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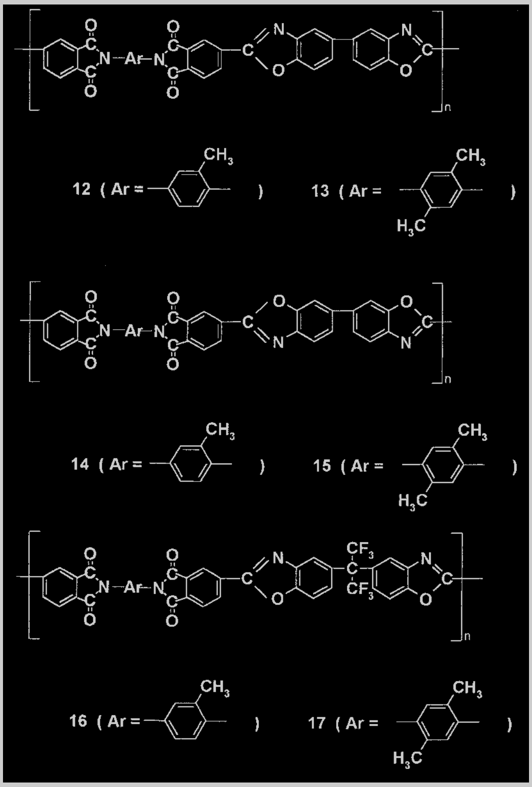
Full Paper: A series of new strictly alternating poly(*o*-hydroxy amide-imide)s with high molecular weight were synthesized by low-temperature solution polycondensation from the preformed imide ring and methyl- or dimethyl-substituted *p*-phenylene-containing diacyl chlorides of 2,5-bis(trimellitimido)toluene or 1,4-bis(trimellitimido)-2,5-dimethylbenzene and three bis(*o*-amino phenol)s. All the poly(*o*-hydroxy amide-imide)s are readily soluble in a variety of organic solvents such as *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc). Transparent and flexible films of these polymers were cast from NMP solutions. The tensile strength of the films ranges from 90–105 MPa and elongation at break from 7–12%. Subsequent thermal cyclodehydration of the poly(*o*-hydroxy amide-imide)s afforded novel rigid-rod and strictly alternating poly(benzoxazole-imide)s. They exhibit glass transition temperatures in the range of 316–345 °C and are stable up to 500 °C in air or nitrogen, with a 10% weight loss temperature in nitrogen ranging from 550–585 °C.



Structures and codes of poly(benzoxazole-imide)s

New rigid-rod and strictly alternating poly(benzoxazole-imide)s containing methyl-substituted *p*-phenylene units in the main chain

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Introduction

Wholly aromatic heterocyclic polymers have been investigated for high-performance application. Aromatic polyimides are widely used in the semiconductor and electronic packaging industry because of their outstanding thermal stability, good insulation properties with low dielectric constant, good adhesion to common substrates, superior chemical stability[1,2]. Aromatic polybenzoxazoles are also a class of heterocyclic polymers that exhibit excellent thermooxidative stability, high tensile modulus and strength, and superior chemical resistance[3,4]. A few rigid-rod polybenzoxazoles have been reported to have potential for fabrication of high-modulus, high-strength fibers[5,6]. However, like 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 are limited. Therefore, attempts have been made to modify the backbone structure and improve their processibility[7–13]. One successful approach is the introduction

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flexible linkages into the polymer backbone to improve processibility. In most of these approaches, fluorinated monomers were introduced into the polymer backbone to enhance the polymer solubility, while retaining the desirable thermoxidation 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[7,10–13]. Similarly, soluble poly(ether benzoxazole)s have been generated and display properties intermediate between the two homopolymers[14,15]. 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 substituent-containing *p*-phenylene moieties as bulky and symmetrical units in the main chain. Recently, we have reported that aromatic poly(amide-imide)s derived from preformed imide ring containing aromatic diimide-diacids, 2,5-bis(trimellitimido)toluene[16] and 1,4-bis(trimellitimido)-2,5-dimethylbenzene[17], had improved solubility with retention of high thermal stability. These resulting poly(amide-imide) films exhibited good mechanical properties. In a continuation of these studies, this article deals with the synthesis and basic characterization of rigid-rod aromatic poly(benzoxazole-imide)s due to their better combination of thermal, mechanical properties as well as improved processing abilities. These more processable polymers with strictly alternating (benzoxazole-benzoxazole)-(imide-imide) sequence can be tailored from the diacid chloride of 2,5-bis(trimellitimido)toluene or (**1**) 1,4-bis(trimellitimido)-2,5-dimethylbenzene containing (**2**) preformed imide rings and bis(*o*-aminophenol)s through the low-temperature solution polycondensation. This yields poly(*o*-hydroxy amide-imide) precursors more stable than poly(benzoxazole amic acid) derived from aromatic diamines containg preformed benzoxazole rings and aromatic dianhydrides and soluble in amidic solvents which were cast into films and then converted to poly(benzoxazole-imide) structures via subsequent thermal cyclodehydration. The properties of these polymers such as solubility, tensile properties, crystallinity, and thermal behavior were examined.

Experimental part

Materials

Commercially obtained 2-methyl-*p*-phenylenediamine dihydrochloride (TCI), 2,5-dimethyl-*p*-phenylenediamine (TCI), and trimellitic anhydride (TCI) were used without further purification. The aromatic bis(*o*-aminophenol) monomers that included 3,3′-dihydroxybenzidine (**4**, TCI), 3,3′-diamino-4,4′-dihydroxy-biphenyl (**3**, TCI) and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (**5**, 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.

2,5-Bis(trimellitimido)toluene and 1,4-bis(trimellitimido)-2,5-dimethylbenzene were prepared by the two-stage procedure that include ring-opening addition of 2-methyl-*p*-phenylenediamine or 2,5-dimethyl-*p*-phenylenediamine with two equivalent amount of trimellitic anhydride, followed by cyclodehydration to the imidodicarboxylic acid by toluene-water azeotropic distillation, according to reported procedures[16,17]. The reaction of the two diimide-diacids with excess thionyl chloride in the presence of a few drops of dimethylformamide (DMF) as a catalyst afforded the corresponding diimide-diacyl chlorides (**1**) and (**2**), respectively. Diacyl chloride **1** was purified by recrystallization from a mixture of hexane and toluene to afford white powders; mp. 264–265 °C.

IR (KBr): 1770 (acyl chloride C═O stretching), 1790 (imide, symmetric C═O stretching), 1737 $\mathrm{cm^{-1}}$ (imide, asymmetric C═O stretching).

$C_{25}H_{12}N_2O_6Cl_2$	Calc.	C 59.19	H 2.38	N 5.52
	Found	C 59.01	H 2.34	N 5.48

Diacyl chloride **2** was purified by recrystallization from toluene to give white needles; mp. 318–319 °C.

IR (KBr): 1770 (acyl chloride C═O stretching), 1790 (imide, symmetric C═O stretching), 1735 $\mathrm{cm^{-1}}$ (imide, asymmetric C═O stretching).

$C_{26}H_{14}N_2O_6Cl_2$	Calc.	C 59.91	H 2.71	N 5.37
	Found	C 59.73	H 2.68	N 5.34

Synthesis of poly(o-hydroxy amide-imide)s

The low-temperature solution polycondensation technique was employed in this investigation. A typical procedure for the preparation of poly(*o*-hydroxy amide-imide)s is as follows. First, 2 mmol of a bis(*o*-aminophenol) was 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 was added, then 2 mmol of diimide-diacyl chloride was 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 viscous gradually. 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-imide)s was measured in NMP at a concentration of $0.5\ \mathrm{g \cdot dL^{-1}}$ at 30 °C.

Preparation of poly(o-hydroxy amide-imide) films and thermal conversion to poly(benzoxazole-imide)s

The prepare the film a solution of about 1.0 g of the poly(*o*-hydroxy amide-imide) sample in 10 mL NMP was poured into a ϕ = 9 cm glass culture dish, which was placed in a 90 °C oven for 12 h to remove the solvent. The obtained semidried polymer film was stripped from the glass substrate and further dried *in vacuo* at 200 °C for 15 h.

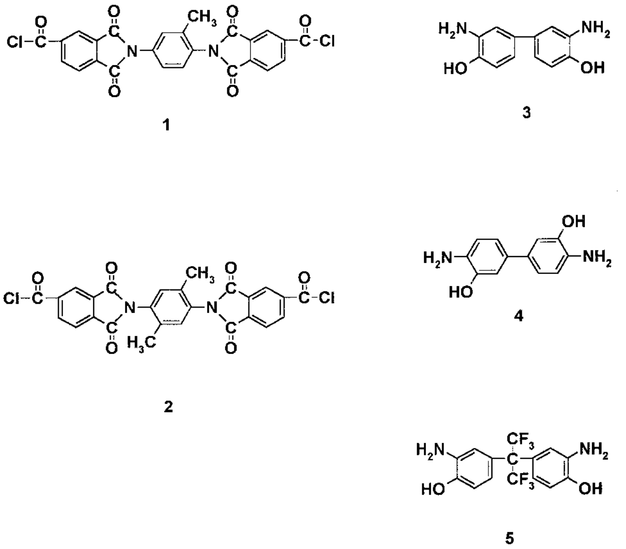
Poly(benzoxazole-imide)s were obtained from the thermal cyclodehydration of poly(*o*-hydroxy amide-imide)s at 380 °C *in vacuo* for 8 h. The conversion was performed in form of films and the inherent viscosities of the poly(benzoxazole-imide)s thus obtained were measured in concentrated sulfuric acid at a concentration of 0.5 g · dL^{-1} at 30 °C.

$(C_{37}H_{18}N_4O_6)_n$	Calc.	C 72.29	H 2.95	N 9.52
	Found	C 73.10	H 2.82	N 9.22

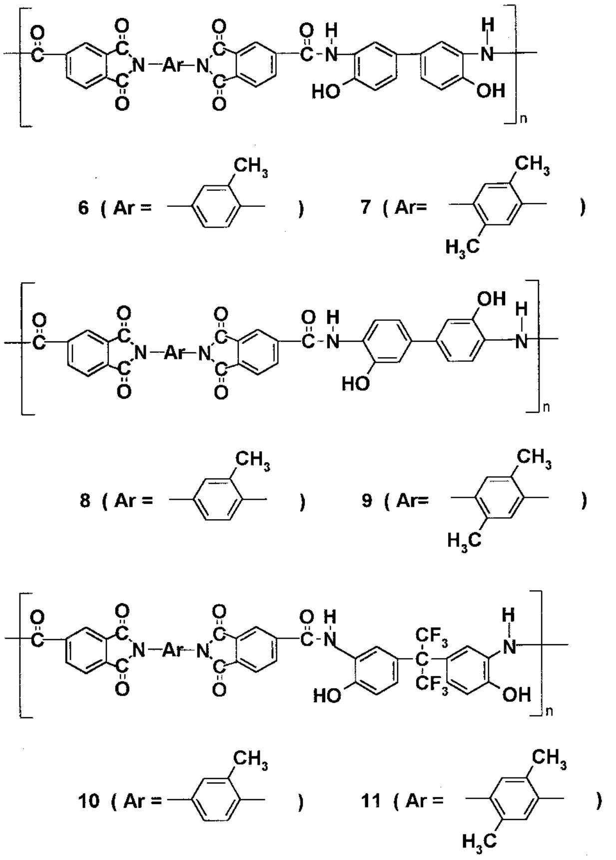
Measurements

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^{-1} 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) 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 cm^3/min) at a heating rate of 10 °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$_\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2 °/min over a range of 2θ = 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.

Scheme 1: Structures and codes of monomers



Scheme 2: Structures and codes of poly(*o*-hydroxy amide-imide)s



Results and discussion

Polymer synthesis

Polybenzoxazoles might be synthesized easily in a one-step procedure using poly(phosphoric acid)[5], phosphorous pentoxide/methanesulfonic acid[18], or trimethylsilyl phosphate[19] as the reaction medium. Isolation and thermal cyclodehydration of soluble poly(*o*-hydroxy amide), derived from the polycondensation of diacid derivatives and bis(*o*-aminophenol)s in a polar solvent, is an alternative method for the production of polybenzoxazole films and fibers[20]. Six poly(*o*-hydroxy amide-imide)s **6**–**11** were prepared readily by the low-temperature solution polycondensation of diimide-diacyl chlorides **1** or **2** with the 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 is generally more preferable than using triethylamine for the preparation of

Tab. 1. Inherent viscosities of poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s

Monomer	Poly(*o*-hydroxy amide-imide)[a]		Poly(benzoxazole-imide)[c]	
	Code	$\frac{\eta_{\text{inh}}}{\text{dL} \cdot \text{g}^{-1}}$ [b]	Code	$\frac{\eta_{\text{inh}}}{\text{dL} \cdot \text{g}^{-1}}$ [b]
1 + **3**	**6**	2.45	**12**	2.32
2 + **3**	**7**	2.20	**13**	2.15
1 + **4**	**8**	1.81	**14**	1.90
2 + **4**	**9**	1.52	**15**	1.62
1 + **5**	**10**	0.90	**16**	0.95[b]
2 + **5**	**11**	0.86	**17**	1.03[a]

[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 °C for 1 h and at room temperature for another 10 h.

[b] Measured at a concentration of 0.5 g · dL^{-1} in NMP at 30 °C.

[c] The conversion of the poly(*o*-hydroxy amide-imide) to the poly(benzoxazole-imide) was carried out by heating at 380 °C for 8 h *in vacuo*.

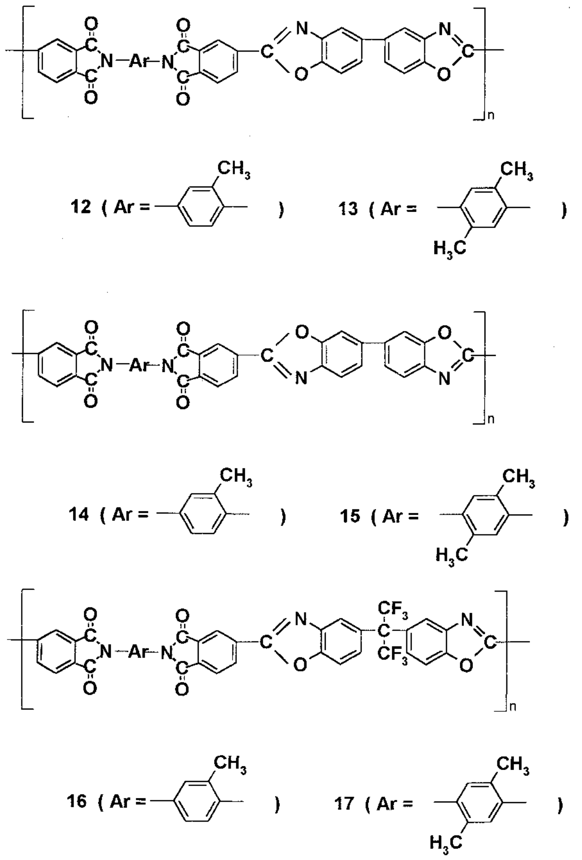
[d] Measured at a concentration of 0.5 g · dL^{-1} in concentrated sulfuric acid at 30 °C, unless otherwise indicated.

higher molecular weight aramides.[21] Structures and codes of the monomers and poly(*o*-hydroxy amide-imide)s are illustrated in Scheme 1 and 2, respectively. The properties of the obtained polymers are summarized in Tab. 1. The inherent viscosities of the resulting poly(*o*-hydroxy amide-imide)s stayed in the range of 0.86–2.45 dL · g^{-1}. It is worth mentioning that the 6F-containing bis(*o*-aminophenol) (**5**)-derived poly(*o*-hydroxy amide-imide)s **10** and **11** were attained with high molecular weights, as evidenced by the inherent viscosity value above 0.8 dL · g^{-1}. This indicates that silylation of bis(*o*-aminophenol) (**5**) reported by Maruyama et al.[7] is not necessary to attain high-molar-mass poly(*o*-hydroxy amide-imide)s in the low-temperature solution polycondensation reaction. All these poly(*o*-hydroxy amide-imide)s were readily soluble in amide-type solvents including NMP and DMAc and could afford free-standing films by means of solution-casting. The films obtained were all flexible and tough. Polymers **6**–**9** are brownish, while polymers **10** and **11** are light yellow in color.

The formation of poly(*o*-hydroxy amide-imide)s was confirmed by means of IR spectroscopy and elemental analysis. The polymers exhibited the broad absorption bands in the region of 2500–3500 cm^{-1} (O—H and N—H str.), 1666 cm^{-1} (amide C═O str.), 1790 cm^{-1} (imide, symmetric C═O str.), and 1735 cm^{-1} (imide, asymmetric C═O str.) (see **11** in Fig. 1).

In the second stage, the poly(*o*-hydroxy amide-imide)s thus obtained were subjected to thermal cyclodehydration. The conversion to poly(benzoxazole-imide)s (**12**–**17**) (Scheme 3) was carried out in the form of films at 380 °C *in vacuo* for about 8 h, and the conversion process

Scheme 3: Structures and codes of poly(benzoxazole-imide)s



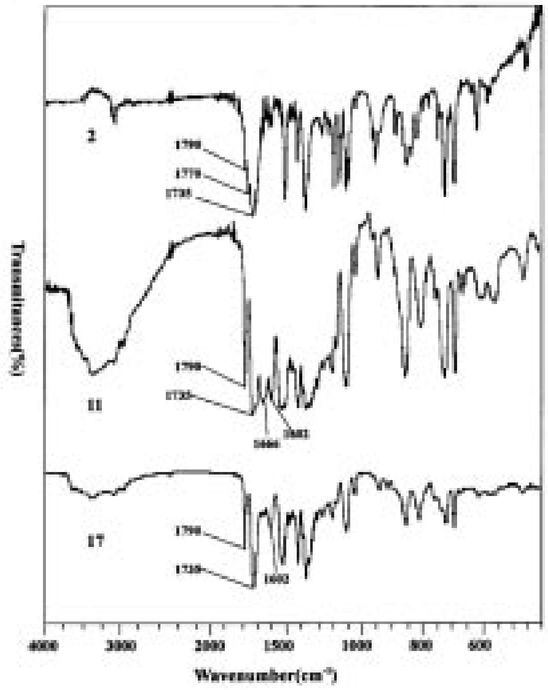


Fig. 1. IR spectra of poly(*o*-hydroxy amide-imide) **11** and poly(benzoxazole-imide) **17** in comparison to the spectrum of the diacyl chloride of 1,4-bis(trimelitimido)-2,5-dimethylbenzene

could be followed by the change in the IR spectra of the films. Fig. 1 shows typical IR spectra of the representative pair of poly(*o*-hydroxy amide-imide) **11** and its corresponding poly(benzoxazole-imide) **17**. The disappearance of the absorption bands around 2500–3500 and 1666 cm^{-1} indicated the completion of the cyclization process, together with the appearance of an absorption at 1602 cm^{-1} characteristic of benzoxazole ring, which was almost overlapped with one of the absorption bands of aromatic C═C str. The elemental analysis values of the transformed polymers agreed well with the values calculated for the polymers with benzoxazole structures. There is sufficient difference in oxygen content between the poly(*o*-hydroxy amide-imide)s and the resulting poly(benzoxazole-imide)s. This conversion could also be monitered by thermogravimetry (TG) and differential scanning calorimetry (DSC) analysis that will be discussed later on. The poly(benzoxazole-imide)s thus obtained, except for **16** and **17**, are insoluble in most organic solvents, while they are soluble in cold concentrated sulfuric acid. The poly(benzoxazole-imide)s derived from diacyl chloride **1** or **2** had inherent viscosities of 0.95–2.32 $dL \cdot g^{-1}$ in concentrated sulfuric acid, indicating that no thermal degradation and decomposition leading to molecular chain scission occurred during the conversion process and during the viscosity determination. This also indicates that the methyl-substituted phenylene linkage-containing poly(benzoxazole-imide)s has good acid-resistance.

Properties of polymers

The solubility of all polymers was evaluated qualitatively and the results are presented in Tab. 2. All of the poly(*o*-hydroxy amide-imide)s were easily soluble in polar aprotic solvents such as NMP, DMAc, DMSO, and DMF at room temperature. Nevertheless, they still exhibited excellent resistance to less polar solvents such as THF, acetone, and ethanol. The poly(*o*-hydroxy amide-imide)s **10** and **11** derived from 2,2-bis-(3-amino-4-hydroxyphenyl)hexafluoropropane) **5** revealed an enhanced solubility. In addition to highly polar solvents, they were also soluble in 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 poly(benzoxazole-imide)s, on the other hand, dissolved all in cold sulfuric acid. Despite the fact that all the poly(benzoxazole-imide)s were amorphous, they were quite insoluble in organic solvents, with the exception of polymers **16** and **17**, which contain the bulky hexafluoropropylene group in the bis(*o*-aminophenol) moieties along the macromolecular backbone. We made a comparison of the solubility of above-mentioned polymers **16** and **17** with those of the poly(benzoxazole-imide)s investigated by Bruma[12)], and found that the latter polymers are only soluble organic solvents, if they contain bulky 6F groups in both the imide and benzoxazole moieties present in the polymers. Thus, the introduction of methyl-substituted *p*-phenylene units into the polymer backbone improves the solubility of the poly(benzoxazole-imide)s in organic solvents.

Wide-angle X-ray diffractograms shown in Fig. 2 indicate all the poly(*o*-hydroxy amide-imide) and poly(benzoxazole-imide) films were amorphous in nature, which may be due to the presence of methyl-substituted *p*-phenylene or hexafluoroisopropylidene linkages in the polymer backbones. All of the poly(benzoxazole-imide)s showed higher chain packing than the corresponding poly(*o*-hydroxy amide-imide)s due to the rigid and planar nature of benzoxazole moieties. Their poor solubility corresponds to close chain packing. All the poly(*o*-hydroxy amide-imide)s could be solution-cast into flexible and

Tab. 2. Solubility behavior of poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s[a)]

Solvent[b)]	Poly(*o*-hydroxy amide-imide)						Poly(benzoxazole-imide)					
	6	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
conc. H_2SO_4	+	+	+	+	+	+	+	+	+	+	+	+
NMP	+	+	+	+	+	+	–	–	–	–	+	+
DMAc	+	+	+	+	+	+	–	–	–	–	+	+
DMF	+	+	+	+	+	+	–	–	–	–	–	–
DMSO	+	+	+	+	+	+	–	–	–	–	–	–
m-cresol	–	–	–	–	–	–	–	–	–	–	–	–
THF	–	–	–	–	+	+	–	–	–	–	–	–
acetone	–	–	–	–	+	+	–	–	–	–	–	–
ethanol	–	–	–	–	–	–	–	–	–	–	–	–
chloroform	–	–	–	–	–	–	–	–	–	–	–	–

[a)] Solubility: +, soluble at room temperature; –, insoluble even on heating.
[b)] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Tab. 3. Tensile properties and thermal behavior of poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s

Poly(*o*-hydroxy amide-imide)						Poly(benzoxazole-imide)			
	tensile properties of polymer films		DSC				DSC	TG	
Code	strength-to-break in MPa	elongation-to-break in %	T_g[a]/°C	T_0[c]/°C	T_p[d]/°C	Code	T_g[e]/°C	T_d[f]/°C	char yield[g] in %
6	102	8	232	270	320	**12**	330	575 (530)	64
7	105	10	[b]	265	325	**13**	338	570 (530)	67
8	99	7	230	270	325	**14**	316	585 (535)	68
9	104	12	[b]	275	335	**15**	317	560 (515)	65
10	90	8	227	270	320	**16**	345	550 (480)	60
11	93	10	223	260	315	**17**	330	555 (470)	62

[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] Difficult to judge.
[c] Extrapolated onset temperature of the endothermic peak.
[d] Endothermic peak temperature.
[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 10 °C/min in nitrogen. Values in parentheses were observed in air.
[g] Residual wt.-% when heated to 800 °C in nitrogen.

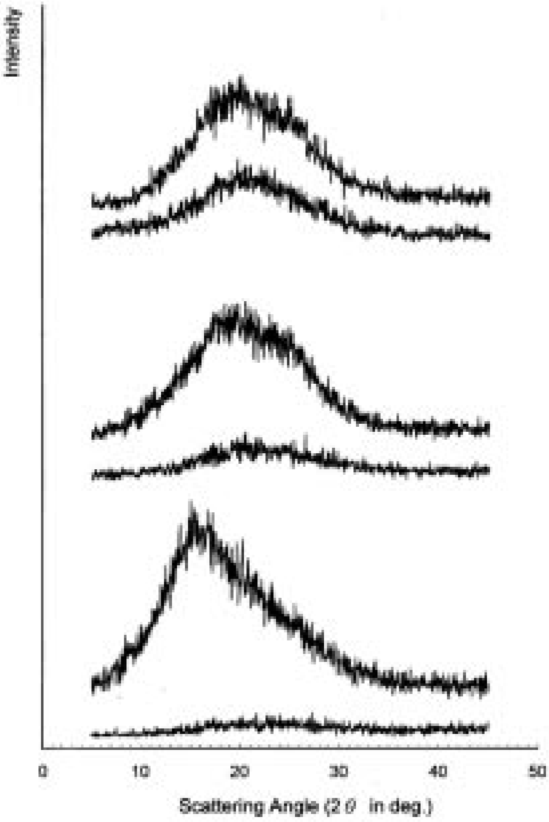


Fig. 2. Wide-angle X-ray diffractograms of some poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s

tough films. These films were subjected to tensile testing, and the results are given in Table 3. The tensile strengths and the elongations at break were in the range of 90–105 MPa and 7–12%, respectively. All the thermally converted poly(benzoxazole-imide) films were also flexible and tough, indicating that no thermal degradation leading to molecular chain scission occurred during the conversion process. However, most of the films shrank or bubbled during the cyclization process; therefore, their mechanical properties were not evaluated. Good-quality and smooth poly(benzoxazole-imide) films may be obtained if under proper tension and lower heating speed.

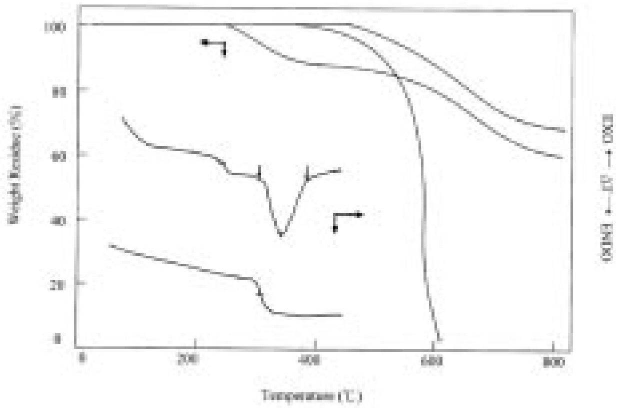


Fig. 3. DSC and TG curves for (A) poly(*o*-hydroxy amide-imide) **8** and (B) poly(benzoxazole-imide) **14**

The thermal behavior of the poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s was investigated by DSC and TG. The poly(*o*-hydroxy amide-imide)s displayed glass transitions between 223–232 °C in the first DSC scan, and exhibited strong endothermic peaks between 260–370 °C, with peak temperatures around 315–335 °C, which are attributed to loss of water during the conversion of the poly(*o*-hydroxy amide-imide) to poly(benzoxazole-imide). Fig. 3 shows a typical pair of

TG and DSC curves for poly(*o*-hydroxy amide-imide) **8** and poly(benzoxazole-imide) **14**. The TG trace of poly(*o*-hydroxy amide-imide) **8** revealed an onset of weight loss around 250 °C and came to an end at about 370 °C. The weight loss was due to the thermal cyclodehydration of the poly(*o*-hydroxy amide-imide), which also agreed well with the strong endothermic peak between 270–370 °C. Poly(benzoxazole-imide) **14** started to lose weight at around 500 °C and left 68% residual char when heated to 800 °C in nitrogen. The baseline shift centered at 230 °C in the first DSC heating trace is ascribed to the glass trasition of the poly(*o*-hydroxy amide-imide) **8**. After rapid cooling from 450 °C, the poly(benzoxazole-imide) **14** formed *in situ* showed a distinct glass transition around 316 °C on the subsequent DSC heating trace. The increased T_g of poly(benzoxazole-imide) **14** when compared to its poly(*o*-hydroxy amide-imide) precursor **8** may be a reflection of an enhanced chain rigidity due to the formation of benzoxazole ring. All the poly(*o*-hydroxy amide-imide)s and poly(benzoxazole-imide)s exhibit a similar DSC and TG behavior, and some of their thermal behavior data are summarized in Tab. 3. All the poly(benzoxazole-imide)s did not lose weight up to 500 °C in nitrogen, and the temperatures at which 10% weight loss was recorded were in the 550–585 °C range in nitrogen. The remained char yields were in excess of 60% at 800 °C in nitrogen. The glass transition temperatures (T_g) of the poly(benzoxazole-imide)s were recorded between 316–345 °C, and found to be about 50 °C higher than those of the corresponding poly(amide-imide)s[16,17] due to the formation of the benzoxazole ring. Thus, the new rigid-rod poly(benzoxazole-imide)s show high thermal stability, with decomposition temperatures over 500 °C and higher T_g, in conjunction with easy processability make these poly(benzoxazole-imide)s attractive for applications in microelectronics, aerospace and related industries as practical materials.

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