

Synthesis and Characterization of Fluorine-Containing Polybenzoxazoles by High-Temperature Direct Polycondensation

Jae Kwan Lee, Ji-Heung Kim,[†] and Young Jun Kim[†]

Department of Chemical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

[†]Department of Textile Engineering, Sungkyunkwan University, Suwon 440-746, Korea

Received March 19, 2003

Key Words : Polybenzoxazole. Fluorine-containing polymer. Polycondensation

Because of their high performance properties, e.g. high glass transition temperature, high melting points, and generally high thermooxidative stability, wholly aromatic polyheterocyclics, such as polybenzimidazoles, polybenzoxazoles (PBO), and polyimides, have long been of interest as heat-resistant fibers and as matrix materials for fiber-reinforced composites.¹⁻³ Several routes have been reported for the synthesis of aromatic poly(benzazole)s: melt polycondensation of dicarboxylic acid diphenyl esters and high-temperature solution polycondensation of dicarboxylic acids⁴ or their derivatives with polyfunctional bis(*o*-diamine), bis(*o*-aminophenol), or bis(*o*-aminothiophenol) monomers in polyphosphoric acid (PPA), a reaction medium. PPA acts as condensing agent and solvent.⁵ Ueda *et al.* developed a modified method for the synthesis of poly(benzazole)s with the use of PPMA (Phosphorous Pentoxide/Methanesulfonic Acid).⁶ Aromatic PBOs were first synthesized in a two-step procedure that involved the polycondensation of bis(*o*-aminophenol)s with aromatic dicarboxylic acid chlorides in solution, forming soluble precursor poly(*o*-hydroxyamide)s, and the thermal cyclodehydration of the precursor polymers, yielding PBOs.⁷ Since then, several different methods of preparing PBOs have been established that employ one-step and two-step processes from the combinations of bis(*o*-aminophenol) derivatives and aromatic dicarboxylic acid analogues.^{8,9}

On the other hand, fluorine-containing polymers have been synthesized and developed as high-performance polymers with unique chemical and physical properties that are not observed with other organic polymers.¹⁰ They possess improved thermal stability, high chemical stability, low adhesion, low refractive index, and so on. An additional benefit of the presence of the C-F bond is the decreased dielectric constant, which fluorinated materials exhibit.

Several different methods have been reported in the literature for the synthesis of 2,5-difluoroterephthalic acid: *i.e.* the oxidation of 2,5-difluoroxylene with nitric acid, carboxylation of lithiobenzoate which is formed by BuLi treatment of difluorobenzoic acid, or multi-step reactions including acylation and subsequent oxidation steps starting from 2,5-difluorotoluene. Previously, Cassidy *et al.* reported the synthesis of polyesters from 2,5-difluoroterephthaloyl chloride with various bisphenols or diols.¹¹ And also the related polyamides were synthesized by Nagata Jr. *et al.*¹²

In our laboratory,^{13,14} 2,5-difluoroterephthalic acid was

synthesized from 1,4-dibromo-2,5-difluorobenzene (I) in two steps: *i.e.* the compound (I) was treated with CuCN in DMF to prepare 2,5-difluoroterephthalonitrile, which was subsequently hydrolyzed to produce 2,5-difluoroterephthalic acid using phosphoric acid. The 2,5-difluoroterephthalic acid was used for the preparation of new poly(benzoxazole)s by high-temperature direct polycondensation with bis(*o*-aminophenol)s in PPA.

Experimental Section

Materials and instrumentation. 1,4-dibromo-2,5-difluorobenzene (98%) was purchased from Fluorochem and used as received. Cuprous cyanide (99%) was purchased from Aldrich Chemical Co. 2,2-Bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (98%) and 3,3-diamino-4,4-dihydroxybiphenyl (99%) were purchased from TCI Co. (Japan) and used without purification. Ferric chloride (97%) and polyphosphoric acid (PPA, 115%) were purchased from Kokusan Chem. (Korea). Other chemicals and solvents were obtained as higher purity available and purified by conventional methods.

IR spectra were obtained on a Unicam 1000 FT-IR spectrometer. NMR spectra were taken on a Varian Unity Inova 500 MHz Spectrometer at room temperature. Thermal analysis (DSC/TGA) was carried out on a Perkin Elmer 7 Series thermal analysis system. Solution viscosity was measured by an Ubbelohde capillary viscometer using sulfuric acid as the solvent.

Synthesis of 2,5-difluoroterephthalic acid. (a) Into the 3-necked flask fitted with condenser, nitrogen inlet, and outlet was added 1,4-dibromo-2,5-difluorobenzene (10 g, 36.77 mmol), cuprous cyanide (7.576 g, 84.59 mmol, 15% molar excess), and DMF (60 mL). The reaction mixture were heated to 155 °C and stirred for 15h. After reaction, the solution was poured into aqueous solution (containing FeCl₃·6H₂O + HCl) at 60-70 °C and the precipitate was filtered off. The solid product was slurried in 10 wt% Na₂CO₃ aqueous solution, filtered and washed with distilled water several times, and then dried in vacuum. The product was purified by sublimation and recrystallization from acetic acid to obtain the desired product, 2,5-difluoroterephthalonitrile, as a white crystalline needle (yield 65%). Mp. 306 °C, ¹H NMR (dmso-*d*₆) 8.37 (s, 2H) ppm. IR 2230 cm⁻¹ (CN stretching). (b) 2,5-Difluoroterephthalonitrile (4 g, 24.68

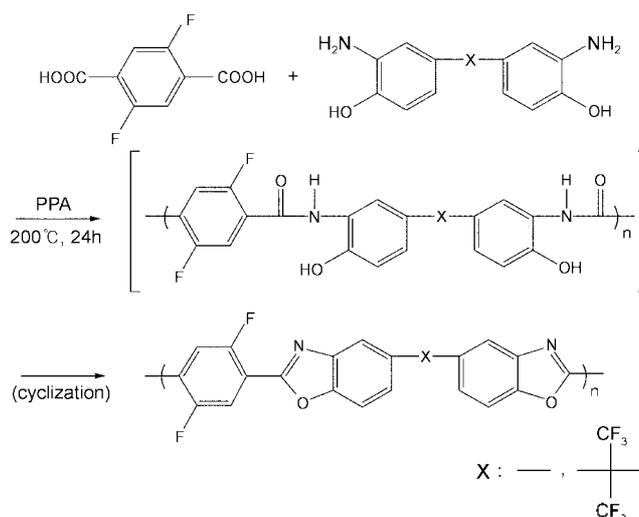
mmol) and phosphoric acid (72 g) were charged into round-bottomed flask with condenser, and stirred for 18h at 180 °C. The reaction mixture was precipitated into large amount of water, filtered and dried. The solid product was recrystallized from acetic acid to obtain white crystal as a pure monomer form (yield *ca.* 80%). Mp. 329 °C. ¹H NMR (dmso-*d*₆) 13.83 (COOH), 7.70 (arom. H) ppm, IR 3050-2650 (O-H), 1700 (carbonyl) cm⁻¹.

Polymerization of 2,5-difluoroterephthalic acid with bis(*o*-aminophenols) by direct polycondensation. 2,5-Difluoroterephthalic acid (1 g, 5 mmol), 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane (1.8122 g, 5 mmol), and polyphosphoric acid (65 g) were stirred and heated to 200 °C, and reacted for 24h. The reaction mixture turned light-yellow as the polymerization was proceeded. The solution was poured slowly into a large amount of distilled water, and the resulting fibrous precipitate was filtered and washed with water and methanol several times before being dried in vacuum at 90 °C. Yield 1.63 g (87.5%). ¹H NMR (CF₃COOD) 7.59 (1H, d), 7.72 (1H, d), 7.90 (1H, s), 8.13 (1H, s) ppm; IR (pellet) 2920, 1610, 1571, 1479, 1432, 1253, 1216, 1137, 1061, 962 cm⁻¹. The same procedure was used for the polymerization reaction with another monomer, 3,3-diamino-4,4-dihydroxybiphenyl, to provide the corresponding polymer with an almost quantitative yield. IR (pellet) 2920, 1733, 1600, 1493, 1452, 1183, 1071, 698 cm⁻¹.

Results and Discussion

Although the preparation of 2,5-difluoroterephthalic acid is known, the method described herein is newly developed in our laboratory and considered to be more simple with high reaction yield. 2,5-Difluoroterephthalic acid (2F2COOH) was synthesized by acid hydrolysis of 2,5-difluoroterephthalonitrile which was derived from nucleophilic bromine displacement reaction of 2,5-dibromo-1,4-difluorobenzene using cuprous cyanide in DMF. Cyanide ion preferentially displaces bromine, a much more reactive halogen atom compared to fluorine, in this particular substitution reaction.¹⁵ Next, conversion of the dinitrile compound to the corresponding acid can be proceeded by both acid and base catalyzed hydrolysis, though, acid hydrolysis using phosphoric acid were employed here to give a high reaction yield. The overall reaction yield was about 55% after purification. The pure monomer was obtained by recrystallization from acetic acid as a colorless crystal.

The polycondensation reaction between 2F2COOH and 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (3A4H6FP) or 3,3-diamino-4,4-dihydroxybiphenyl (3A4HBP)



Scheme 1

was conducted at 200 °C in excess of PPA, a well-known condensing reagent. Both polymer products were obtained in high yields and possessed relatively high molecular weights estimated from their solution viscosities. The results of polymerization are shown in Table 1, with their thermal data. The polymer from 3A4HBP monomer possessed very high viscosity (4.0 dl/g), probably due to higher molecular weight and its chain rigidity. It was difficult to get a reasonable concentration for NMR measurement, and the polymer tended to form fiber from the viscous solution, when pulled out by using tweezer. Figure 1 shows IR spectra of both polymers exhibiting a characteristic C=N stretching band around 1600 cm⁻¹ based on benzoxazole ring.

Figure 2, shows the TGA thermograms of the prepared poly(benzoxazole)s and the thermal data are included in Table 1 shown above. Both polymers exhibited excellent thermal stability with no weight loss up to 500 °C. Polymer (I) containing aliphatic hexafluoroisopropylidene group exhibit relatively poor stability compared to polymer (II) of wholly aromatic and rigid structure. Polymer (II) did not show a weight loss up to as high as 600 °C and the residual weights at 800 °C was 69% under nitrogen. The glass transition temperature of polymer (I) was observed weakly by DSC at around 340 °C. No transition, however, was noticed from the polymer (II).

As are expected from these type of aromatic polymers, both of the prepared polymers showed limited solubility in organic solvents, but were soluble in strong acids such as concentrated sulfuric acid or trifluoroacetic acid (for polymer (I)). Hexafluoroisopropylidene group is generally known to

Table 1. Results of Polymerization and the Thermal Properties

code	yield (%)	inherent viscosity ^a (dl/g)	5% weight loss (°C) in N ₂ (Air)	10% weight loss (°C) in N ₂ (Air)	residual weight % at 800 °C, N ₂
(I) 3A4H6FP	87.5	0.92	539 (532)	572 (540)	41
(II) 3A4HBP	97.4	4.00	621 (574)	683 (586)	69

^a0.5 g/dl concentration in H₂SO₄ (98%) at 25 °C.

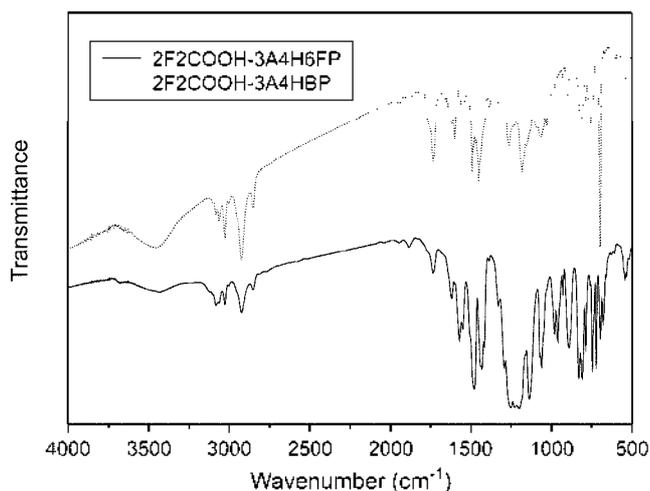


Figure 1. FT-IR spectra of polymer (I) and (II).

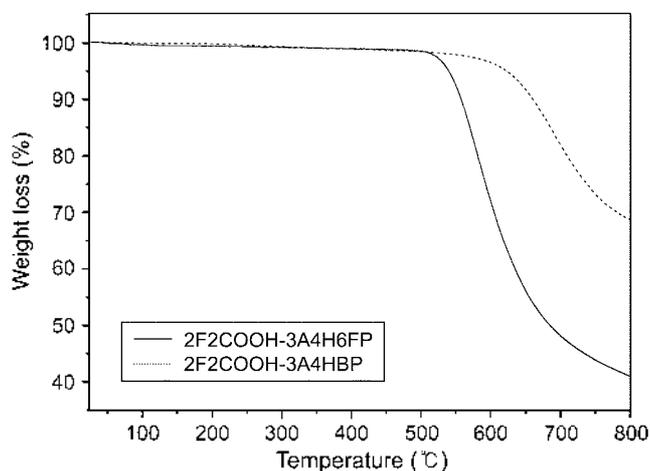


Figure 2. TGA Thermograms of Polymer (I) and (II) (at a heating rate of 10 °C/min in nitrogen).

improve the solubility of various types of aromatic polymers. As are generally known, fiber spinning can be a choice of processing method for these rigid-rod polymers like aramid Kevlar or PBI.

To summarize, 2,5-difluoroterephthalic acid monomer was synthesized from hydrolysis of 2,5-difluoroterephthalonitrile which was derived from 1,4-dibromo-2,5-difluorobenzene *via* bromine substitution reaction with cyanide nucleophile. The monomer was used for the direct polycondensation with bis(*o*-aminophenols) in PPA to prepare new polybenzoxazoles. High molecular weight polymers could be prepared, and the resulting polymers exhibited excellent thermal stability. These polymers are totally insoluble in most organic solvents, but are soluble in strong acids such as concentrated sulfuric acid.

Acknowledgement. This work was supported by research grants from MOCIE, and by the Brain Korea 21 Project.

References

- Hergenrother, P. M. *High Performance Polymers and Composites*, Kroschwitz, J. I., Ed.; John Wiley & Sons: 1991.
- Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980; Ch. 6, pp 154-158.
- Wolfe, J. F. *Encyclopedia of Polymer Science and Engineering*, Wiley Interscience: New York, 1985; Vol. 11, pp 601-635.
- Vogel, H.; Marvel, C. C. *J. Polym. Sci.* **1961**, *50*, 511.
- Iwakura, Y.; Uno, K.; Imai, Y. *J. Polym. Sci. Part A, Polym. Chem.* **1964**, *2*, 2605.
- Ueda, M.; Sato, M.; Mochizuki, A. *Macromolecules* **1985**, *18*, 2723.
- Kubota, T.; Nakanishi, R. *J. Polym. Sci., Part B: Polym. Lett.* **1964**, *2*, 655.
- Imai, Y.; Maeda, Y.; Takeuchi, H.; Park, K.-H.; Kakimoto, M. A.; Kurosaki, T. *J. Polym. Sci. Part A, Polym. Chem.* **2002**, *40*, 2656.
- Kim, J.-H.; Lee, J. K. *Bull. Korean Chem. Soc.* **2001**, *22*(9), 999.
- Fluoropolymers I (Topics in Applied Chemistry)*; Hougham, G.; Cassidy, P. E.; Johns, K.; Davidson, T., Eds.; Kluwer Academic: Plenum Publishers: New York, 1999; Ch. 9.
- Person, D. V.; Fitch, J. W.; Cassidy, P. E.; Kono, K.; Reddy, V. S. *Reactive & Functional Polymers* **1996**, *30*, 141.
- Nagata, Jr. M.; Tsutsumi, N.; Kiyotsukuri, T. *J. Polym. Sci. Part A, Polym. Chem.* **1988**, *26*(1), 235.
- Kim, J.-H.; Lee, J. K.; Kim, Y. J.; Won, J. C.; Choi, K.-Y. *Macromolecular Research* **2002**, *10*(5), 241.
- Kim, J.-H.; Bang, S. W.; Kim, Y. J. *Bull. Korean Chem. Soc.* **2000**, *21*(9), 896.
- Ellis, G. P.; Romney-Alexander, T. M. *Chem. Rev.* **1987**, *87*, 779.