

A series of new poly(*o*-hydroxyamide)s having high molecular weights were synthesized by low-temperature solution polycondensation of 4,4'-(1,4-naphthalenedioxy)dibenzoyl chloride and 4,4'-(2,6-naphthalenedioxy)dibenzoyl chloride with three bis(*o*-aminophenol)s. Subsequent thermal cyclodehydration of the poly(*o*-hydroxyamide)s affords novel polybenzoxazoles. All the poly(*o*-hydroxy-

amide)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 266–279 °C and are stable up to 500 °C in air or nitrogen, with a 10% weight loss in nitrogen in a temperature range of 570–635 °C.

Preparation and characterization of aromatic polybenzoxazoles bearing ether and 1,4-naphthalene or 2,6-naphthalene units in the main chain

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Aromatic polybenzoxazoles are a class of heterocyclic polymers that exhibit outstanding thermooxidative 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, as with aromatic polyimides they are generally difficult to process because of their poor thermal processibility and poor solubility in conventional organic solvents. As a consequence, potential applications have been limited. Therefore, attempts have been made to modify the backbone structure and improve their processibility^{5–11}. One successful approach is to introduce flexible linkages into the polybenzoxazole backbone in order to increase processibility. In most of these approaches, fluorinated monomers were introduced into the polymer backbone to enhance the polymer solubility, while retaining the desirable thermooxidation stability. For example, by the incorporation of the 2,2-hexafluoroisopropylidene (6F) group into the polybenzoxazole backbone solubility was enhanced, while favorable thermooxidative stability and high glass transition temperatures were retained^{5,8–11}. Similarly, soluble poly(ether benzoxazole)s have been generated and display properties intermediate between the two homopolymers^{12,13}. 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, we are interested in the potential usefulness of naphthyl moieties as bulky and symmetrical units in the main chain. Recently, we have reported that aramids derived from 4,4'-(1,4-naphthylenedioxy)dibenzoic acid¹⁴ and 4,4'-(2,6-naphthylenedioxy)dibenzoic acid¹⁵ had improved solubility with retention of high thermal stability. These resulting polyamide films exhibit good mechanical properties. The present article deals with the synthesis and basic characterization of flexible aromatic polybenzoxazoles bearing both ether and 1,4-naphthylene or 2,6-naphthylene units. These polymers were prepared in solution by the reaction of 4,4'-(1,4-naphthylenedioxy)dibenzoyl chloride or 4,4'-(2,6-naphthylenedioxy)dibenzoyl chloride with bis(*o*-aminophenol)s at low-temperatures. The properties of these polymers including solubility, tensile properties, crystallinity, and thermal behavior were examined.

Experimental part

Materials

4,4'-(1,4-Naphthylenedioxy)dibenzoic acid and 4,4'-(2,6-naphthylenedioxy)dibenzoic acid were prepared by the nucleophilic fluorodisplacement reaction of *p*-fluorobenzonitrile with 1,4-dihydroxynaphthalene and 2,6-dihydroxy-

naphthalene, respectively, followed by the hydrolysis reaction of the dinitrile compounds in potassium hydroxide solution, according to reported procedures^{14,15}. The reaction of the two dicarboxylic acids with excess thionyl chloride in the presence of a few drops of *N,N*-dimethylformamide (DMF) as a catalyst affords diacyl chlorides 4,4'-(1,4-naphthalenedioxy)dibenzoyl chloride (**1**) and 4,4'-(2,6-naphthalenedioxy)dibenzoyl chloride (**2**), respectively. Diacyl chloride **1** was purified by recrystallization from a mixture of hexane and toluene to afford white needles; mp. 167–168 °C (lit¹⁶ 167–168 °C), diacyl chloride **2** was purified by recrystallization from toluene to give white needles; mp. 185–186 °C (lit¹⁶ 185–186 °C). The aromatic bis(*o*-aminophenol) monomers that included 3,3'-dihydroxybenzidine (TCI), 3,3'-diamino-4,4'-dihydroxy-biphenyl (TCI) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (TCI) were of high purity and used as received. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Commercially obtained anhydrous lithium chloride was dried under vacuum at 180 °C for 8 h.

Synthesis of poly(*o*-hydroxyamide)s

The low-temperature solution polycondensation technique was employed in this investigation. A typical procedure of preparing poly(*o*-hydroxy amide)s is as follows. First, 2 mmol of a bis(*o*-aminophenol) were dissolved in 10 mL of NMP and maintained at –10 °C ~ 0 °C in an ice-acetone bath. To the solution 0.6 mL of propylene oxide were added, then 2 mmol of diacyl chloride were added, and the reaction was carried out at –10 °C ~ 0 °C for about 1 h and then at room temperature overnight (for about 10 h). As the polycondensation proceeded, 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*-hydroxy amide)s was measured in DMAc at a concentration of 0.5 g/dL at 30 °C.

Preparation of poly(*o*-hydroxy amide) films and thermal conversion to polybenzoxazoles

A polymer solution for preparing the film was made by dissolving about 0.6 g of the poly(*o*-hydroxyamide) sample in 6 mL of DMAc. The solution was poured into a $\psi = 9$ cm 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 cyclodehydration 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 concentration of 0.5 g/dL at 30 °C.

Measurements

IR spectra were recorded on a Jasco IR-700 infrared spectrometer. Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N analyzer at the National Taiwan University (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 calorimeter equipped with a Sinku Riko TA-7000 thermal analyzer was used to determine the thermal transitions. Heating rate was 20 °C/min. Glass transition temperatures (T_g s) were read at the middle of the change in the heat capacity. Thermogravimetry (TG) was analyzed using a DuPont 951 thermogravimetric 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 diffraction measurements were performed at room temperature (about 25 °C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered CuK α 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 determined using an Instron universal tester, model HT-9102 (Hung Ta Instrument Co., Taiwan), with a load cell of 10 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 might be synthesized easily in a one-step procedure using poly(phosphoric acid)³, phosphorous pentoxide/methanesulfonic acid¹⁷, or trimethylsilyl phosphate¹⁸ as the reaction medium. Isolation and thermal cyclodehydration of soluble poly(*o*-hydroxyamide), derived from the polycondensation of diacid derivatives and bis(*o*-aminophenol)s in polar solvent, is an alternative method for the production of polybenzoxazole films and fibers¹⁹. Six poly(*o*-hydroxyamide)s **6**–**11** were prepared readily by the low-temperature solution polycondensation of diacyl chlorides **1** or **2** with three structurally different bis(*o*-aminophenol)s **3**, **4**, and **5** in NMP solution in the presence of propylene oxide as the acid acceptor at –10 °C ~ 0 °C for 1 h and at room temperature for another 10 h. The low-temperature polycondensation using propylene oxide as the acid acceptor was generally more preferable than that using triethylamine for the preparation of higher molecular weight aramids²⁰. Structures and codes of the monomers and poly(*o*-hydroxyamide)s are illustrated in Fig. 1 and 2, respectively. The results of the polymerizations are summarized in Tab. 1. The inherent viscosities of the resulting poly(*o*-hydroxyamide)s stay in the range of 0.66–1.55 dL/g. It is worth mentioning that the 6F-containing bis(*o*-aminophenol) (**5**)–

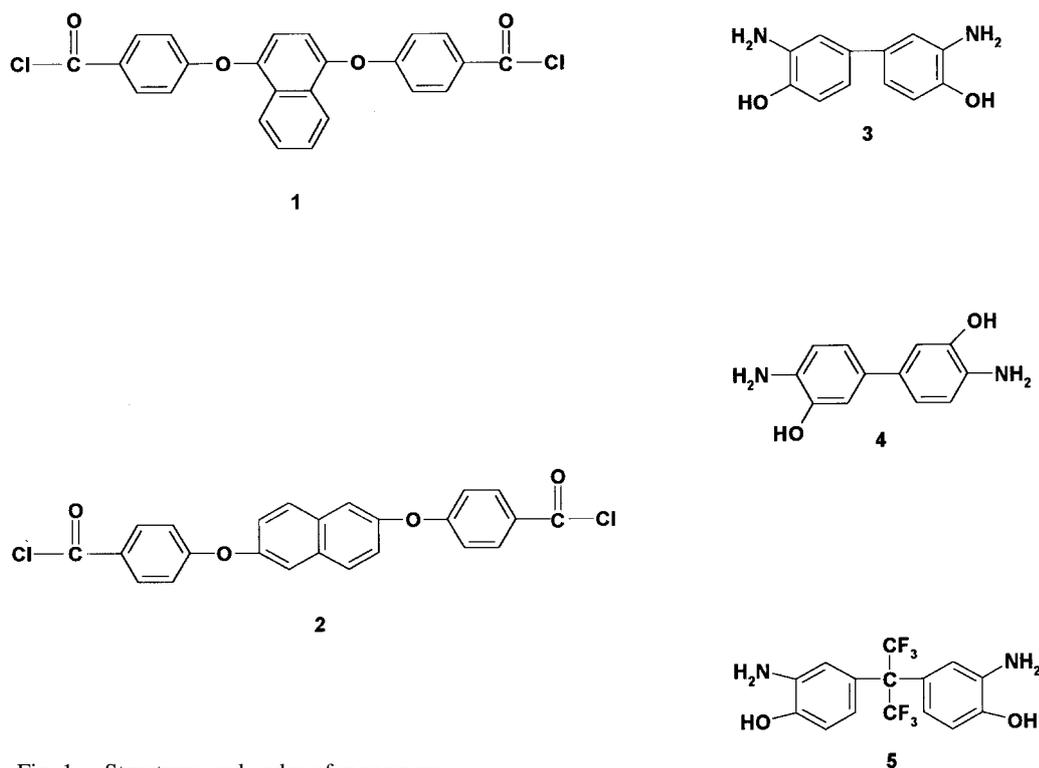
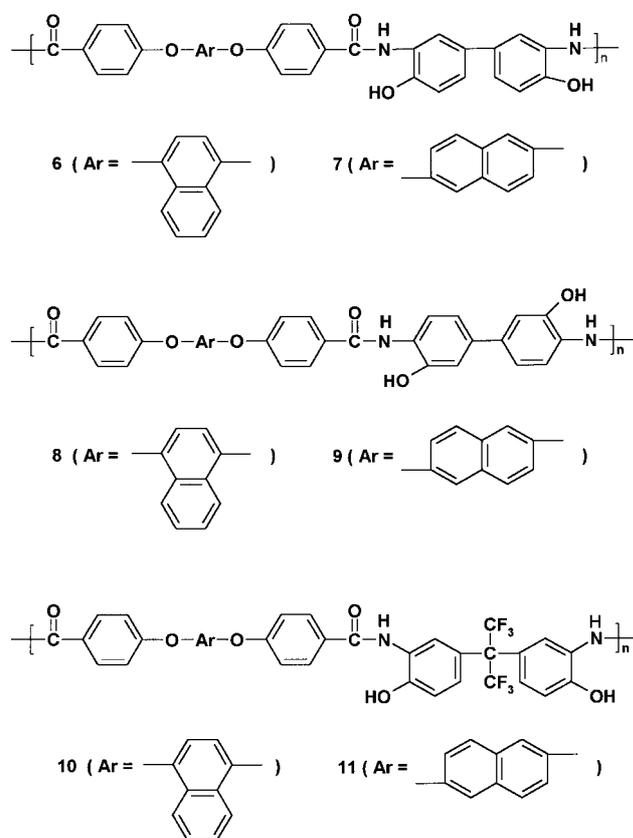


Fig. 1. Structures and codes of monomers

Fig. 2. Structures and codes of poly(*o*-hydroxyamide)sTab. 1. Inherent viscosities of poly(*o*-hydroxyamide)s and polybenzoxazoles

Monomers	Poly(<i>o</i> -hydroxyamide) ^{a)}		Polybenzoxazole ^{c)}	
	Code	$\frac{\eta_{inh}^b}{dL/g}$	Code	$\frac{\eta_{inh}^b}{dL/g}$
1 + 3	6	1.35	12	0.88
2 + 3	7	1.55	13	0.55
1 + 4	8	1.15	14	0.82
2 + 4	9	1.31	15	0.53
1 + 5	10	0.66	16	0.44
2 + 5	11	0.71	17	0.32

a) Polymerization was carried out with 2 mmol of each monomer in 10 mL of NMP in the presence of 0.6 mL of propylene oxide at $-10-0^\circ\text{C}$ for 1 h and at room temperature for another 10 h.

b) Measured at a concentration of 0.5 g/dL in DMAc at 30°C .

c) The conversion of the poly(*o*-hydroxyamide) to the polybenzoxazole was carried out by heating at 300°C for 8 h *in vacuo*.

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

derived poly(*o*-hydroxyamide)s **10** and **11** are attained with high molecular weights, as evidenced by the inherent viscosity value around 0.7 dL/g. It seems to be that silylation of bis(*o*-aminophenol) (**5**) reported by Maruyama et al.⁵⁾ is not a necessary step to attain high-molar-mass poly(*o*-hydroxyamide)s in the low-temperature

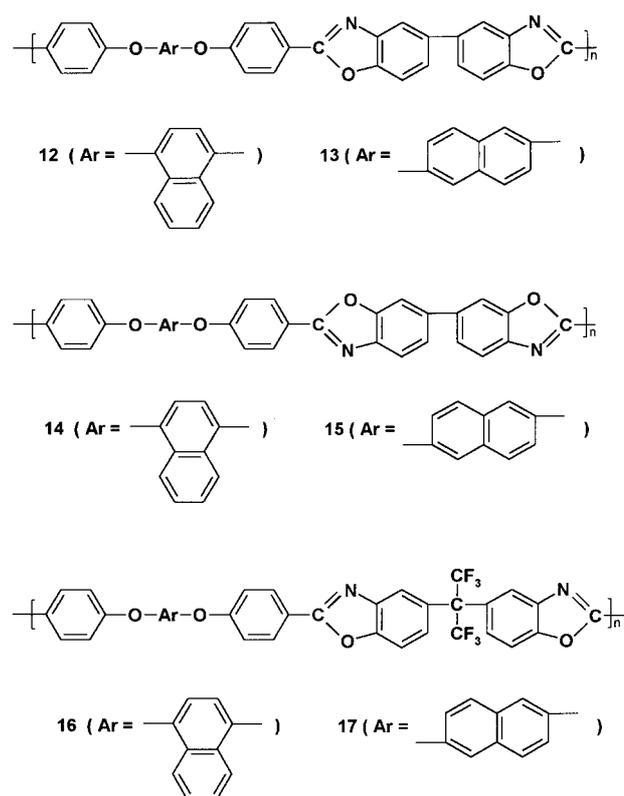


Fig. 3. Structures and codes of polybenzoxazoles

solution polycondensation reaction. All these poly(*o*-hydroxyamide)s are readily soluble in amide-type solvents including NMP and DMAc and could afford free-standing films by means of solution casting. The films obtained are all flexible and tough. Polymers **6–9** are brownish, while polymers **10** and **11** are light yellow in color.

The formation of poly(*o*-hydroxyamides) was confirmed by means of IR spectroscopy and elemental analy-

sis. The polymers exhibit broad absorption bands in the region of 2500–3500 cm⁻¹ (O–H and N–H str.) and 1650 cm⁻¹ (amide C=O str.).

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 could be observed the change in the IR spectra of the films. Fig. 4 shows typical IR spectra of the representative pair of poly(*o*-hydroxyamide) **7** and its corresponding polybenzoxazole **13**. The complete disappearance of the absorption bands around 2500–3500 and 1650 cm⁻¹ indicate the completion of the cyclization process, together with the appearance of an absorption at 1602 cm⁻¹ characteristic of the benzoxazole ring, which is almost overlapped 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. This conversion could also be monitored by the thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis that will be discussed later on. The polybenzoxazoles thus obtained, except for **16** and **17**, are insoluble in most organic solvents, while they are soluble in cold concentrated sulfuric acid. The polybenzoxazoles derived from these diacyl chlorides have inherent viscosities of 0.32–0.88 dL/g in concentrated sulfuric acid.

Properties of polymers

The solubility of all the polymers was evaluated qualitatively and the results are presented in Tab. 2. All of the poly(*o*-hydroxyamide)s are easily soluble in polar aprotic solvents such as NMP, DMAc, DMSO, and DMF at room

Tab. 2. Solubility behavior of poly(*o*-hydroxyamide)s and polybenzoxazoles^{a)}

Solvent ^{b)}	Poly(<i>o</i> -hydroxyamide)						Polybenzoxazole					
	6	7	8	9	10	11	12	13	14	15	16	17
conc. H ₂ SO ₄	+	+	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	–	–	–	–	+h	+h
DMAc	+	+	+	+	+	+	–	–	–	–	–	–
DMF	+	+	+	+	+	+	–	–	–	–	–	–
DMSO	+	+	+	+	+	+	–	–	–	–	–	–
<i>m</i> -Cresol	–	–	–	–	+	+h	–	–	–	–	–	–
THF	–	–	–	–	+	+	–	–	–	–	–	–
Acetone	–	–	–	–	+	+	–	–	–	–	–	–
Ethanol	–	–	–	–	–	–	–	–	–	–	–	–
Chloroform	–	–	–	–	–	–	–	–	–	–	–	–

^{a)} Solubility: +, soluble at room temperature; +h, soluble on heating; –, insoluble even on heating.

^{b)} NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

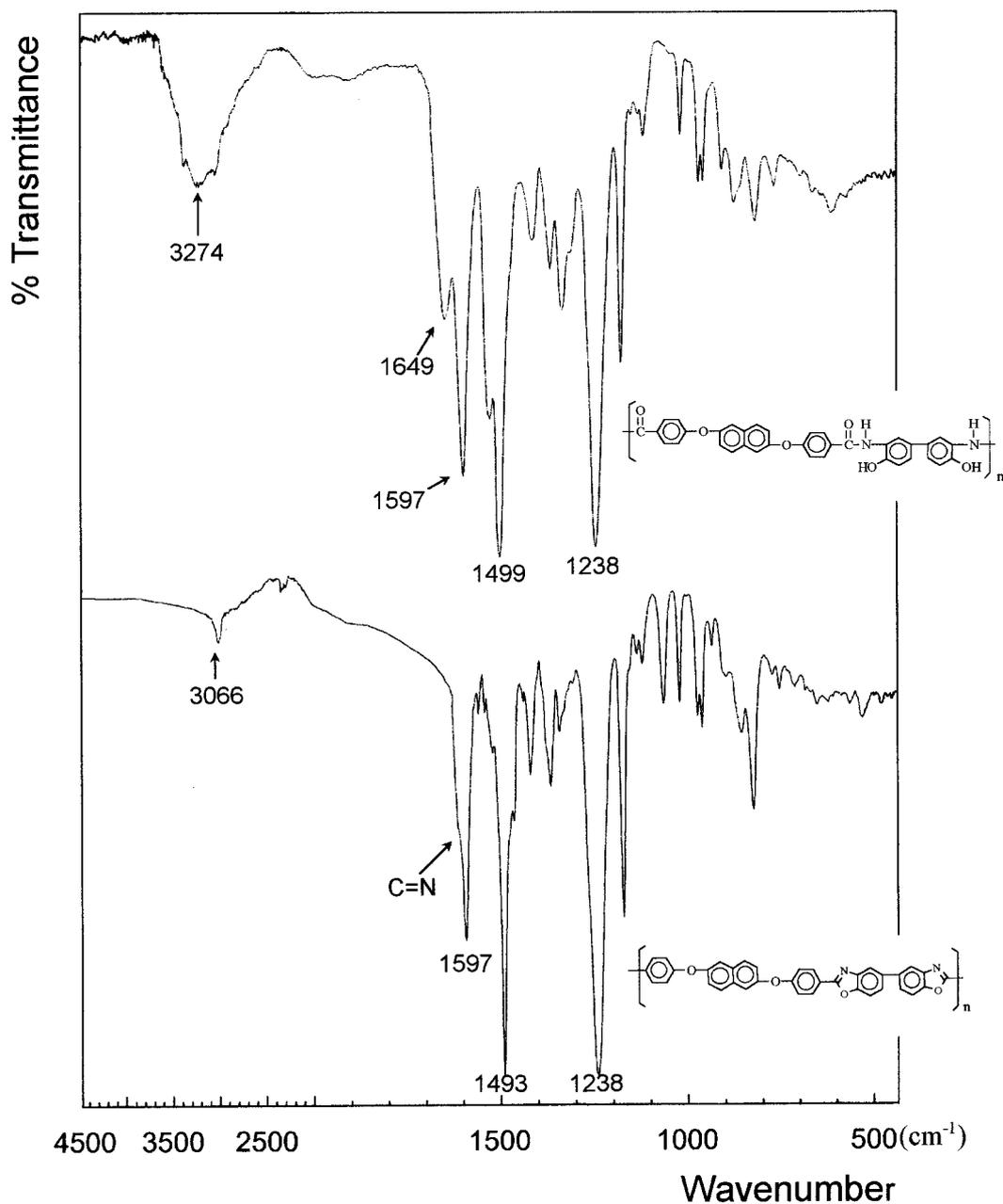


Fig. 4. IR spectra of poly(*o*-hydroxyamide) **7** and polybenzoxazoles **13**

temperature. Nevertheless, they still exhibit excellent resistance to less polar solvents such as *m*-cresol, THF, chloroform, acetone, and ethanol. The poly(*o*-hydroxyamide)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 to prevent close chain packing, and allow solvent molecules to diffuse into the polymer chains.

The polybenzoxazoles, on the other hand, dissolve only in cold sulfuric acid. Despite the fact that all the polyben-

zoxazoles are amorphous, they are quite insoluble in organic solvents, with the exception of polymers **16** and **17**, which contain the bulky 6F group in the bis(*o*-aminophenol) moieties along the macromolecular backbone.

The absence of crystallinity of the prepared poly(*o*-hydroxyamide) and polybenzoxazole films were confirmed by wide-angle X-ray diffraction studies. The amorphous nature of these polymers may be due to the presence of flexible naphthalenedioxy ether linkages in the polymer backbones. All of the polybenzoxazoles show higher chain packing than the corresponding poly(*o*-hydroxyamide)s due to the rigid and planar nature

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

Poly(<i>o</i> -hydroxyamide)						Polybenzoxazole			
Code	Tensile properties of polymer films		DSC ^{a)}			Code	DSC	TG	
	strength-to-break in MPa	elongation-to-break in %	$T_0^b/^\circ\text{C}$	$T_p^c/^\circ\text{C}$	$T_f^d/^\circ\text{C}$		$T_g^e/^\circ\text{C}$	$T_d^f/^\circ\text{C}$	char yield ^{g)} in %
6	81	11	210	268	335	12	266	615 (570)	73.7
7	92	9	213	271	347	13	271	615 (575)	75.0
8	83	10	211	265	340	14	273	625 (575)	72.5
9	91	8	209	258	357	15	275	635 (580)	74.6
10	75	11	211	255	348	16	277	570 (550)	61.7
11	79	9	213	254	361	17	279	570 (555)	62.8

- 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) Endothermic peak temperature.
 d) Extrapolated final temperature of the endothermic peak.
 e) Midpoint temperature of baseline shift on the second DSC heating trace of the sample after rapid cooling from 450 °C in nitrogen.
 f) 10% wt.-loss temperature at a heating rate of 20 °C/min in nitrogen. Values in parentheses were observed in air.
 g) Residual wt.-% when heated to 800 °C in nitrogen.

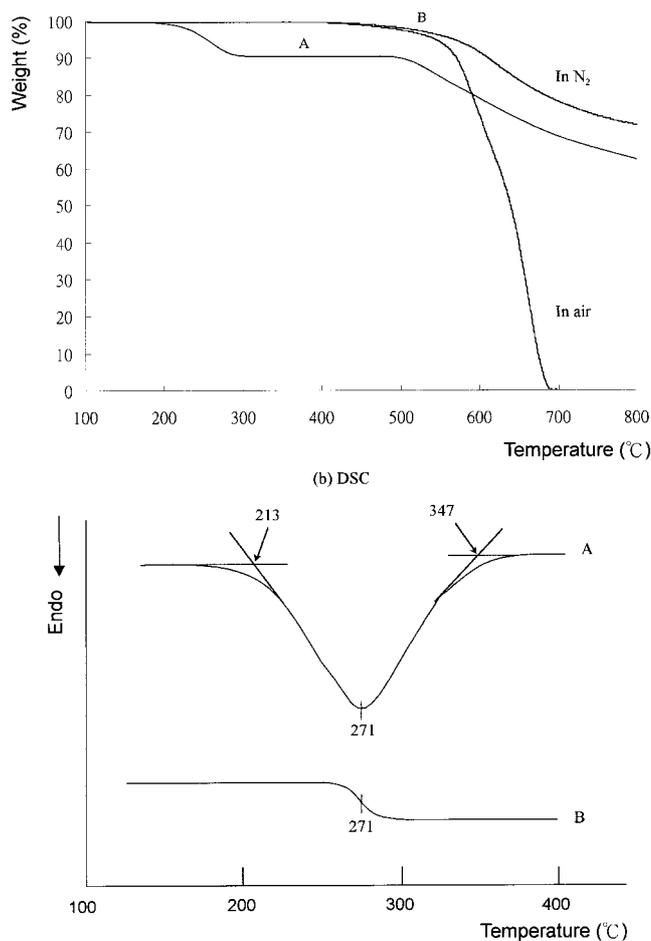


Fig. 5. (a) TG curves for (A) poly(*o*-hydroxyamide) **7** and (B) polybenzoxazole **13** at a heating rate of 20 °C/min; (b) DSC curves for (A) poly(*o*-hydroxyamide) **7** and (B) polybenzoxazole **13** at a heating rate of 20 °C/min in nitrogen

of benzoxazole moieties. Their poor solubility is reflective of close chain packing. All the poly(*o*-hydroxyamide)s can be solution-cast into flexible and tough 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 75–92 MPa and 8–11%, respectively. All the thermally converted polybenzoxazole films are also flexible and tough, indicating that no thermal degradation leading to molecular chain scission occurred during the conversion process. However, most of the films shrink during the cyclization process; therefore, their mechanical properties were not evaluated. Good-quality and smooth polybenzoxazole films may be obtained under proper tension and slower heating speed.

The thermal behavior of the poly(*o*-hydroxyamide)s and polybenzoxazoles was investigated by DSC and TG. All the poly(*o*-hydroxyamide)s exhibit strong endothermic peaks between 209–361 °C in the first DSC scan, with peak temperatures around 254–271 °C, which are attributed to loss of water during the conversion of the poly(*o*-hydroxy amide) to polybenzoxazole. Fig. 5a and 5b show a typical pair of TG and DSC curves for poly(*o*-hydroxyamide) **7** and polybenzoxazole **13**. The TG trace of poly(*o*-hydroxyamide) **7** reveals an onset of weight loss around 200 °C that comes to an end at about 300 °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 213–347 °C. Polybenzoxazole **13** starts to lose weight at around 500 °C and leaves 75.0% residual char when heated to 800 °C in nitrogen. After rapid cooling from 450 °C in the first DSC heating trace, the polybenzoxazole (**13**) formed *in situ*

shows a distinct glass transition around 271 °C on the subsequent DSC heating trace. The increased T_g of polybenzoxazole **13** when compared to its poly(*o*-hydroxyamide) precursor **7** may be a reflection of an enhanced chain rigidity due to the formation of the benzoxazole ring. All the poly(*o*-hydroxyamide)s and polybenzoxazoles exhibit a similar DSC and TG behavior, and their thermal behavior data are summarized in Tab. 3. All the polybenzoxazoles do not lose weight up to 500 °C in air or nitrogen, and the temperatures at which 10% weight loss are recorded are in the 570–635 °C range in nitrogen. All of them exhibit char yields in excess of 61.7% at 800 °C in nitrogen. Their glass transition temperatures (T_g s) are recorded between 266–279 °C. The large window between T_g and the decomposition temperature make these polybenzoxazoles attractive for practical processing.

Conclusions

Six poly(*o*-hydroxyamide)s with high molar masses have been prepared from 4,4'-bis(1,4-naphthalenedioxy)dibenzoyl chloride (**1**) and 4,4'-bis(2,6-naphthalenedioxy)dibenzoyl chloride (**2**) with bis(*o*-aminophenol)s by the low-temperature solution polycondensation. All the poly(*o*-hydroxyamide)s are easily soluble in a variety of organic solvents and can be cast into flexible and tough films from their polymer solutions. They can be transformed to the corresponding polybenzoxazoles at elevated temperatures and reveal a dramatically decreased solubility but higher T_g s when compared to their corresponding poly(*o*-hydroxyamide) prepolymers. All the polybenzoxazoles show excellent thermal stability. Thus, the prepared polybenzoxazoles are promising candidates for new high performance polymeric materials.

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