

Macromolecular Research

Volume 10, Number 5 October 31, 2002

© Copyright 2002 by The Polymer Society of Korea

Synthesis and Characterization of Poly(amic acid)s from a Novel Aromatic Diamine with Bilaterally Attached Benzoxazole Groups

Ji-Heung Kim* and Jae Kwan Lee

Department of Chemical Engineering, Center for Advanced Functional Polymers, Sungkyunkwan University, Korea

Young Jun Kim

Department of Textile Engineering, Center for Advanced Functional Polymers, Sungkyunkwan University, Korea

Jong Chan Won and Kil-Young Choi

Division of Advanced Materials, Korea Research Institute of Chemical Technology, Korea

Received May 16, 2002; Revised Aug. 22, 2002

Abstract : A new aromatic diamine monomer containing benzoxazole substituents was prepared by a multi-step synthesis starting from 1,4-dibromo-2,5-difluorobenzene. This bulky and disc-shaped monomer was polymerized with commercial dianhydride monomers to give several different poly(amic acid)s with their inherent viscosities in the range of 0.24-0.35 dL/g. The prepared polymers were soluble in typical polar aprotic solvents. Thermal imidization to the corresponding polyimides were investigated by using FT-IR, DSC and TGA.

Keywords : thermally stable polymers, polyimides, benzoxazole group.

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 thermally stable polymers synthesized are aromatic,

rigid-rod type polymers that have difficulties in processing due to their low solubility and high glass transition or melting temperatures. Therefore, compromises have been necessary between thermal stability and processability. 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 (eg. Kapton by Dupont) is a familiar and successfully applied example of this approach and one of the most important materials among polymers

*e-mail : kimjh@skku.ac.kr

1598-5032/10/241-05 © 2002 Polymer Society of Korea

for electronic applications.⁴⁻⁷

We have been studying on 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 and T_g of the polymers and also push the neighboring polymer chain apart, leading to amorphous or lower crystallinity due to less packed structure. Previously, 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 or Ullmann condensation reaction.⁸⁻¹⁰ Above aryl difluoride compound was proved to possess reactivity high enough for the nucleophilic displacement reaction toward 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 derived a novel diamine monomer by reacting benzoxazole-substituted aryl difluoride compound with aminophenolate in DMAc. The synthesis and characterization of both monomer and several poly(amic acid)s derived from it were discussed. Their thermal imidization behavior was also investigated by using FT-IR, DSC, and TGA.

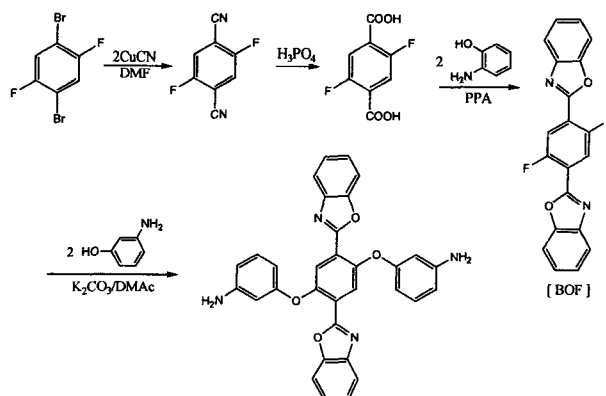
Experimental

Chemicals and Instruments. 1,4-Dibromo-2,5-difluorobenzene, 98%, was purchased from Fluorochem. 2-Aminophenol and 3-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 Chem. (Korea). Several dianhydride monomers including 1,2,4,5-benzene-tetracarboxylic dianhydride (pyromellitic dianhydride; PMDA), 97%, 4,4'-oxydiphthalic dianhydride (ODPA), 97%, 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPTA), 97%, and 4,4'-(hexafluoro isopropylidene)diphthalic anhydride (6FDA), 99%, were purchased from Aldrich, and purified by sublimation. *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidinone (NMP) were dried over CaH_2 and freshly distilled before use.

Infrared spectra were obtained on a Unicam 1000 FT-IR spectrometer. ^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. The molecular weight data were obtained by gel permeation chromatography (GPC, Waters) using DMF as eluent at a flow rate of

1 mL/min. Polystyrene standards were used to calibrate the molecular weight.

Synthesis of 1,4-bis(3-aminophenoxy)-2,5-bis(2-benzoxazolyl)benzene (AP3BOX). The aromatic diamine monomer, AP3BOX, was synthesized by multi-step reaction as shown in Scheme I. 1,4-Bis(2-benzoxazolyl)-2,5-difluorobenzene (BOF) was prepared by polyphosphoric 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. 2,5-Difluoroterephthalonitrile was prepared by bromine substitution of 1,4-dibromo-2,5-difluorobenzene using CuCN in DMF. BOF was purified by sublimation [melting point (DSC): 333.5 °C]. The detailed procedure for BOF synthesis was reported in our previous communication.⁸ The final AP3BOX monomer was synthesized by quantitative nucleophilic displacement reaction between BOF and 3-aminophenolate which was formed *in-situ* in DMAc by treating 3-aminophenol with potassium carbonate, as described in the following procedure; Into the three-necked flask equipped with Dean-Stark trap, nitrogen inlet, and condenser, 3-aminophenol (0.6423 g, 5.886 mmol) and equimolar K_2CO_3 were added and dissolved in DMAc. Then a 10 mL of 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 mol) was added in solid with additional 5 mL of DMAc. The reaction mixture was stirred for about 20 h at a controlled temperature between 150~155 °C. The resulting solution was poured into a large amount of distilled water. The precipitated powder was filtered and washed repeatedly with water before drying under vacuum over P_2O_5 for several days; m.p. 325 °C (by DSC), IR 3379 (NH), 2935, 1729, 1613 (C=N), 1490, 1453, 1248, 1197 (C-O-C), 753 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$) 7.84, 7.77, 7.42, 7.08, 6.38, 6.35, 6.33, 5.33 (-NH₂) ppm. ^{13}C NMR ($\text{DMSO}-d_6$) 160.3, 158.6, 151.8, 151.4, 142.1, 131.6, 127.3, 126.2, 123.0, 122.9, 121.3, 112.2, 111.1, 107.0, 105.0 ppm.



Scheme I

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, 0.8 g (1.1593 mmol) of AP3BOX was added and dissolved completely in 10 mL of NMP. The flask was placed in water bath chilled with ice, and then 0.4713 g (1.1593 mmol) of OPA was added with an additional 3 mL of NMP. The reaction mixture was stirred for 20 h under nitrogen flow at the temperature of about 10 °C. The resulting slightly viscous solution was precipitated into a 300 mL of water. The powder was filtered, washed several times with water and methanol, and then dried under vacuum over P₂O₅ at room temperature for several days. All the other poly(amic acid)s were also prepared using different dianhydrides according to the same procedure.

Results and Discussion

Synthesis of Aromatic Diamine Monomer Containing Benzoxazole Group. A new aromatic diamine monomer, AP3BOX, was synthesized by multi-step reaction shown in Scheme I. In our previous study, it was demonstrated that two bilaterally substituted benzoxazolyl group possessing strong electron-withdrawing effect functioned effectively as an activating group for the well-known nucleophilic aromatic displacement reaction of halide (fluoride or bromide) positioned ortho to the benzoxazole group. The reaction proceeded clean at mild reaction condition in DMAc using phenolate or thiophenolate nucleophilic reagent to give the substitution product quantitatively.^{7,8} Here the same reaction was employed to synthesize AP3BOX monomer under controlled reaction temperature in nitrogen atmosphere. The substitution reaction proceeded clean, and the expected product was separated in pure form as analyzed by thin layer chromatography and ¹H NMR spectroscopy. The IR, ¹H and ¹³C NMR spectra of the monomer are shown in Figures 1 and 2, respectively. From the IR analysis, the characteristic absorption band of NH stretching at 3400 cm⁻¹, and aromatic C-O-C at 1197 cm⁻¹ were observed. Also NMR spectra showed well-defined peaks matching well with the structure of monomer.

Synthesis and Characterization of Poly(amic acid)s. Poly(amic acid)s were prepared by condensation polymerization of the diamine monomer with several dianhydrides in NMP (Scheme II). The polymerization yields were 72~91%, and the inherent viscosity values were in the range of 0.24~0.35 dL/g (measured in DMAc at the concentration of 0.5 g/dL). It seems that purity and deviation from exact stoichiometry in the small scale reaction is responsible for such low-to-medium molecular weight. The polymerization results together with their thermal data (to be discussed later) are presented in Table I. The ¹H-NMR spectra of the prepared poly(amic acid)s are shown in Figure 3. Aromatic protons appeared at 6.9~8.2 ppm, and NH

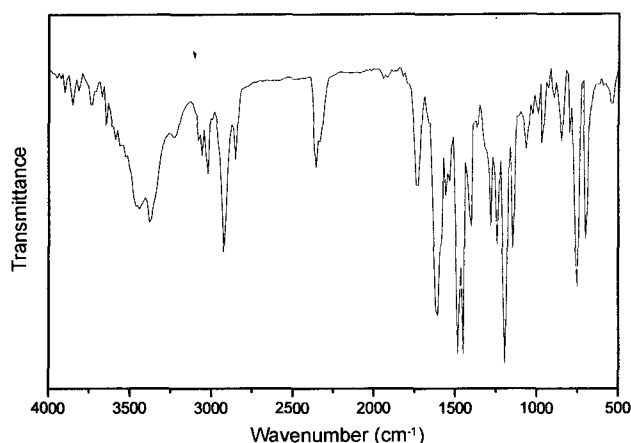


Figure 1. FT-IR spectrum of diamine monomer (AP3BOX).

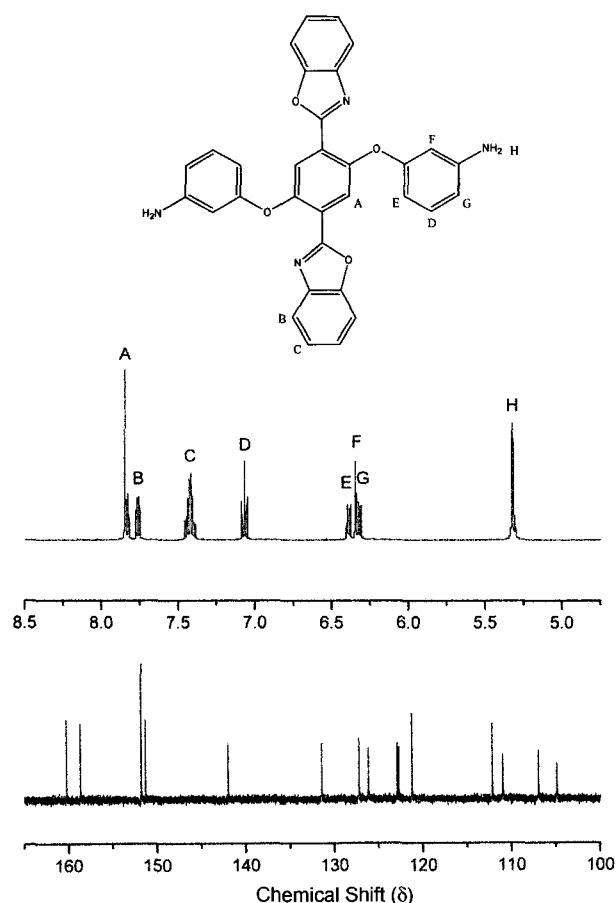
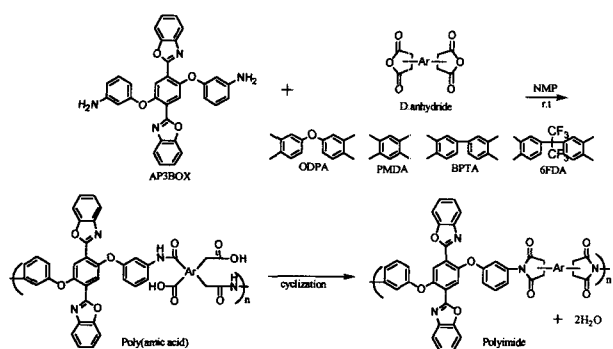


Figure 2. ¹H and ¹³C NMR spectra of diamine monomer (AP3BOX).

protons of amide groups appeared at 10.5~10.7 ppm. IR spectra of the polymers showed characteristic amide and acid absorption bands at 1662, 1539, and 1426 cm⁻¹.

Thermal Imidization to Polyimides. Thermal imidization



Scheme II

of poly(amic acid)s was investigated by DSC, TGA and FT-IR measurements. Figure 4 shows the DSC thermograms of different poly(amic acid)s. The imidization endotherms appeared at the temperature range between 200 and 280 °C. In case of PMDA or BPTA, additional small exothermic transitions appeared at around 350~330 °C, presumably due to the crystallization of the resulting polyimides. From the second heating scan of polymer samples obtained from ODPA and 6FDA, glass transitions were observed at 247 and 261 °C, respectively. Typical TGA thermograms of the poly(amic acid) (AP3BOX-BPTA) are shown in Figure 5. The first weight loss at the temperature range of 200~260 °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 500 °C before decomposition. The rescan curve after the first heating to 300 °C are shown as a dotted line. The TGA curves of all the samples after curing are shown in Figure 6. The decomposition onsets were observed at 470~500 °C, and the residual weights at 800 °C were in the range of 53~56 wt%. The relative thermal stability was to be in order of BPTA > 6FDA > PMDA ~ ODPA, though the exact comparison was difficult due to the relatively low molecular weight of the prepared polymers. The structural changes during the imidization were observed by FT-IR (Figure 7). The absorption bands of amide groups at 1662, 1539, and 1416 cm^{-1} disappeared after curing, and

Table I. Inherent Viscosities and Thermal Properties of Polymers

Dianhydride	Yield (%)	η_{inh}^a (dl/g)	T_{imid}^b	T_g^c (°C)	T_c^d (°C)	$T_{5\%}^e$ (°C)	Char Yield ^f (%)
ODPA	88.7	0.24	205~239	247	-	480	53.5
PMDA	91.1	0.35	215~260	-	352	496	52.9
BPTA	74.5	0.26	221~258	-	336	523	56.2
6FDA	72.1	0.28	218~260	261	-	507	54.7

^aMeasured with 0.5 g/dL in DMAc at 25 °C. ^bTemperature range of imidization measured by DSC.

^cGlass transition temperature observed by DSC (2nd scan). ^dTemperature of crystallization observed by DSC.

^eTemperature of 5% weight loss measured by TGA. ^fResidual weight % at 800 °C.

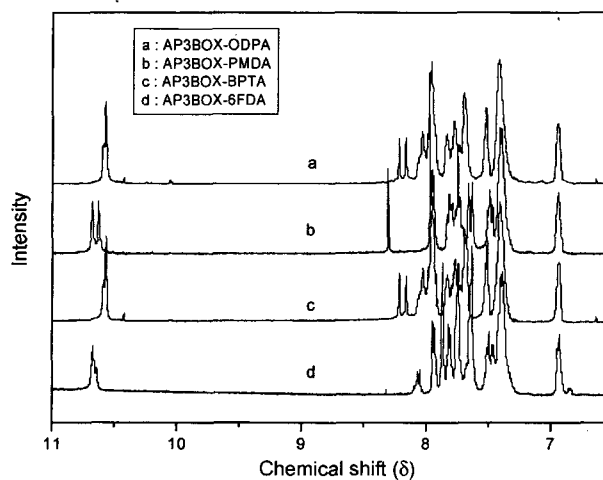
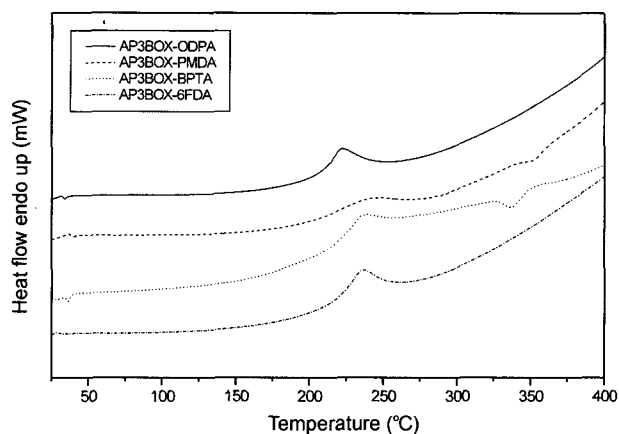
Figure 3. ^1H NMR spectra of poly(amic acid)s.

Figure 4. DSC thermograms of poly(amic acid)s.

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.

The results of solubility test of poly(amic acid)s are

Table II. Solubility of Poly(amic acid)s

(○ : soluble, × : insoluble)

	NMP	DMAc	DMF	DMSO	Pyridine	<i>m</i> -Cresol	THF	Acetone	Chloroform
AP3BOX-ODPA	○	○	○	○	○	○	×	×	×
AP3BOX-PMDA	○	○	○	○	○	×	×	×	×
AP3BOX-BPTA	○	○	○	○	○	×	×	×	×
AP3BOX-6FDA	○	○	○	○	○	×	○	×	×

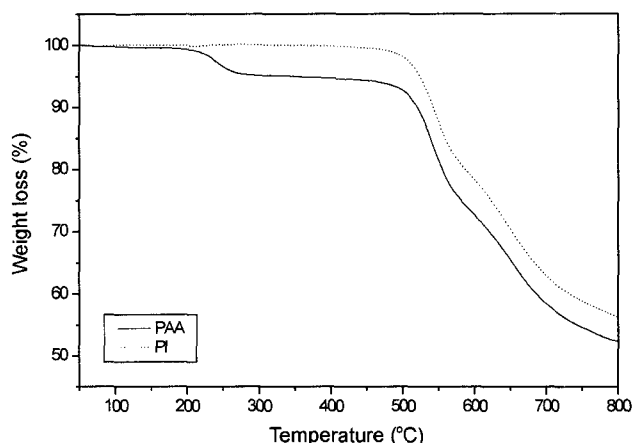


Figure 5. Typical TGA thermograms of poly(amic acid), AP3BOX-BPTA, before and after imidization curing.

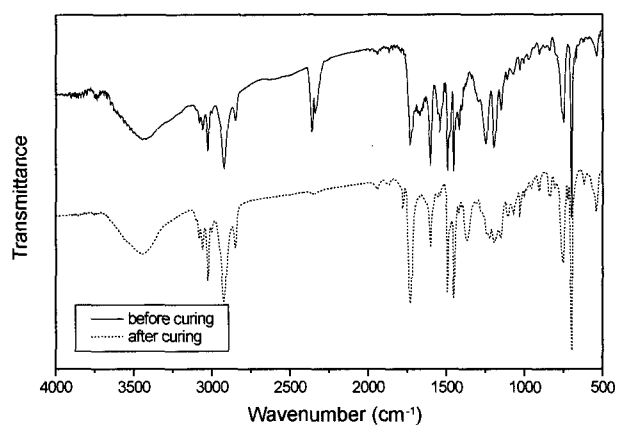


Figure 7. FT-IR spectral change upon imidization curing (sample: AP3BOX-PMDA).

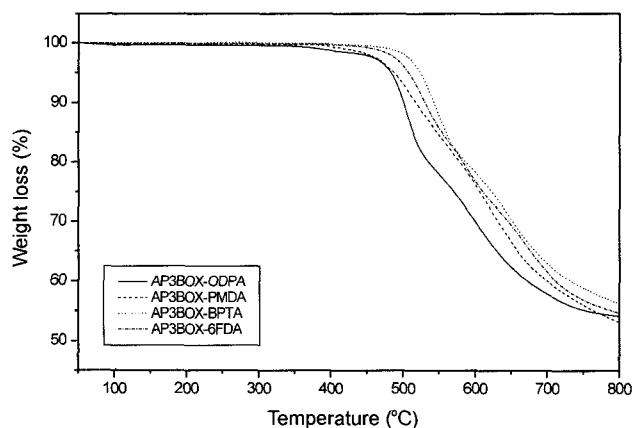


Figure 6. TGA thermograms of various polyimides.

shown in Table II. The polymers possessed good solubility in polar aprotic solvents including DMF, DMAc, NMP, DMSO, and pyridine. Poly(amic acid)s containing more flexible linkages such as those from ODPA and 6FDA were also soluble in *m*-cresol or tetrahydrofuran. The cured polyimides, however, were mostly insoluble in common organic solvents, but soluble in strong acids like sulfuric acid and trifluoroacetic acid.

Acknowledgement. This study was supported by research grants No. B62-A08-5406-03-2-3 from Ministry of Commerce, Industry and Energy (MOCIE).

References

- (1) R. R. Luise, *Applications of High Temperature Polymers*, CRC Press, Boca Raton, 1997.
- (2) H. R. Kricheldorf, *Handbook of Polymer Synthesis, Part B*, Marcel Dekker, New York, 1992.
- (3) R. J. Cotter, *Engineering Plastics, A Handbook of Polyarylethers*, Gordon and Breach Publishers, Switzerland, 1995.
- (4) H. R. Kricheldorf, *Progress in Polyimide Chemistry*, Springer-Verlag, Berlin, 1999.
- (5) M. K. Ghosh and K. L. Mittal, *Polyimides: Fundamentals and Applications*, Marcel Dekker, New York, 1996.
- (6) M. Ree, T. J. Shin, and S. W. Lee, *Korea Polym. J.*, **9**(1), 1 (2001).
- (7) K. U. Jeong, J.-J. Kim, and T.-H. Yoon, *Korea Polym. J.*, **8**(5), 215 (2000).
- (8) J. I. Lee, L. Y. Kwon, J.-H. Kim, K. Y. Choi, and D. H. Suh, *Die Angew. Makromol. Chem.*, **254**, 27 (1998).
- (9) J.-H. Kim and S. W. Bang, *Polymer J.*, **32**, 118 (2000).
- (10) J.-H. Kim, S. W. Bang, and Y. J. Kim, *Bull. Korean Chem. Soc.*, **21**(9), 896 (2000).