Synthesis and Properties of Aromatic Polyimide, Poly(benzoxazole imide), and Poly(benzoxazole amide imide)

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ABSTRACT: Two series of heterocyclic aromatic polymers were synthesized from 4,4′-(4,4′-isopropylidenediphenoxy)-bis(phthaltic anhydride) and 2,2′-bis(3,4-dicarboxyphenyl)-hexafluoropropane dianhydride by two-step method. The inherent viscosities were in the range of 24–45 cm^3/g. The effects of the rigid benzoxazole group in the backbone of copolymer on the thermal, mechanical, and physical properties were investigated. These polymers exhibit good thermal stability. The temperatures of 5% weight loss (T_5) of these polymers are in the range of 403–530°C in air and 425–539°C in nitrogen. The chard yields of these polymers are in the range of 15–24% in air and 54–61% in nitrogen. These polymers also have high glass-transition temperatures and a low coefficient of thermal expansion and good mechanical properties. The poly(benzoxazol imide) has a higher tensile strength and modulus than those of neat polyimide. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2301–2312, 2009

Key words: polyimides; thermal properties; dielectric properties; poly(benzoxazole)

INTRODUCTION

Polymers that contain heterocyclic members, such as imide, isocyanurates, and benzimidazole, typically exhibit outstanding thermo-oxidative stability, high tensile modulus and strength, and superior chemical resistance.[1] Aromatic polyimides are high-performance heterocyclic polymers. Polyimides possess good mechanical properties and high thermal stability and good solvent resistance. Therefore, they have been used in electronic packaging, adhesives, films, automobiles, and aircraft parts, for example.[2]

However, when polyimide is to be employed in a hostile environment, many of its properties must be improved. For instance, when polyimide is used in aerospace, it must endure radiation.[3] Thermal and mechanical properties should improve as the temperature increases. The properties of polyimide can be improved in two ways. The first method is the dispersion of inorganic filler in the polyimide matrix. However, the adhesion between inorganic filler and polymer matrix is typically poor, so the surface of the inorganic filler should be modified.[3] Our previous works [4–6] have demonstrated that multiwalled carbon nanotube (MWCNT) can be utilized to reinforce the polyimide matrix. Modified MWCNTs can significantly improve the mechanical properties of the polyimide.[4–6] The second method for improving the properties of polyimide is to design an appropriate molecular structure of the polymer.

The incorporation of other functional groups can improve the properties of the polyimide. For instance, polyimide incorporating with ether, amide, or ester functional groups into polyimide can improve its flexibility of the composite.[7–9] Benzoxazole is a rigid-rod molecule with a polymeric structure that contains a benzoxazole backbone and may have a higher modulus and higher strength.[10–18] In this work a high thermal stability and good solvent resistance poly (benzoxazoles imide) polymer develop. A novel polyimide polymer that contains heterocyclic benzoxazole rings was synthesized.

The monomers, 4,4′-(4,4′-isopropylidenediphenoxy) bis(phthaltic anhydride) (IPDA), 2,2′-bis(3,4-dicarboxy-phenyl)hexafluoropropane dianhydride (6FDA), and trimellitic dianhydride chloride (TAC) were reacted with 3,3′-dihydroxy-4,4′-diaminobiphenyl (HAB) in two-step method.[11,12] Poly(benzoxazole imide) and poly(benzoxazole amide imide) copolymers were prepared. The properties of these polymers, solubility, thermal behavior, mechanical properties, and dielectric constant, were studied.

EXPERIMENTAL SECTION

Materials

Both HAB (99.7%) and 4,4′oxydianiline (4,4-ODA) (99.8%) were supplied by the Wakayama Seika
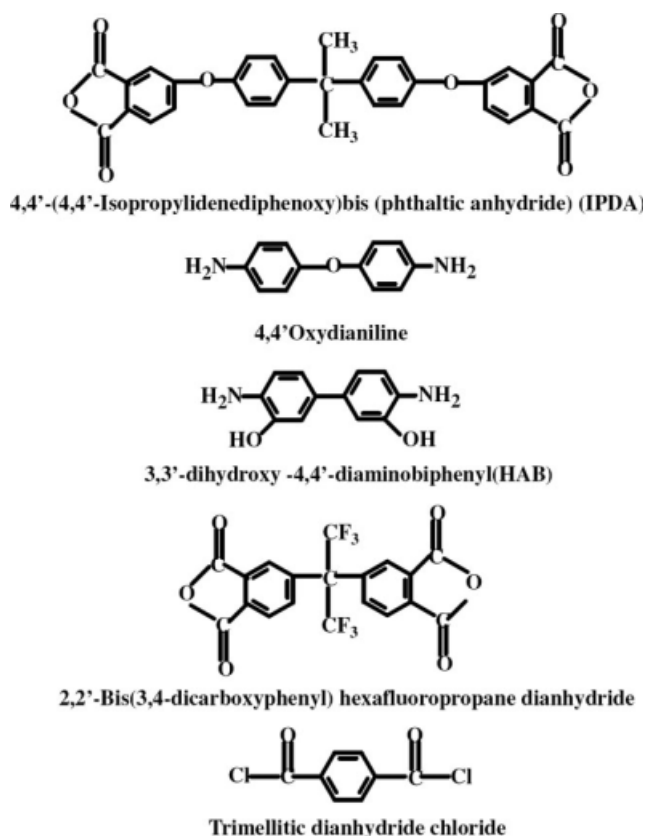
Scheme 1 Structures and codes of monomers.

(Wakayama City, Japan). IPDA (99%) was obtained from Aldrich Chemicals (St. Louis, MO) and recrystallized from acetic anhydride (Showa Chemical Co., Gyoda City, Saotama, Japan) before being dried at 150°C prior to reaction. 6FDA (99.7%) was received from Chriskev Company (Lenexa, KS) and was dried at 150°C prior to reaction. Trimellitic dianhydride chloride (TMAC) (99.7%) was obtained from the Aldrich (St. Louis, MO). N-Methyl-2-pyrrolidone (NMP) was purified by distillation at reduced pressure over calcium hydride and was stored over 4 Å molecular sieves. Scheme 1 presents the structures and codes of the monomer.

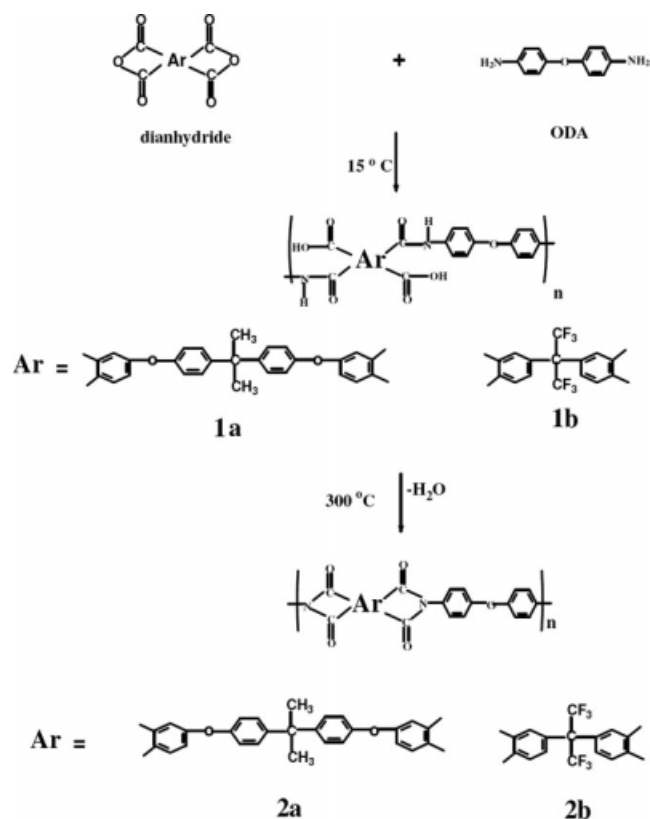### Synthesis of the polyimides and poly(benzoxazole imide)

Synthesis of polyimide

The following procedure was employed to prepare IPDA: 5 mmol 4,4'ODA was dissolved in 20 mL NMP and kept at 15°C for 30 min, and then 5 mmol IPDA was added. This reactive solution continued to be stirred for 6 h to obtain a viscous poly(amic acid) (PAA) solution. The inherent viscosity of the polymer was 37 cm^3/g, as measured in NMP at a concentration of 0.005 g/cm^3 at 30°C. The PAA was converted into polyimide by thermal imidization method. The PAA solution was

cast on a glass plate by a doctor's blade and placed put in an oven at 120°C for 30 min to remove the solvent. The PAA film was stripped from the glass plate, further dried, and underwent imidization by heating from 150°C for 0.5 h, to 250°C at 0.5 h, and 300°C for 1 h. The film was yellow in color and transparent. The method of synthesis of polyimide from IPDA and ODA is also employed to that from 6FDA and ODA. The inherent viscosity of the 6FDA-derived polyimide **1b** was 45 cm^3/g, as measured in NMP at a concentration of 0.005 g/cm^3 at 30°C. Scheme 2 presents the structures and of the synthesis of polyimide.

Synthesis of poly(benzoxazole imide) from IPDA, HAB, and TMAC

Five millimole HAB was dissolved in 20 mL NMP and was kept at 15°C for 30 min; then 2.5 mmol IPDA was added. This reactive solution was stirred for 1 h. The mixture was placed in a high temperature oven at 200°C for 1 h. After the amic acid ring had been closed, 2.5 mmol TMAC was added. The solution was kept at room temperature for 6 h to obtain a viscous PAA solution. The inherent viscosity of the polymer was 24 cm^3/g, as measured in NMP at a concentration of 0.005 g/cm^3 at 30°C. The PAA solution was cast on a glass plate using a doctor's blade and placed in an oven at 120°C for 30 min to remove the solvent. The PAA film was stripped from the glass plate and was

Scheme 2 Synthesis of the polyimide.
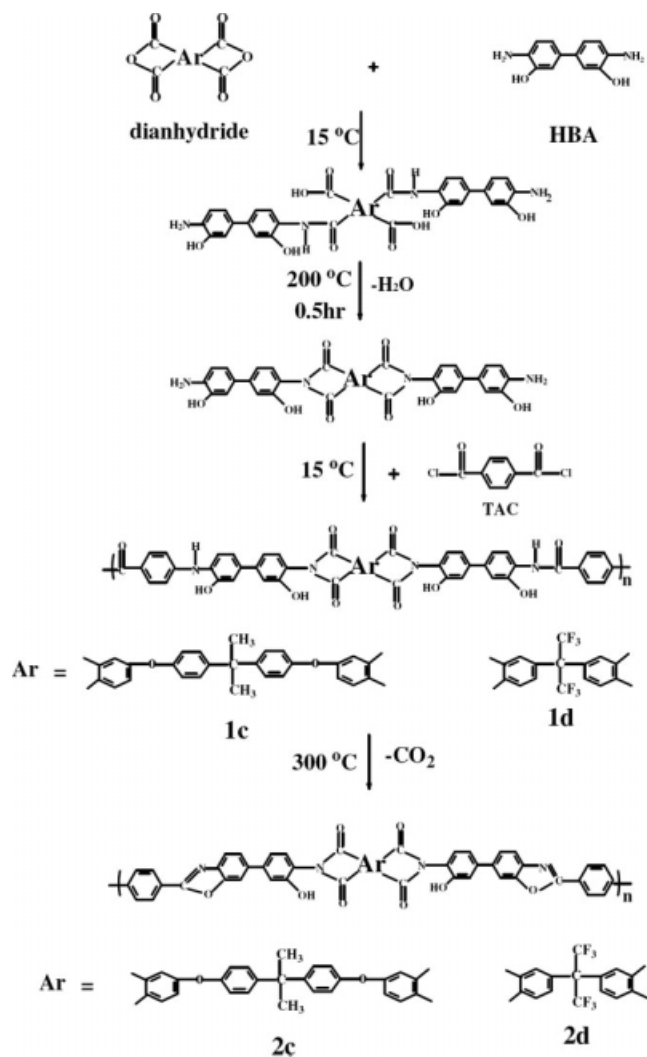
Scheme 3 Synthesis of the poly(benzoxazole imide).

room temperature for 6 h to obtain a viscous PAA solution. The inherent viscosity of the polymer was 28 cm³/g, as measured in NMP at a concentration of 0.005 g/cm³ at 30°C. The PAA solution was cast on a glass plate by using a doctor's blade and then placed in an oven at 120°C for 0.5 h to remove the solvent. The PAA film was stripped from the glass plate and then further dried and imidized by the following sequence: 150°C for 0.5 h, to 250°C for 0.5 h, and 300°C for 1 h to obtain a dark brown film. The synthesis of poly(benzoxazole amide imide) (**1f**) from 6FDA, ODA, HAB, and TMAC was the same as that from IPDA, ODA, HAB, and TMAC. The inherent viscosity of the 6FDA-derived poly(benzoxazole amide imide) (**1f**) was 26 cm³/g, as measured in NMP at a concentration of 0.005 g/cm³ at 30°C. Scheme 4 present the structures and synthesis of poly(benzoxazole amide imide).
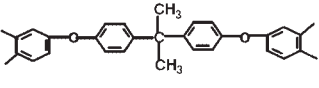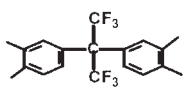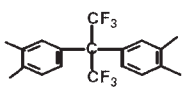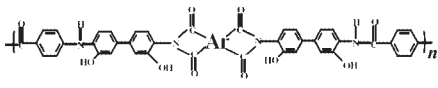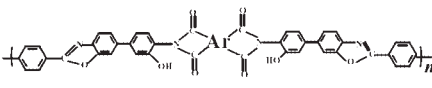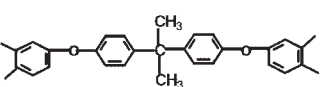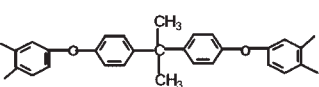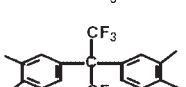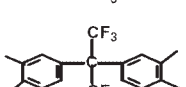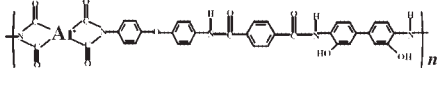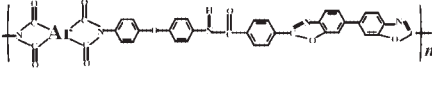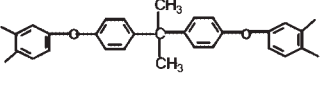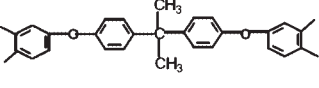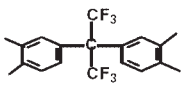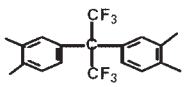
Property measurements

IR spectra were obtained by using a Jasco 460 FTIR spectrometer with 16 scans in the range 400–4000

then further dried and imidized by sequential heating from 150°C for 0.5 h, to 250°C for 0.5 h, to 300°C for 1 h to obtain a dark brown film. The method of synthesis poly(benzoxazole imide) from IPDA, HAB, and TMAC is also applied to that from 6FDA, HAB, and TMAC. The inherent viscosity of the 6FDA-derived poly(benzoxazole imide) (**1d**) was 33 cm³/g, as measured in NMP at a concentration of 0.005 g/cm³ at 30°C. Scheme 3 presents the structures and synthesis of poly(benzoxazole imide).
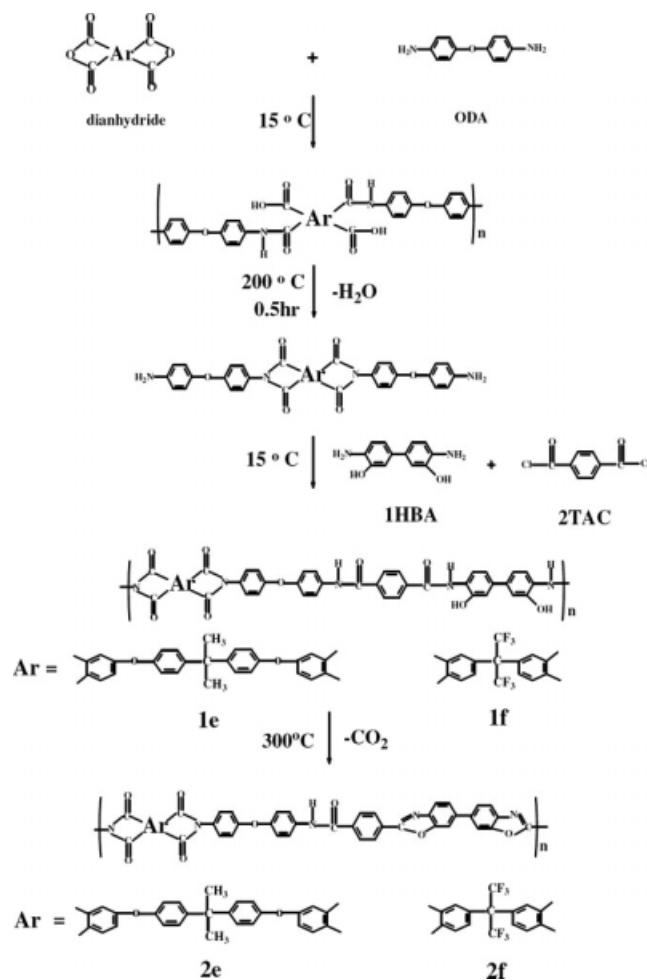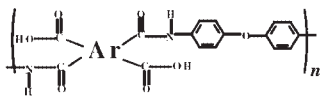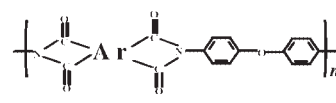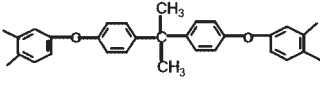
Synthesis of poly(benzoxazole amide imide), IPDA, ODA, HAB, and TMAC

Five millimole ODA was dissolved in 20 mL NMP and kept at 15°C for 30 min, and then 2.5 mmol IPDA was added. This reactive solution was stirred for 1 h. The mixture was placed in a high temperature oven at 200°C for 1 h. After the amic acid ring was closed, 5 mmol TMAC was added, and then 2.5 mmol HAB was added. The solution was kept at

Scheme 4 Synthesis of the poly(benzoxazole amide imide).

TABLE I
Code and Structures of Polymers

Polyamic Acid → 300°C imidization → **Polyimide**

Ar	code		Ar	code
(structure with CH$_3$/CH$_3$)	1a		(structure with CH$_3$/CH$_3$)	2a
(structure with CF$_3$/CF$_3$)	1b		(structure with CF$_3$/CF$_3$)	2b

Poly o-hydroxy amide imide → 300°C imidization → **Poly(benzoxazole imide)**

Ar	code		Ar	code
(structure with CH$_3$/CH$_3$)	1c		(structure with CH$_3$/CH$_3$)	2c
(structure with CF$_3$/CF$_3$)	1d		(structure with CF$_3$/CF$_3$)	2d

Poly o-hydroxy amide imide → 300°C imidization → **Poly(benzoxazole amide imide)**

Ar	code		Ar	code
(structure with CH$_3$/CH$_3$)	1e		(structure with CH$_3$/CH$_3$)	2e
(structure with CF$_3$/CF$_3$)	1f		(structure with CF$_3$/CF$_3$)	2f

cm^{-1}. NMR spectra were recorded by using a Bruker DSX 400 Hz spectrometer in dimethyl sulfoxide. Intrinsic viscosity (IV) was measured in NMP solution at 30°C by using an Ubbelohde no. 100 viscometer. Molecular weight was measured by using a Shimadzu GPC. Polystyrene was used as a relative standard. Thermogravimetric analysis (TGA) was performed on powdered samples by using a DuPont TA TGA-40 at a heating rate of 20°C/min under nitrogen and in an atmosphere of air. The coefficient of thermal expansion (CTE) of polyimide film was determined by using a TA 2940 thermal mechanical analyzer with a tensile force of 0.5 N on the film at a heating rate 10°C/min. The glass transition temperature (T_g) was taken from the inflection point of the dimensional change versus temperature curve. The mechanical properties of the cast film were tested by using a Hung Ta Instrument HT-9102, with a load cell of 100 kg. The dielectric constant was determined by using an Agilent 4284A LCR in 1 MHz.

RESULTS AND DISCUSSION

Synthesis of polymers

A series of novel polymers were prepared from two dianhydrides, IPDA and 6FDA, with diamine ODA, diacid chloride TACl, and bis(o-aminophenols) HBA. The respective reaction schemes are illustrated in Schemes 1–3. Table I presents two series of IPDA- and

TABLE II
Intrinsic Viscosities (IV) and Molecular Weights of Poly(amic acid hydroxyamide)s

Polymer Code	IPDA-derived polymer			6FDA-derived polymer		
	1IPDA + 1ODA **1a**	0.5IPDA + 1HBA + 0.5TMAC **1c**	0.25IPDA + 0.5ODA 0.25HBA + 0.5TMAC **1e**	16FDA + 1ODA **1b**	0.56FDA + 1HBA + 0.5TMAC **1d**	0.256FDA + 0.5ODA 0.25HBA + 0.5TMAC **1f**
IV^a (dL/g)	0.37	0.24	0.28	0.45	0.33	0.26
$M_w{}^b \times 10^4$ (g/mol)	5.43	4.12	4.41	5.50	4.82	4.34
$M_n{}^b \times 10^4$ (g/mol)	2.91	2.34	2.49	2.94	2.71	2.26
M_w/M_n	1.86	1.76	1.77	1.87	1.78	1.92

[a] Measured at a polymer concentration of 0.5 g/dL in 15 mL NMP 30°C.
[b] Relative to polystyrene standards, using DMF as eluent.

6FDA-derived polymers and their chemical structures. Table II summarizes the intrinsic viscosity and molecular weight of the synthesized polymers. The intrinsic viscosities of these polymer precursors are in the range of 24–45 dL/g. GPC analysis indicates their weight-averaged molecular weights (M_w) and number-averaged molecular weights, and polydispersity indices were in the ranges of 41,200–55,000, 22,600–29,400, and 1.76–1.92, respectively.

Determination chemical structures of polyimides by FTIR

The chemical structures of IPDA-derived polyimide (**2a**), poly(benzoxazole imide) (**2c**), and poly(benzoxazole amide imide) (**2e**) are identified by FTIR. Figure 1 presents the FTIR spectra of IPDA-derived precursors and polymers. The characteristic absorption peaks of the IPDA polyamic acid **1a** are at 3400 cm^{-1} (O—H and N—H stretch) and 1650 cm^{-1} (amide C=O).
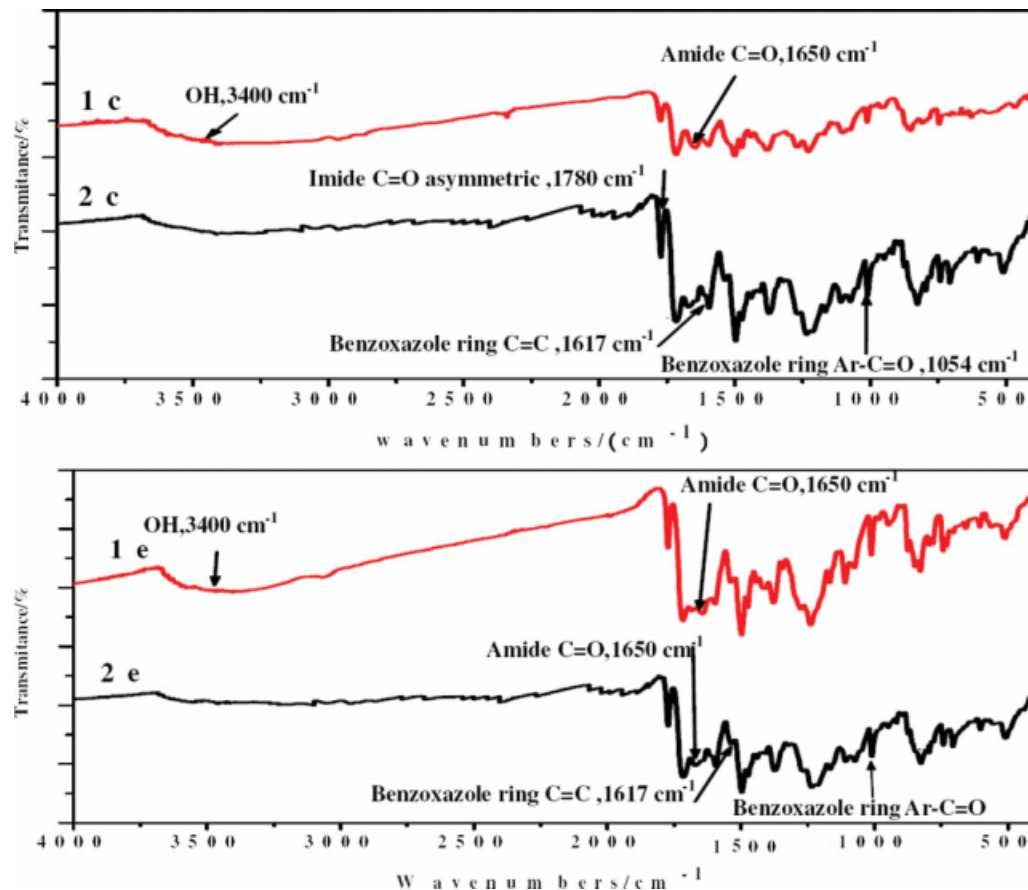

Figure 1 FTIR spectra of the IPDA-derived polymer. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com.]

Following thermal imidization, the characteristic FTIR peaks of the IPDA polyimide **2a** are at 1780 cm^{-1} (asymmetric C=O stretch), 1720 cm^{-1} (symmetric C=O stretch), while the peak of the amic acid at 3400 cm^{-1} (O—H stretch) is smaller and reveals weaker absorption. The absorption associated with the peak at 1650 cm^{-1} (amide C=O) decreased. The peaks of imide at 1720 cm^{-1} (symmetric C=O stretching) became sharper. These observations verify that poly-amic acid will form polyimide linkage by thermal cyclohydration. The characteristic absorption peaks of the IPDA poly(o-hydroxyl amide) (**1c**) are at 3400 cm^{-1} (O—H and N—H stretching) and 1650 cm^{-1} (amide C=O). In the second stage, the dehydration of o-hydroxyl amide forms polybenzoxazole. The characteristic FTIR peaks of the hydroxy-containing IPDA poly(benzoxazole imide) (**2c**) are at 3400–3100 cm^{-1} (board O—H stretching), 1720 cm^{-1} (imide symmetric C=O stretching), while those of benzoxazole functional are at 1617 cm^{-1} (C=N stretching) and 1054 cm^{-1} (Ar—C—O stretching). Therefore, the peak at 1650 cm^{-1} (amide C=O) disappeared, and the peak at 3400 cm^{-1} (O—H stretching) became smaller and boarder peak. The benzoxazole characteristic peaks at 1617 cm^{-1} (C=N stretching), 1054 cm^{-1} (Ar—C—O stretching) appeared. The thermal cyclohydration of o-hydroxyl amide forms hydroxyl-containing poly(benzoxazole imide) as revealed by the spectra. Figure 1 presents the FTIR spectra of the characteristic pair of poly(o-hydroxy amide imide) (**1e**) and its corresponding poly(benzoxazole amide imide) (**2e**). The characteristic FTIR peaks of the IPDA poly(benzoxazole amide imide) (**2e**) are at 1720 cm^{-1} (imide symmetric C=O stretching), 1650 cm^{-1} (amide C=O stretching); those of benzoxazole are at 1617 m^{-1} (C=N stretching), 1054 cm^{-1} (Ar—C—O stretching). The disappearance of the absorption peaks around 3400 cm^{-1} (O—H stretch) upon thermal cyclization, and the appearance of peaks at 1617 cm^{-1} (C=N stretching) and 1054 cm^{-1} (Ar—C—O stretching)are characteristic of the benzoxazole ring. The characteristic absorption bands of the amide group appeared at 1650 cm^{-1} (C=O stretching) and those of the benzoxazole group appeared at 1617 m^{-1} (C=N stretching), 1054 cm^{-1} (Ar—C—O stretching), indicating that poly(benzoxazole amide imide) had been synthesized. Figure 2 presents the FTIR spectra of the 6FDA-derived polymers polyimide (**2b**), poly(benzoxazole imide) (**2d**), and poly(benzoxazole amide imide) (**2f**). The 6FDA-derived polymer exhibits the same phenomenon as the IPDA-derived polymer upon thermal cyclization. The characteristic FTIR peaks of the 6FDA polyimide (**2b**) are at 1780 cm^{-1} (asymmetric C=O stretching) and 1720 cm^{-1} (symmetric C=O stretching). The characteristic FTIR peaks of the hydroxy-containing of 6FDA poly(benzoxazole imide) (**2d**) are at the 3400 cm^{-1} (board O—H stretching), 1720 cm^{-1} (imide

symmetric C=O stretching),while those of the benzoxazole ring 1617 cm^{-1} (C=N stretching) and 1054 cm^{-1} (Ar—C—O stretching). The characteristic FTIR peaks of the 6FDA poly(benzoxazole amide-imide) (**2f**) are at 1720 cm^{-1} (symmetric C=O stretching) and 1650 cm^{-1} (amide C=O stretching), while those of benzoxazole are at 1617 cm^{-1} (C=N stretching) and 1054 cm^{-1} (Ar—C—O stretching).

Functional groups of polyimide by ^{13}C-NMR

Figure 3 presents the ^{13}C-NMR spectra of IPDA-derived polymers **2c** and **2e**. The characteristic NMR peaks of the hydroxyl-containing poly(benzoxazole imide) (**2c**) showed that: the carbonyl group in the imide ring appeared at 167 ppm; the carbon atom in the benzoxazole ring appeared at 163 ppm; carbon atoms in the aromatic hydroxyl exhibited at 150 ppm; and the carbon of isopropyl was at 42 ppm. The characteristic NMR peaks of the poly(benzoxazole amide imide) (**2e**) showed the carbonyl group of imide ring appeared at 167 ppm. The carbon atom in the amide group and carbon atom in the benzoxazole group were expected at 165 and 163 ppm but they were difficult to observe and assign at these peaks. The peaks of the benzoxazole carbon atom and the amide carbon atom appeared over-lapped at 163.7 ppm.[10] The carbon species in isopropyl was at 42 ppm. Figure 4 presents the ^{13}C-NMR spectra of the 6FDA-derived polymers **2d** and **2f**. The characteristic NMR peaks of the hydroxyl-containing poly(benzoxazole imide) (**2d**) exhibited the following: the carbonyl group of the imide ring was shown at 167 ppm; carbonyl of benzoxazole ring appeared at 163 ppm; carbon in the aromatic hydroxyl was at 150 ppm; and carbon of the fluorinated isopropyl was at 66 ppm. The characteristic ^{13}C-NMR spectra of the **2f** poly(benzoxazole amide imide) showed that the carbonyl of imide ring was at 167 ppm. The characteristic peaks of the specific amide carbon and benzoxazole carbon were not clearly observed. The peaks of the benzoxazole ring carbon and the amide carbon at 163.7 ppm over-lapped. The peak of the carbon in fluorinated isopropyl was at 66 ppm.

Solubilities of polymer

The solubilities of the synthesized polymers were evaluated qualitatively and the results are presented in Table III. The polyamic acid and poly(hydroxyamide-amic acid) precursors were soluble in various polar solvents such as NMP, DMAC, DMF, and THF at room temperature. Following cyclization, these polymer precursors were converted to polyimide, poly(benzoxazole imide), and poly(benzoxazole amide imide) by thermal imidization. The polyimides **2a** and
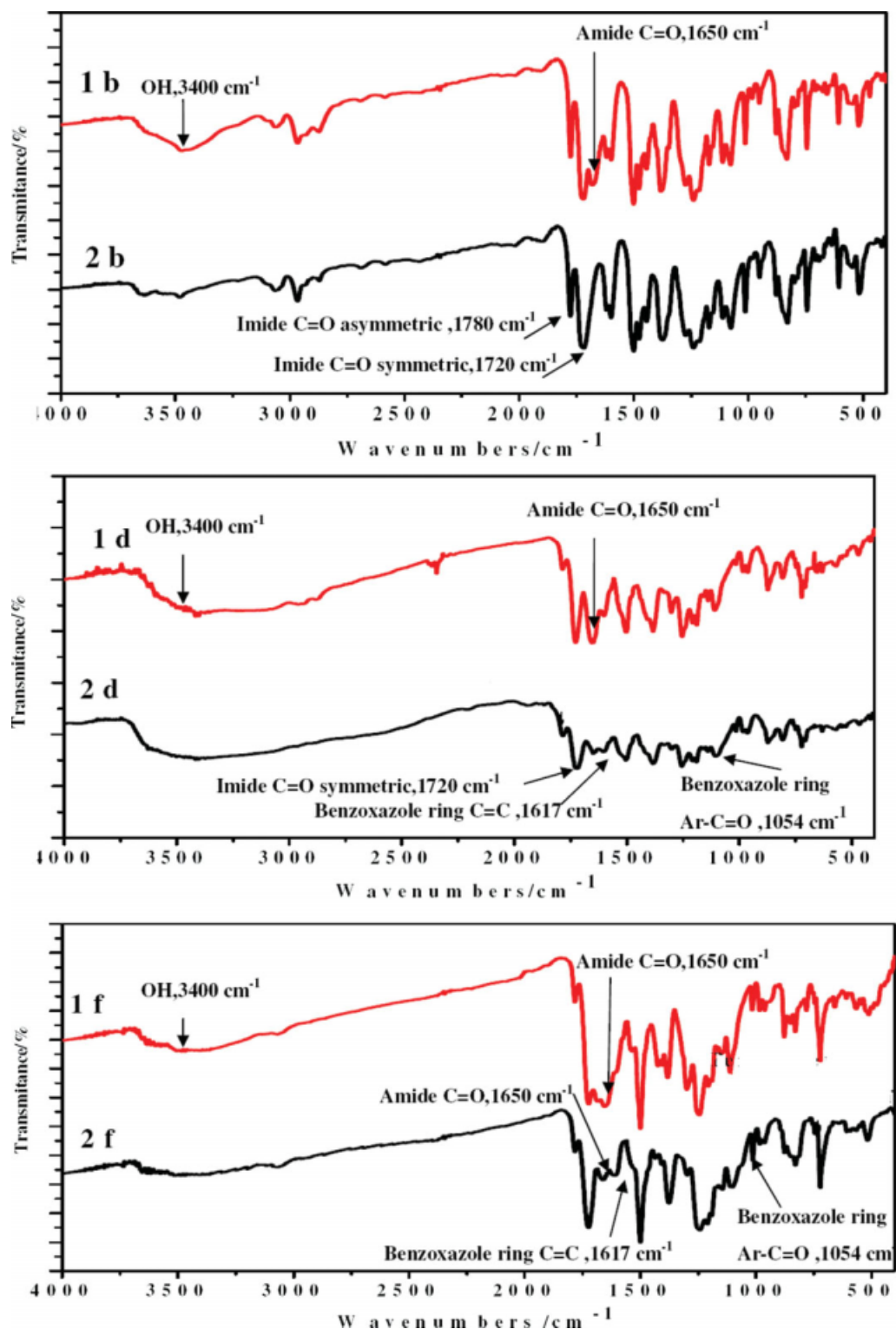
Figure 2 FTIR spectra of the FTIR of the 6FDA-derived polymer. [Color figure can be viewed in the online issue which is available at www.interscience.wiley.com.]

2b may have swollen in polar solvents such as NMP, DMAC, and DMF, but the poly(benzoxazole imide) and poly(benzoxazole amide imide) copolymers did not dissolve in any organic solvents. The introduction of the rigid benzoxazole group into the backbone of co-polymer markedly improved the chemical resistance.

Thermal properties of polymers

Table IV summarizes the thermal properties of the polymers. The thermal stability of the polymer was evaluated by TGA at a heating rate of 20°C/min in air and a nitrogen atmosphere. The 5% weight loss

Figure 3 ^{13}C-NMR spectra of IPDA-derived polymer **2c** and **2e**.

temperatures of (T_5) of the IPDA-derived polymers were in the range of 403–530°C in air, and 425–539°C in nitrogen. The chard yields of IPDA-derived polymer were in the range of 15–24% in air, and 55–60% in nitrogen. Figure 5 presents TGA of poly(benzoxazole imide) (**2c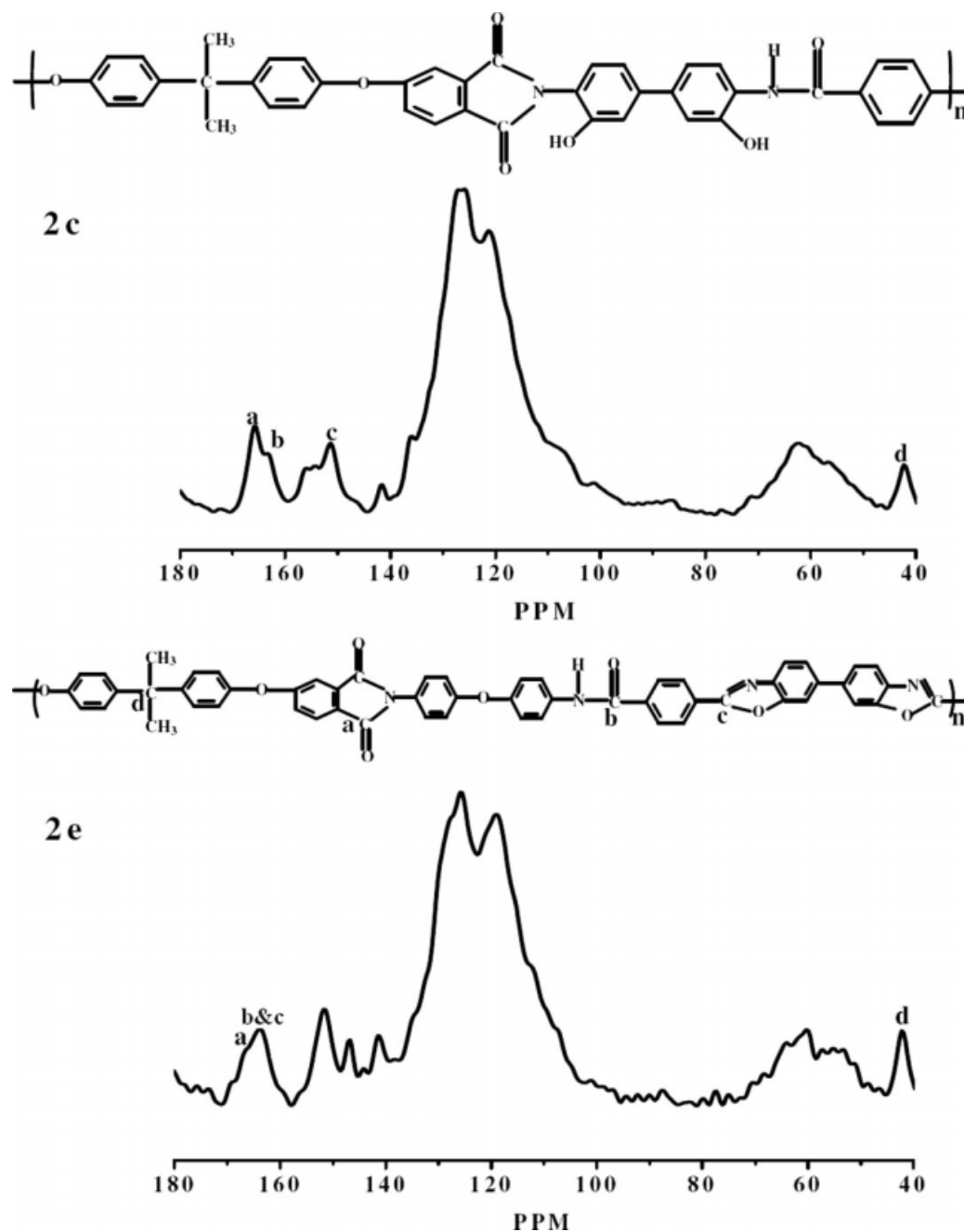**) indicated 23.2% weight loss occurred between 350 and 600°C, because hydroxyl imide was rearranged to form a carboxy-benzoxazole intermediate following the decarboxylation. Carbon dioxide was released above 350°C to form a fully aromatic benzoxazole film.[12] Changes of structures of hydroxyl-imide to benzoxazole by thermal conversion

are illustrated in Scheme 5. The 5% weight loss temperatures (T_5) of 6FDA-derived polymers were in the range of 412–508°C in air and 427–508°C in nitrogen. Figure 5 indicates the chard yield of the 6FDA-derived polymer was in the range 20–25% in air, and 54–61% in nitrogen. The weight loss of 6FDA poly(benzoxazole imide) (**2d**) was 22.3% between 350 and 600°C, because carbon dioxide was released to form the benzoxazole group in the polymer backbone. The chard yields of these novel heterocyclic aromatic polymers exceeded 50% in nitrogen. The introduction of the highly thermally stable benzoxazole group was
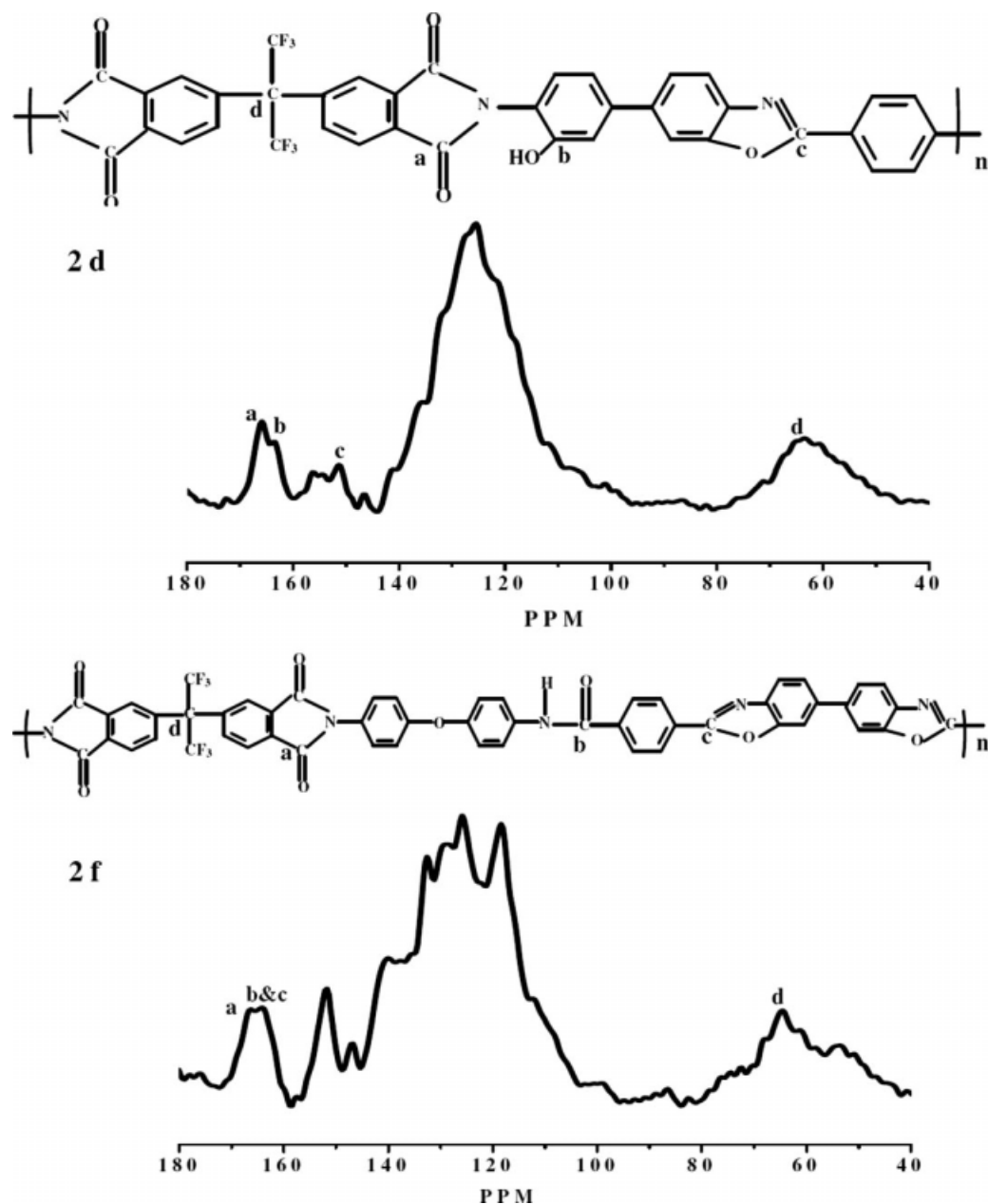
Figure 4 ^{13}C-NMR spectra of IPDA-derived polymer **2c** and **2e**.

TABLE III
Solubility of Poly(amic acid hydroxyamides) and Poly(benzoxazoles)

| Solvent | IPDA-derived polymer | | | | | | 6FDA-derived polymer | | | | | |
	1a	2a	1c	2c	1e	2e	1b	2b	1d	2d	1f	2f
NMP	+	*	+	−	+	−	+	*	+	−	+	−
DMAC	+	*	+	−	+	−	+	*	+	−	+	−
DMF	+	*	+	−	+	−	+	*	+	−	+	−
THF	+	−	+	−	+	−	+	−	+	−	+	−

+, soluble; −, insoluble; *, swelling
NMP, *N*-methyl-2-pyrrolidone; DMAC, dimethylacteamide; THF, tetrahydrofuran; DMF, dimethylformamide.

TABLE IV
Thermal Properties of Poly(benzoxazole imides)

Polymer	CTE[a] (ppm/°C)	T_g[b] (°C)	T_d[c] 5% loss (°C)		Chard yield[d] (%)	
			In air	In N_2	In air	In N_2
2a	74	255	530	539	24	55
2c	42	358	403	425	19	57
2e	53	336	448	454	15	60
2b	73	306	508	508	21	54
2d	36	374	412	427	25	58
2f	52	353	440	460	20	61

[a] **2a–2f** measured in the temperature range of 150–250°C by TMA.
[b] Determined by TMA at a heating rate of 10°C/min.
[c] T_d = 5% weight loss, as determined by TGA at a heating rate of 20°C/min.
[d] Chard yield, as determined by TGA at a heating rate of 20°C/min to 800°C.

introduced to the polymer backbone, which will increase the char yield of polymer. The TGA data show that these polymers possess high thermo-oxidative stability. Table IV presents the results of the thermal mechanical analysis (TMA) of these cured polymer films. The T_g and in-plane CTE of the IPDA-derived polymers were tested, which are in the range of 255–358°C and 42–74 ppm/°C, respectively. Figure 6
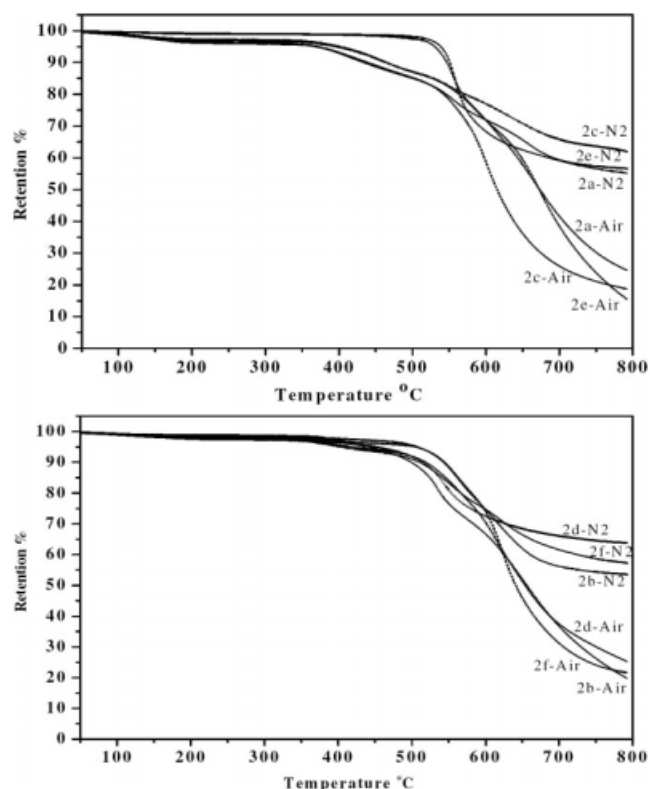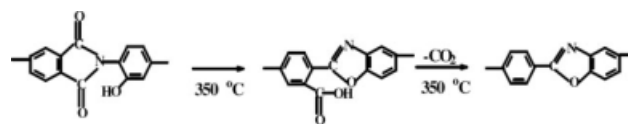
Scheme 5 Scheme of hydroxyl-imide to benzoxazole by thermal conversion.

presents Poly(benzoxazole imide) (**2c**) and poly(benzoxazole amide imide) (**2e**) contain rigid benzoxazole group in the backbone, which show higher T_g and lower CTE than those of polyimide (**2a**). The chain rigidity was increased due to the formation of benzoxazole ring in polymer main chain. The T_g and in-plane CTE of the 6FDA-derived polymers were in the range of 306–374°C and 36–73 ppm/°C, respectively. Owing to the same reason, poly (benzoxazole imide) (**2d**) and poly(benzoxazole amide imide) (**2f**) contain rigid benzoxazole group in backbone, which will possess higher T_g and lower CTE than those of polyimide (**2b**). The IPDA-derived polymer showed lower T_g value than that of 6FDA-derived polymer due to the presence of the flexible isopropylidine linkage.

Mechanical properties of polymers

Table V presents the mechanical properties of the polymer films with various chemical structures. Two

Figure 5 TGA curves for the poly(benzoxazole amide imide) and poly(benzoxazole imide) at a heating rate of 20°C/min in nitrogen and air.
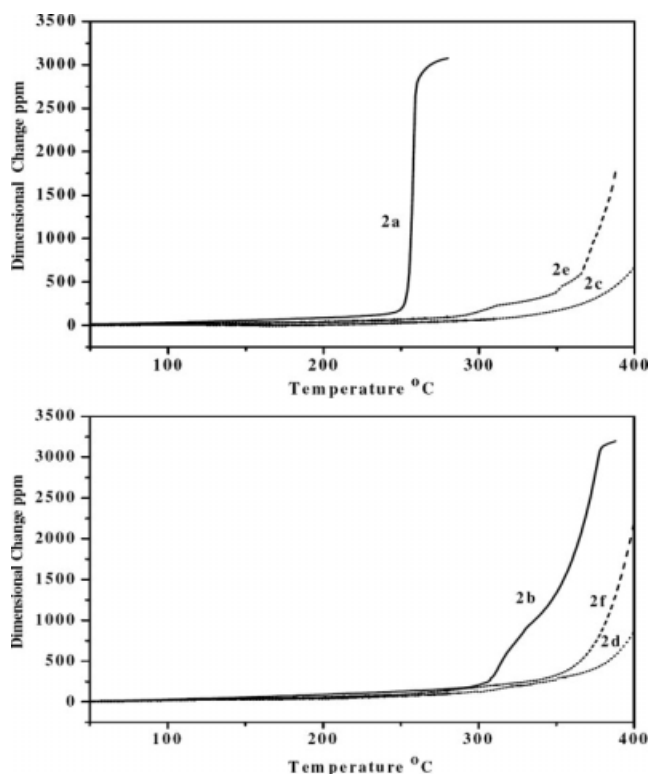
Figure 6 TMA curves for the poly(benzoxazole amide imide) and poly(benzoxazole imide) at a heating rate of 10°C/min in nitrogen and air.

TABLE V
Mechanical Properties of Poly(benzoxazole imides)

Polymer	Imide content (%)	Benzoxazole content (%)	Amide content (%)	Tensile strength[a] (MPa)	Elongation at break[a] (%)	Tensile modulus[a] (GPa)
2a	100			92	11.3	1.7
2c	50	50		112	8.3	2.1
2e	33.3	33.3	33.3	103	9.2	1.9
2b	100			97	12.2	1.9
2d	50	50		124	7.6	2.3
2f	33.3	33.3	33.3	111	10.2	2.0

[a] Determined from stress–strain curves by Huang Ta tensile strength tester.

series of IPDA and 6FDA-derived polymers show good mechanical properties. The tensile strength and tensile modulus of IPDA-derived polymer were in the ranges of 92–112 MPa and 1.7–2.1 GPa, respectively. The tensile strength of polyimide (**2a**) was 92 MPa; its tensile modulus was 1.7 GPa. Because about 33 mol % of the rigid benzoxazole group was introduced to the poly(benzoxazole amide imide) (**2e**) backbone, the tensile strength and tensile modulus of poly(benzoxazol amide imide) (**2e**) are 103 MPa and 1.9 GPa, which were higher than those of polyamide (**2a**). When the benzoxazole group content was increased to 50 mol % as in poly(benzoxazole imide) (**2c**), the tensile strength and the tensile modulus of poly(benzoxazol imide) are increased to 112 MPa and 2.1 GPa, which were higher than those of polyimide (**2a**) by 20%. The chain rigidity was increased due to the formation of benzoxazole ring in the polymer main chain, such that the tensile strength and modulus of the polymer increased. The tensile strength and tensile modulus of the 6FDA-derived polymer were in the ranges 97–124 and 1.9–2.3 MPa, respectively. Poly(benzoxazole imide) (**2d**) and poly(benzoxazole amide imide) (**2f**), whose backbone contains a rigid benzoxazole group, have a higher tensile strength and tensile modulus than those of polyimide **2b**. The IPDA-derived polymer showed lower tensile strength and tensile modulus value than those of 6FDA-derived polymer because the IPDA-derived polymers possess flexible isopropylidine linkage.

Dielectric property of the polymers

Table VI presents the dielectric constants of various polyimide and polybenzoxazole polymer films. The dielectric constants of the IPDA-derived polymer at 1 MHz are in the range of 3.45–3.73. The dielectric constant of polyimide polymer **2a** is 3.52. When the benzoxazole group content was increased to 50 mol %, as in poly(benzoxazol imide) (**2c**), the dielectric constant of poly(benzoxazol imide) was lower than that of polyimide **2a**. Benzoxazole does not contain polar car-

bonyl groups, which have a lower Dk than that of polyimide. The Dk of poly(benzoxazole imide) (**2c**) is 3.45, which is lower than that of polyimide **2a** (3.52) with similar chemical structure. When the nonpolar benzoxazole group was introduced to the polymer backbone, the Dk will be lower. The Dk of poly(benzoxazole amide imide) (**2e**) is 3.73, which is higher than that of polyimide **2a** (3.52). The polar amide group was introduced to the polymer backbone, which will increase the Dk. The dielectric constants of 6FDA-derived polymers were in the range of 3.25–3.52. Poly(benzoxazole imide) (**2d**) has higher benzoxazole group content in backbone, which shows lower dielectric constant 3.25 than those of polyimide polymer **2b** (3.31). From these data, one can see that the fluorinated polyimide **2b**, poly(benzoxazole imide) (**2d**), and poly(benzoxazole amide imide) (**2f**) show lower dielectric constants than those of the corresponding nonfluorinated polyimide (**2a**), poly(benzoxazole imide) (**2c**), and poly(benzoxazole amide imide) (**2e**). The drop in the dielectric constants of fluorinated polymer might be attributed to the presence of bulky CF_3 group. The strong electronegativity of fluorine causes low polarizability of C—F bond; consequently, the free volume will be increased. These effects may reduce the dielectric constant of the polymer.

CONCLUSION

Two series of heterocyclic polymers with rigid benzoxazole group in polymer backbone have been

TABLE VI
Electrical Properties of Poly(benzoxazole imides)

Polymer	Dielectrical constant 1 MHz (dry)
	Dk
2a	3.52
2c	3.45
2e	3.73
2b	3.31
2d	3.25
2f	3.52

synthesized from IPDA and 6FDA with HBA and TACl by the two-step method. These benzoxazole groups contained polymers that were insoluble in organic polar solvent and exhibited better chemical resistance than neat polyimide. These polymers also showed good thermal stability, where the T_gs are between 285 and 376°C. The thermal degradation temperatures of these polymers of 5% weight loss were above 400°C in air, and above 440°C in nitrogen atmosphere. These polymers showed low CTE between 36 and 76 ppm. These polymers also possess extremely good mechanical properties; the tensile strengths are in the range of 92–124 MPa and tensile modulus is in the range of 1.7–2.3 GPa. By introducing the rigid-rod benzoxazole group into the polymer, the thermal properties, T_gs and CTE, and the mechanical properties, tensile strength and tensile modulus, were also enhanced significantly.

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