

Synthesis and Characterization of Novel Aromatic Condensation Polymers Containing Rigid Benzoxazole Pendent Groups

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Received 8 July 2003; accepted 13 October 2003

ABSTRACT: A new aromatic diamine monomer containing benzoxazole substituents was prepared by a multistep synthesis starting from 1,4-dibromo-2,5-difluorobenzene. The diamine was polymerized with commercial aromatic dianhydride or dicarboxylic acid chloride monomers to provide several different poly(amic acid)s and polyamides with their inherent viscosities in the range of 0.24–0.46 dL/g.

Thermal properties of these polymers including thermal imidization of poly(amic acid)s into polyimides were investigated by using FTIR, DSC, and TGA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 178–185, 2004

Key words: polycondensation; polyamides; polyimides; benzoxazole group; thermal properties

INTRODUCTION

The production of thermally stable organic polymers has been the subject of many research efforts for the past 30 years because of the growing application of thermally stable polymers in the fields of aerospace and electronics.^{1–3} Most of the thermally stable polymers synthesized are aromatic, rigid-rod-type polymers that have difficulties in processing because of their low solubility and high glass transition or melting temperatures. Therefore, compromises have been necessary between thermal stability and processibility. A common approach has been to synthesize a flexible soluble precursor, which upon subsequent heat treatment cyclizes intramolecularly to produce the final thermally stable, rigid polymers. A condensation-type polyimide (e.g., Kapton by DuPont) is a familiar and successfully applied example of this approach and one of the most important materials among polymers for electronic applications.^{4–7} Another general approach includes the incorporation of flexible linkage and/or *meta*-catenated structure instead of *para*- to obtain lower glass transition temperature and enhanced solubility characteristics.

Recently, we studied the synthesis of novel monomer and polymers, especially where rigid benzoxazole

groups are bilaterally attached to the aromatic backbone. The lateral benzoxazole moiety should improve the thermal stability with an increase of glass transition temperature of the polymers and also push the neighboring polymer chain apart, leading to amorphous or lowered crystallinity due to the less packed structure. In our previous work, we have synthesized novel aryl 1,4-dihalide monomers substituted with two benzoxazole group attached at *ortho*-position (2,5-) to halogen atom and studied their reactivity on the nucleophilic aromatic substitution (S_NAr) or Ullmann condensation reaction.^{8–10} The above aryl difluoride compound has been proven to sufficiently possess high reactivity for the nucleophilic displacement reaction by phenolate or thiophenolate with an almost quantitative conversion. Also, the difunctional compound could be used successfully as a monomer for the synthesis of various poly(arylene ether)s and poly(arylene sulfide)s.

In this study, we synthesized a novel diamine monomer by reacting benzoxazole-substituted aryl difluoride compound with 4-aminophenolate in *N,N*-dimethylacetamide (DMAc). The synthesis and characterization of two different types of condensation polymers [i.e., poly(amic acid)s and polyamides] from this new monomer are discussed.

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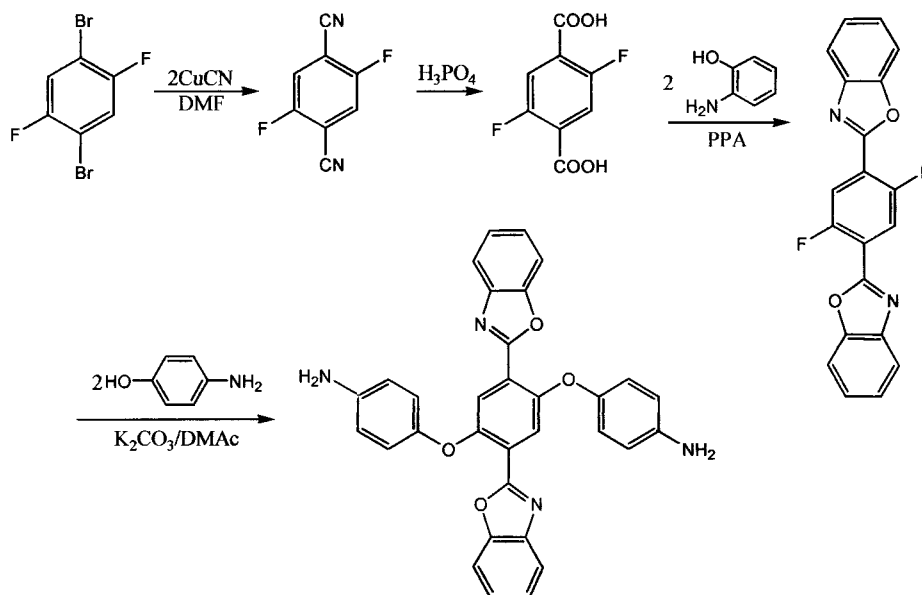
Contract grant sponsor: Brain Korea 21 Project in 2003.

Contract grant sponsor: MOCIE; contract grant number: B62-A08-5406-03-2-3.

EXPERIMENTAL

Chemicals and measurements

1,4-Dibromo-2,5-difluorobenzene (98%) was purchased from Fluorochem (United Kingdom).



Scheme 1 Synthesis of 1,4-bis(4-aminophenoxy)-2,5-bis(2-benzoxazolyl)benzene (AP4BOX).

2-Aminophenol and 4-aminophenol were purchased from Aldrich and sublimed before use. Cuprous cyanide (99%) and potassium carbonate (99.5%) were purchased from Aldrich and used as received. Ferric chloride (97%) and polyphosphoric acid (115%) were purchased from Kokusan Chemicals (Korea). Several dianhydride monomers including 1,2,4,5-benzenetetracarboxylic dianhydride (pyromellitic dianhydride; PMDA, 97%), 4,4'-oxydiphthalic dianhydride (ODPA, 97%), and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99%), and also terephthaloyl chloride (TPC) were purchased from Aldrich and purified by sublimation. Isophthaloyl chloride (IPC) from Aldrich was distilled under reduced pressure before use. Sebacyl chloride (SC, 99%) was purchased from Aldrich and used as received. *N,N*-dimethylformamide (DMF), DMAc (purchased from Aldrich), and 1-methyl-2-pyrrolidinone (NMP) were dried over CaH_2 , and freshly distilled before use.

Infrared spectra were obtained on a Perkin-Elmer FTIR spectrometer (Model Spectrum 2000). ^1H - and ^{13}C -NMR spectra were taken on a Varian Unity Inova 500 MHz spectrometer. Thermal analysis was carried out on a Perkin-Elmer DSC/TGA7 series thermal analysis system at a heating rate of 10 deg/min under nitrogen. Viscosities of the polymer solutions were measured in an Ubbelohde capillary viscometer at 25°C.

Synthesis of 1,4-bis(4-aminophenoxy)-2,5-bis(2-benzoxazolyl)benzene (AP4BOX)

Aromatic diamine monomer, AP4BOX, was synthesized by multistep reaction as shown in Scheme 1. 1,4-Bis(2-benzoxazolyl)-2,5-difluorobenzene(BOF)

was prepared by poly(phosphoric acid) (PPA) catalyzed condensation reaction between 2-aminophenol and 2,5-difluoroterephthalic acid. 2,5-Difluoroterephthalic acid was prepared by acid hydrolysis of 2,5-difluoroterephthalonitrile, which was derived by bromine substitution of 1,4-dibromo-2,5-difluorobenzene using CuCN in DMF. The detailed procedure for the BOF synthesis was reported in our previous communication.⁸ Final AP4BOX monomer was synthesized by nucleophilic displacement reaction between BOF and 4-aminophenolate that was formed *in situ* in DMAc by treating 4-aminophenol with potassium carbonate. A typical procedure for this last step of reaction was described as follows: Into the three-necked flask equipped with Dean-Stark trap, nitrogen inlet,

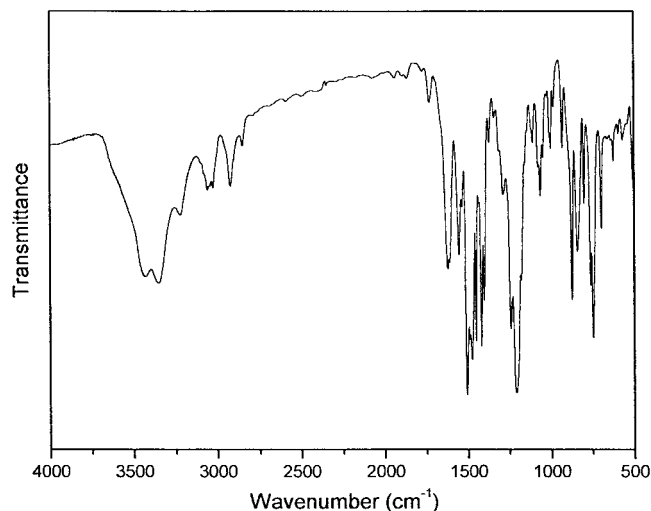


Figure 1 FTIR spectrum of diamine monomer (AP4BOX).

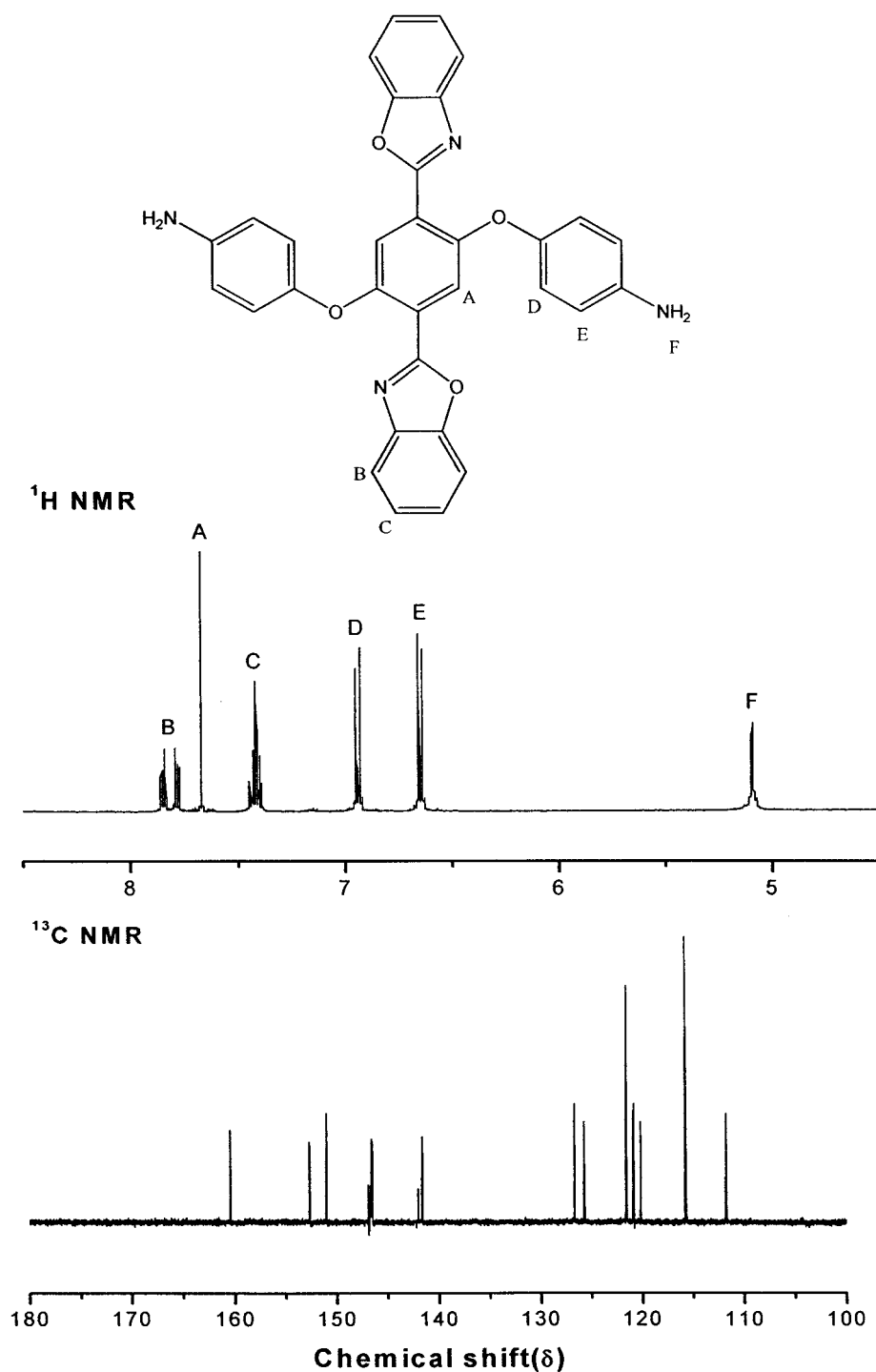
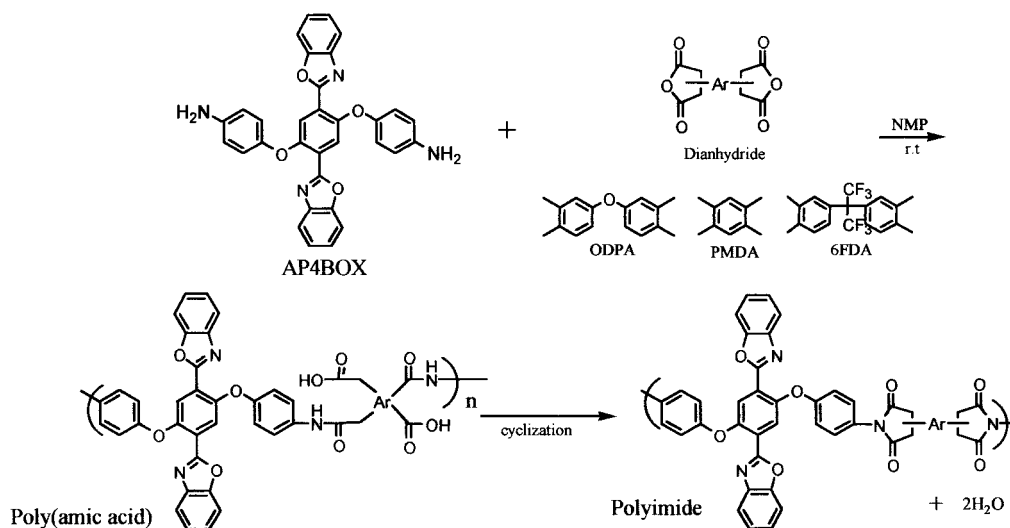


Figure 2 ^1H - and ^{13}C -NMR spectra of diamine monomer (AP4BOX).

and condenser, 4-aminophenol (0.6423 g, 5.886 mmol) and equimolar K_2CO_3 were added and dissolved in DMAc. Then, 10 mL toluene was added. The reaction mixture was heated to 140°C and stirred for 6 h to distill-off toluene as an azeotropic mixture to remove water completely. The reaction bath was then cooled to about 80°C , and BOF (1 g, 2.871 mmol) was added in solid with an additional 5 mL DMAc. The reaction

mixture was stirred for about 20 h at a controlled temperature between 150 and 155°C . The resulting solution was poured into a large amount of distilled water. The precipitated powder was filtered and washed repeatedly with water and methanol before being dried under vacuum over P_2O_5 for several days. Yield, 1.4 g (92%). m.p., 350.5°C (by DSC), IR 3352 (NH), 2925, 1729, 1603 (C=N), 1558, 1505, 1423, 1248, 1208 (C—



Scheme 2 Synthesis of poly(amic acid)s from AP4BOX.

O—C), 875, 747 cm^{-1} . $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): 7.84 (d, 2H), 7.79 (d, 2H), 7.67 (s, 2H), 7.42 (m, 4H), 6.94 (d, 4H), 6.66 (d, 4H), 5.20 (NH_2) ppm. $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$): 160.40, 152.65, 150.99, 146.60, 146.50, 141.65, 126.68, 125.70, 121.54, 120.89, 120.81, 120.13, 115.75, 111.78 ppm. ANAL. calcd for $\text{C}_{32}\text{H}_{22}\text{N}_4\text{O}_4$: C, 72.99; H, 4.21; N, 10.64. Found: C, 71.82; H, 4.14; N, 10.56.

Synthesis of poly(amic acid)s

A typical procedure for the synthesis of poly(amic acid) is described below: Into the 100-mL three-necked flask equipped with condenser, nitrogen inlet, and magnetic stirrer, 0.7406 g (1.4065 mmol) of AP4BOX was added and dissolved completely in 14 mL NMP. The flask was placed in a water bath chilled with ice; then 0.4363 g (1.4065 mmol) of ODPA was added with an additional 3 mL NMP. The reaction mixture was stirred for 20 h under nitrogen flow at a temperature of about 10°C. The resulting viscous solution was precipitated into 300 mL water. The powder was filtered, washed several times with water, and then dried under vacuum over P_2O_5 at 80°C for several

days. Yield: 1.07 g (91%). The other poly(amic acids) from different dianhydride monomers have also been prepared by using the same procedure.

Synthesis of polyamides

A typical procedure for the synthesis of a polyamide is described below: Into the 100-mL three-necked flask equipped with condenser, nitrogen inlet, and magnetic stirrer, 0.8313 g (1.5788 mmol) of AP4BOX was added and dissolved completely with 2 equiv TEA in 15 mL NMP, including 5 wt % LiCl. The flask was placed in a water bath chilled with ice, and then 0.3205 g (1.5788 mmol) terephthaloyl chloride (or isophthaloyl chloride or sebacoyl chloride) was added with an additional 5 mL NMP under nitrogen. The reaction mixture was stirred for 20 h under nitrogen flow at room temperature (about 20°C). The resulting viscous solution was precipitated into 300 mL water. The powder was filtered, washed several times with water and methanol, and then dried under vacuum over P_2O_5 at 80°C for 2 days. Yield: 1.03 g (99%).

TABLE I
Results of Polymerization and Thermal Properties of Poly(amic acid)s

	Yield (%)	$\eta_{\text{inh}}^{\text{a}}$ (dL/g)	$T_{\text{imid}}^{\text{b}}$ (°C)	After curing (polyimide)		
				T_{g}^{c} (°C)	$T_{5\%}^{\text{d}}$ (°C)	Char Yield ^e (%)
AP4BOX-PMDA	87.5	0.46	223~285	—	502	50.2
AP4BOX-6FDA	91.3	0.43	225~280	294	512	55.0
AP4BOX-ODPA	91.0	0.31	218~261	267	533	56.5

^a Measured with 0.5 g/dL in DMAc at 25°C

^b Temperature range of imidization endotherm measured by DSC (weak and broad)

^c T_{g} observed by DSC 2nd scan after first scan to 400°C

^d Temperature of 5% weight loss

^e Residual weight % at 800°C in N_2

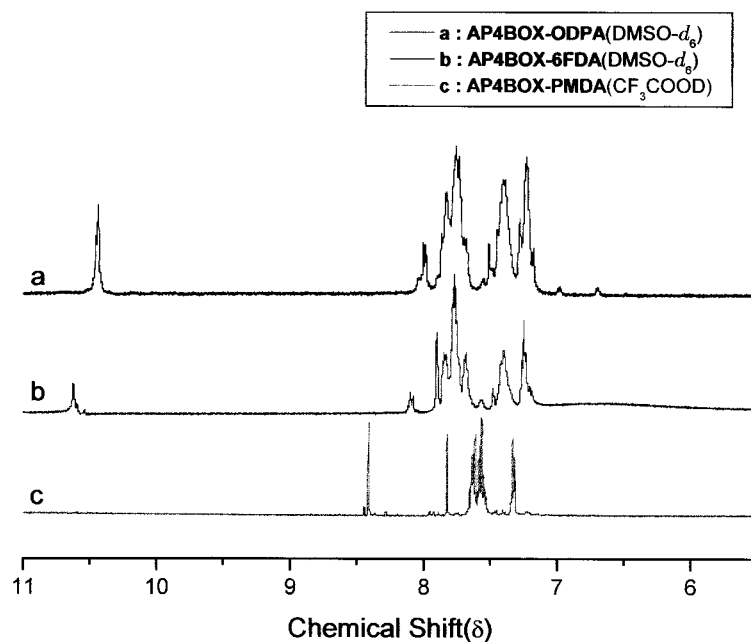


Figure 3 $^1\text{H-NMR}$ spectra of poly(amic acids).

RESULTS AND DISCUSSION

Synthesis of aromatic diamine monomer containing benzoxazole pendent groups

A new aromatic diamine monomer, AP4BOX, was synthesized by multistep reactions, as shown in Scheme 1. In our previous study, it was demonstrated that two bilaterally substituted benzoxazolyl groups, possessing strong electron-withdrawing effect, functioned effectively as an activating group for nucleophilic aromatic displacement reaction of fluoride positioned ortho to the benzoxazole group. The reaction

proceeded clean at rather mild reaction conditions in DMAc by using phenolate or thiophenolate nucleophilic reagent to give the expected substitution product almost quantitatively.^{7,8} Here, the same reaction was employed to synthesize AP4BOX monomer under controlled reaction temperature in nitrogen atmosphere. The substitution reaction was found to proceed clean again, and the desired product could be separated in pure form as analyzed by thin-layer chromatography and $^1\text{H-NMR}$ spectroscopy. The FTIR, NMR ($^1\text{H-}$ and $^{13}\text{C-}$) spectra of the monomer are

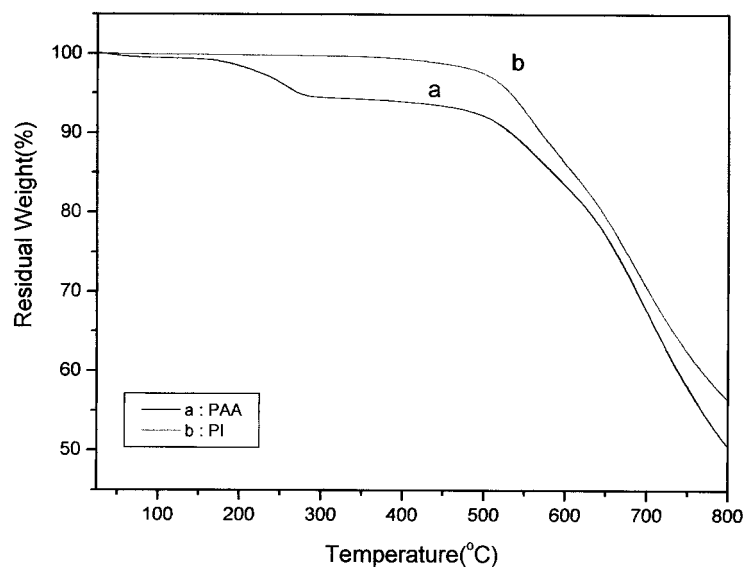


Figure 4 Typical TGA thermograms of poly(amic acid), AP4BOX-PMDA, before and after imidization curing.

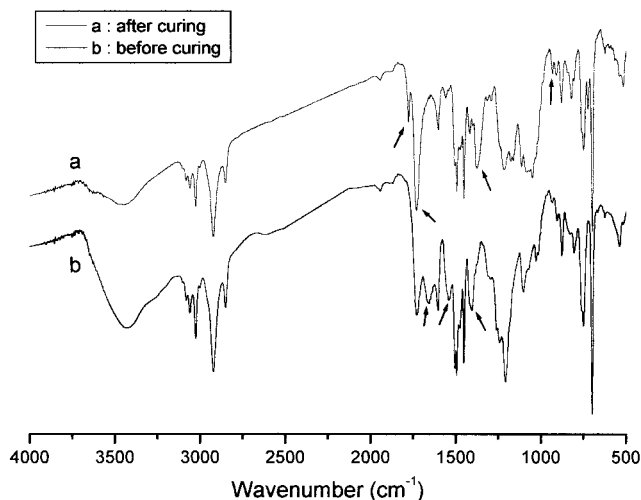


Figure 5 FTIR spectral change upon imidization curing (sample: AP4BOX-6FDA).

shown in Figures 1 and 2, respectively. From the IR analysis, the characteristic absorption band of NH stretching at 3352 cm^{-1} , and aromatic C—O—C at 1208 cm^{-1} , were observed. $^1\text{H-NMR}$ spectrum showed amine (NH_2) protons at 5.2 ppm, and all the aromatic protons at 6.6–7.8 ppm were matched well with the structure. In addition, the $^{13}\text{C-NMR}$ spectrum showed all of the 14 different carbon atoms expected for the monomer's structure.

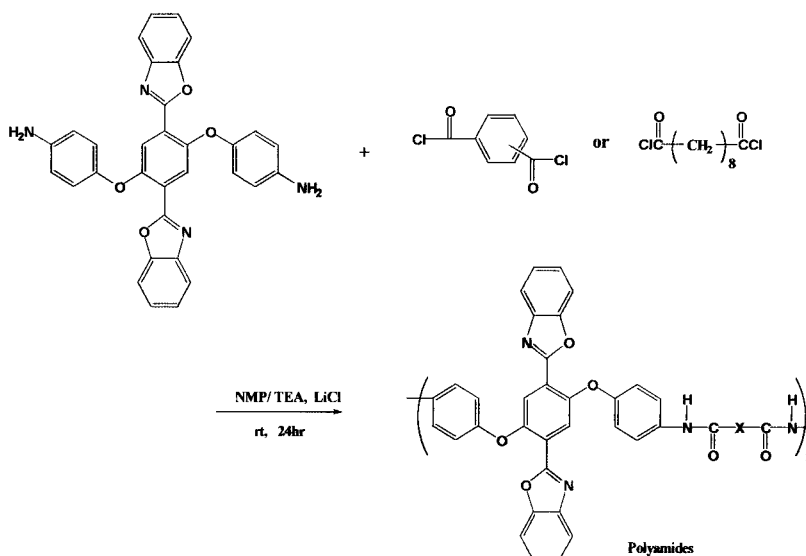
Synthesis and characterization of poly(amic acid)s

Poly(amic acid)s were prepared by low-temperature polycondensation between the diamine monomer (AP4BOX) and three different dianhydrides in NMP (Scheme 2). The polymerization reaction yield was

88–91%, and the inherent viscosity values were in the range of 0.32–0.46 dL/g (measured in DMAc at the concentration of 0.5 g/dL). The polymerization results together with their thermal data (to be discussed later) are presented in Table I. Poly(amic acid) from 6-FDA could be cast into a flexible light-brown film, but, the others were brittle. The $^1\text{H-NMR}$ spectra of the prepared poly(amic acid)s are shown in Figure 3. Aromatic protons appeared at 7.2–8.5 ppm, and NH protons of amide groups appeared at around 10.6 ppm. IR spectra of the polymers showed similar characteristic amide and carboxylic acid absorption bands at 1657, 1540, and 1407 cm^{-1} in all polymers.

Thermal cyclization into polyimides

Thermal imidization curing of poly(amic acid)s was monitored by DSC, TGA, and FTIR measurements. DSC thermograms of different poly(amic acid)s exhibited the imidization endotherms in a broad temperature range between 200 and 280°C . For the polymer samples obtained from ODPA and 6FDA, the glass transitions of the cured polyimides were observed weakly at 267 and 294°C , respectively, from the second heating after the first scan to 400°C . Typical TGA thermograms of the poly(amic acid) (AP4BOX-PMDA) are shown in Figure 4. The first weight loss at the temperature range of $200\text{--}260^\circ\text{C}$ represents the water release accompanying imidization process with the value of about 4.5 wt %, matching closely with the theoretical value (4.4 wt %). The cured polyimide remained stable up to about 500°C before decomposition. The rescan curve after the first heating to 300°C is shown as a dotted line. The TGA curves of different poly(amic acids) samples, after imidization by simple dynamic heating to 400°C at a heating rate of $10^\circ\text{C}/$



Scheme 3 Synthesis of polyamides from AP4BOX.

TABLE II
Results of Polymerization and Thermal Properties of Polyamides

	Yield (%)	η_{inh}^a (dL/g)	T_g^b (°C)	T_c^c (°C)	$T_{5\%}^d$ (°C)	Char Yield ^e (%)
AP4BOX-TPC	98.1	0.45	—	289	464	41.1
AP4BOX-IPC	96.3	0.31	242	—	430	49.6
AP4BOX-SC	91.5	0.24	179	300–350 (T_m^{395})	429	35.2

^a Measured with 0.5 g/dL in H₂SO₄ at 25°C

^b T_g observed by DSC 1st scan

^c T_c crystallization endotherm

^d Temperature of 5% weight loss

^e Residual weight % at 800°C in N₂

min under nitrogen, showed the decomposition onsets at 470–500°C, and the residual weights at 800°C were in the range of 53–56 wt % under nitrogen. The structural changes during the imidization were observed by FTIR (Fig. 5). The absorption bands of amide groups at 1662, 1539, and 1416 cm⁻¹ disappeared after curing, and the characteristic imide absorption bands at 1780 and 1732 cm⁻¹ (C=O asymmetric and symmetric stretching), 1368 cm⁻¹ (C–N stretching), and 836 cm⁻¹ (C=O bending) were observed, suggesting the structural conversion from amide acids to the corresponding imides.

Synthesis and characterization of polyamides with benzoxazole pendants

Two aromatic acid chlorides (i.e., terephthaloyl and isophthaloyl chloride) and an aliphatic sebacoyl chloride were used for the preparation of polyamides (Scheme 3). The polymerization results together with their thermal data are presented in Table II. Polyamide from terephthaloyl chloride showed crystallization exotherm at around 289°C, but the glass transition was not observed by DSC. Instead, the polymer from isophthaloyl chloride showed only glass transition at 242°C. Polyamide from aliphatic sebacoyl chloride exhibited glass transition at 179°C and, interestingly, broad crystallization exotherm at 300–350°C with the following strong melting endothermic peak at 395°C. These polymers possessed good thermal stability, showing no weight loss up to 400°C in both air and nitrogen. The ¹H-NMR spectra of the prepared polyamides are shown in Figure 6. Aromatic protons appeared at 7.2–8.5 ppm, but we do not observe the NH protons of the amide groups because of exchange with the acidic solvent (trifluoroacetic acid-*d*). In Figure 6(c), additional signals of the aliphatic protons of the sebacoyl moiety appear at 2.85, 2.01, and 1.59 ppm, respectively. IR spectra of the polymers showed characteristic amide absorption bands similarly at 1657, 1540, and 1407 cm⁻¹, and also strong C–O–C absorptions at 1240 cm⁻¹.

The results of the solubility test on both poly(amic acids) and polyamides are shown in Table III. Poly(amic acids) containing more flexible linkages such as those from ODPa and 6FDA were soluble in polar aprotic

solvents, including DMF, DMAc, NMP, DMSO, and pyridine. Poly(amic acid) from PMDA, however, was soluble only in NMP, suggesting limited solubility due to a rather rigid chain structure. The cured polyimides were mostly insoluble in common organic solvents, including those mentioned above.

Polyamide samples showed rather different solubility in various solvents according to the different monomers. As expected, polymers from isophthaloyl chloride and sebacoyl chloride showed better solubility, dissolving in some polar organic solvents, which are compared to the very limited solubility of polymer from terephthaloyl chloride, only soluble in strong acids.

CONCLUSION

A new aromatic diamine monomer containing bilaterally substituted benzoxazole groups was synthesized and used for typical condensation polymerizations with commercially available aromatic dianhydride or dicarboxylic acid chloride monomers to provide sev-

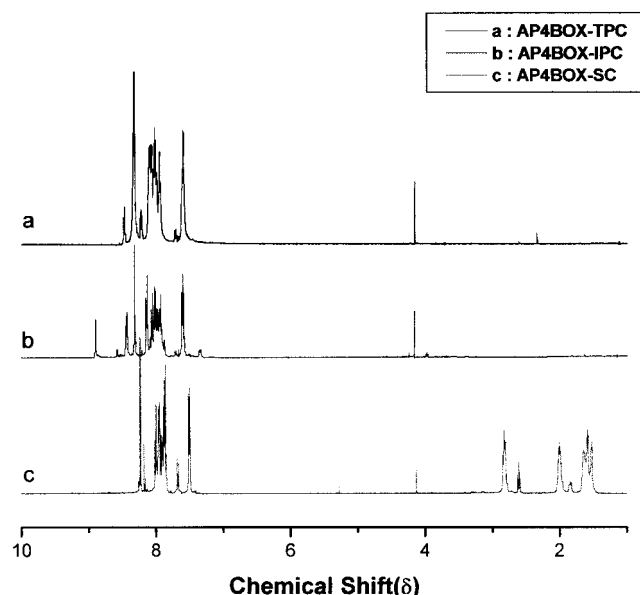


Figure 6 ¹H-NMR spectra of polyamides.

TABLE III
Solubility of Poly(amic acid)s and Polyamides

		NMP	DMAc	DMF	DMSO	Pyridine	m-Cresol	Acetone	TFAA	H ₂ SO ₄
PAA	PMDA	○	×	×	×	×	×	×	—	—
	6FDA	○	○	○	○	○	×	×	—	—
	ODPA	○	○	○	○	○	×	×	—	—
PA	TPC	×	×	×	×	×	×	×	○	○
	IPC	○	△	×	×	×	×	×	○	○
	SC	△	△	△	△	×	×	×	○	○

○: soluble, △: soluble by heating, ×: insoluble

eral different poly(amic acids) and polyamides. The polymers with their inherent viscosities in the range of 0.24–0.46 dL/g were separated and characterized on their thermal and solubility properties, including thermal imidization of poly(amic acid)s into polyimides.

This work was supported by the Brain Korea 21 Project in 2003 and also by a research grant from MOCIE (No. B62-A08-5406-03-2-3).

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