cold sulfuric acid. Despite the fact that the polybenzoxazoles are amorphous, they were quite insoluble in organic solvents, with the exception of polymer **17**, which contains the bulky 6F group in both the diacid and the bis(*o*-aminophenol) moieties along the macromolecular backbone.

Wide-angle X-ray diffractograms indicate that all poly(*o*-hydroxyamide) and polybenzoxazole films are amorphous, which may be due to the presence of flexible ether and isopropylidene or hexafluoroisopropylidene linkages in the polymer backbones. All poly(*o*-hydroxy-amide)s could be solution-cast into flexible and tough

Tab. 2.　Solubility behavior of poly(o-hydroxyamide)s and polybenzoxazoles[a)]

Solvent[b)]	Poly(o-hydroxyamide)						Polybenzoxazole					
	6	7	8	9	10	11	12	13	14	15	16	17
conc. H_2SO_4	d	+	d	+	d	+	d	+	d	+	d	+
NMP	+	+	+	+	+	+	–	–	–	–	–	+
DMAc	+	+	+	+	+	+	–	–	–	–	–	+
DMF	+	+	+	+	+	+	–	–	–	–	–	–
DMSO	+	+	+	+	+	+	–	–	–	–	–	–
m-Cresol	–	–	–	–	+	+h	–	–	–	–	–	–
THF	–	–	–	–	+	+	–	–	–	–	–	–
Acetone	–	–	–	–	+	+h	–	–	–	–	–	–
Ethanol	–	–	–	–	–	–	–	–	–	–	–	–
Chloroform	–	–	–	–	–	–	–	–	–	–	–	–

[a)]　Solubility: +, soluble at room temperature; +h, soluble on heating; –, insoluble even on heating; d: decomposed.
[b)]　DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Tab. 3.　Tensile properties and thermal behavior data of poly(o-hydroxyamide)s and polybenzoxazoles

Poly(o-hydroxyamide)						Polybenzoxazole			
	Tensile properties of polymer films		DSC				DSC	TG	
Code	strength-to-break in MPa	elongation to-break in %	T_g[a)] /°C	T_o[b)] /°C	T_p[c)] /°C	Code	T_g[d)] /°C	T_d[e)] /°C	char yield[f)] %
6	99	8	152	246	297	12	224	572 (548)	65.1
7	102	10	–[g)]	253	311	13	231	582 (591)	65.1
8	99	7	165	253	300	14	223	569	61.5
9	104	10	–	243	298	15	225	579	65.3
10	85	8	176	221	294	16	218	564	60.7
11	93	10	–	235	289	17	218	567	55.0

[a)]　Temperature at the middle point 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)]　Endotherm peak temperature.
[d)]　Midpoint temperature of baseline shift on the second DSC heating trace of the sample after rapid cooling from 450 °C in nitrogen.
[e)]　10% weight-loss temperature at a heating rate of 20 °C/min in nitrogen; values in parentheses were observed in air.
[f)]　Residual wt.-% when heated to 800 °C in nitrogen.
[g)]　Difficult to judge.

films. These films were subjected to tensile testing, and the results are given in Tab. 3. The tensile strengths and the elongations at break are in the range of 93–104 MPa and 7–10%, respectively. The 6F diacyl chloride-derived poly(o-hydroxyamide)s exhibit slightly higher strength and toughness than the isopropylidene-containing polymers. All thermally converted polybenzoxazole films are also flexible and tough. However, most of the films shrank or bubbled during the cyclization process; therefore, their mechanical properties were not evaluated. Good-quality and smooth polybenzoxazole films may be obtained if a carefully designed heating program is employed.

The thermal behavior of the poly(o-hydroxyamide)s and polybenzoxazoles was investigated by DSC and TG. The isopropylidene diacyl chloride (1)-based poly(o-hydroxyamide)s display distinct glass transitions between 152–176 °C in the first DSC scan. All poly(o-hydroxyamide)s exhibit strong endothermic peaks between 220–350 °C, with peak temperatures around 289–311 °C, which are attributed to the loss of water during the conversion of poly(o-hydroxyamide) to polybenzoxazole. Fig. 5 shows a typical pair of TG and DSC curves for poly(o-hydroxyamide) 10 and polybenzoxazole 16. The TG trace of poly(o-hydroxyamide) 10 reveals that the weight loss started around 230 °C and came to an end at about 350 °C. The weight loss is due to the thermal cyclodehydration of the poly(o-hydroxyamide), which also agrees well with the strong endothermic peak between 221–355 °C. Polybenzoxazole 16 started to lose weight at around 510 °C and left 65.5% residual char when heated to 800 °C in nitrogen. The baseline shift centered at
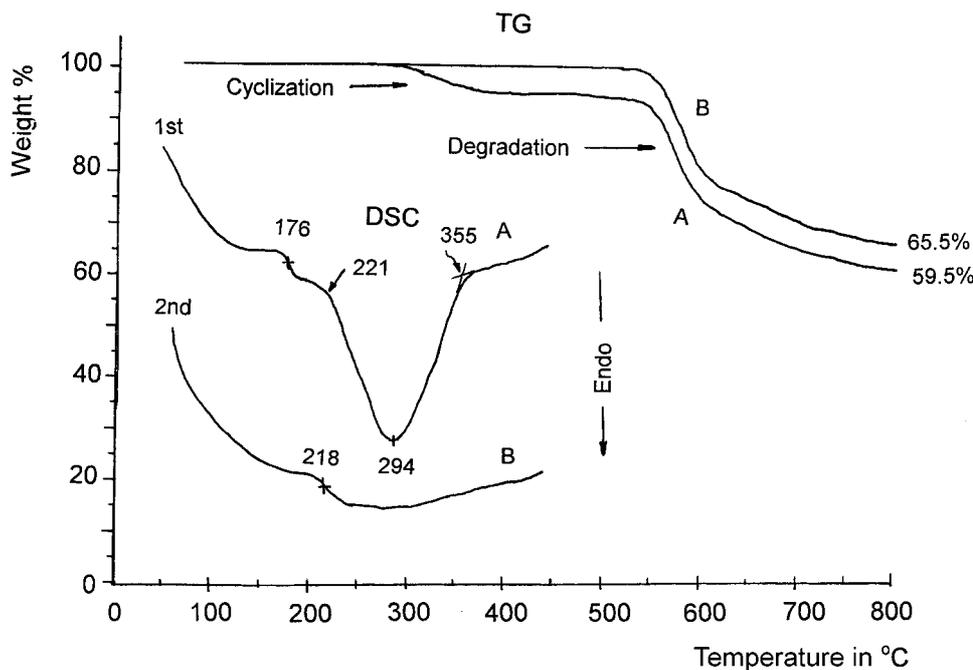
Fig. 5. DSC and TG curves for (A) poly(o-hydroxyamide) **10** and (B) polybenzoxazole **16** at a heating rate of 20 °C/min in nitrogen

176 °C in the first DSC heating trace is ascribed to the glass transition of poly(o-hydroxyamide) **10**. After rapid cooling from 450 °C, polybenzoxazole (**16**) formed *in situ* showed a distinct glass transition around 218 °C on the subsequent DSC heating trace. The increased T_g of polybenzoxazole **16** when compared to its poly(o-hydroxyamide) precursor **10** may be a reflection of an enhanced chain rigidity due to the formation of benzoxazole rings. All poly(o-hydroxyamide)s and polybenzoxazoles exhibit a similar DSC and TG behavior, and some of their thermal behavior data are summarized in Tab. 3. All polybenzoxazoles do not lose weight up to 500 °C in air or nitrogen, and the temperatures at which 10% weight-loss was recorded are in the 553–607 °C range in nitrogen. Char yields are >55.0% for all of them when heated to 800 °C in nitrogen. Their glass transition temperatures (T_g's) are between 218–231 °C. The large window between T_g and the decomposition temperature makes these polybenzoxazoles attractive for practical processing.

Conclusions

Six poly(o-hydroxyamide)s with high molar masses have been prepared from 4,4′-[isopropylidenebis(1,4-phenylene)dioxy]dibenzoyl chloride (**1**) and 4,4′-[hexafluoroisopropylidenebis(1,4-phenylene)dioxy]-dibenzoyl chloride (**2**) with bis(o-aminophenol)s by low-temperature solution polycondensation. All poly(o-hydroxyamide)s were easily soluble in a variety of organic solvents and could be cast into flexible and tough films from their polymer solutions. They have T_g's between 152–176 °C and could be transformed to the corresponding polybenzoxazoles at elevated temperatures. The polybenzoxazoles revealed a dramatically decreased solubility but higher T_g's when compared to their corresponding poly(o-hydroxyamide) prepolymers. All polybenzoxazoles showed excellent thermal stability. Thus, the prepared polybenzoxazoles are promising candidates for new high performance polymeric materials.

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