Oxidative Polymerization of 2,6-Difluorophenol to Crystalline Poly(2,6-difluoro-1,4-phenylene oxide)

Ryohei Ikeda,[†,‡] Hozumi Tanaka,[‡] Hiroshi Uyama,[§] and Shiro Kobayashi*[,§,⊥]

Joint Research Center for Precision Polymerization−Japan Chemical Innovation Institute, NIMC, Tsukuba, Ibaraki, 305-8565, Japan; Toyo Ink Mfg. Co., Ltd., 27, Wadai, Tsukuba, Ibaraki, 300-4247, Japan; Department of Materials Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan; and National Institute of Materials and Chemical Research (NIMC), Tsukuba, Ibaraki, 305-8565, Japan

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ABSTRACT: Oxidative polymerization of 2,6-difluorophenol was performed using the Fe−salen complex and hydrogen peroxide as catalyst and oxidizing agent, respectively. The resulting polymer obtained at 60 °C in 1,4-dioxane was partly soluble in tetrahydrofuran and insoluble in chloroform, benzene, and hexafluorobenzene. The molecular weight of the THF-soluble part was in the range of several thousands. NMR and IR analysis showed the formation of poly(2,6-difluoro-1,4-phenylene oxide). In the DSC trace of second scan, the crystallization temperature and melting point were observed, indicating that the Fe−salen complex enabled the synthesis of crystalline poly(phenylene oxide) from 2,6-difluorophenol for the first time.

Introduction

Fluorine-containing polymers have unique properties as functional materials in comparison with those of hydrocarbon polymers.[1] The most famous example is Teflon, which is based on tetrafluoroethylene. Teflon coating provides excellent chemical and environmental resistance.

For the past decades, enzymatic synthesis of polyphenols has been extensively investigated.[2] Peroxidases induced the oxidative polymerization of phenol derivatives under mild reaction conditions to produce a new class of polyphenols in good yields.[3] This process does not use toxic formaldehyde, and their synthetic procedure is very facile. A soluble polyphenol was obtained from nonsubstituted phenol in aqueous methanol.[4] In the peroxidase-catalyzed polymerization of a phenol derivative having a methacryloyl group, the phenolic moiety was chemoselectively polymerized to give a polymer having the methacryloyl group in the side chain.[5]

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was first synthesized by an oxidative polymerization of 2,6-dimethlphenol using a copper/amine catalyst.[6] Blends of PPO and polystyrene are widely used as engineering plastics in industrial fields.[7] PPO has glass transition temperature (T_g) of 210 °C and no melting point (T_m). The crystalline PPO derivative, poly(2,6-diphenyl-1,4-phenylene oxide) ($T_m = 480$ °C), was synthesized from 2,6-dipenylphenol using the copper/amine catalyst.

Peroxidase and laccase catalysts were also active for the polymerization of 2,6-dimethylphenol.[8] The resulting polymer consisted exclusively of the 1,4-oxyphenylene unit; on the other hand, a small amount of Mannish base and 3,5,3′5′-tetramethyl-4,4′-diphenoquinone units are contained in the commercially available PPO.[7] These enzymes catalyzed the polymerization of 3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid), yielding a PPO derivative having a carboxylic acid group at one end and a phenolic group at the other,[9] where the elimination of hydrogen and carbon dioxide from the monomer was involved. Interestingly, conventional chemical oxidation catalysts did not induce the polymerization of syringic acid. Recently, we have first achieved regioselective oxidative polymerization of a phenol derivative using a tyrosinase model complex as catalyst, leading to crystalline 2,6-unsubstituted PPO.[10] The complex also catalyzed the regioselective polymerization of 2,5-dimethylphenol to give the crystalline PPO derivative with T_m higher than 300 °C.[11]

A fluorine-containing PPO derivative has much potential as new polymeric materials since it has excellent performances due to a PPO backbone bearing fluorine substituents. It was reported that poly(2,6-difluoro-1,4-phenylene oxide) (**2**) was synthesized by anionic polymerization of 5,7-difluoro-1-oxaspiro[2.5]octa-4,7-dien-6-one.[12] This method, however, involves tedious multistep procedures including monomer synthesis and, hence, may not be suitable for preparative synthesis of **2**. Very recently, we have found that 2,6-difluorophenol (**1**) was polymerized by peroxidase catalyst.[13] This is the first example of the oxidative polymerization of fluorine-containing phenols. However, the elimination of fluorine atom partly took place to give the polymer with complicated structure.

Recently, we have found that Fe(III)−salen efficiently catalyzed the oxidative polymerization of 2,6-dimethylphenol and bisphenol A[14] and also the polymerization of cardanol to a cross-linkable polyphenol.[15] We regarded Fe−salen as model complex of peroxidase having a heme as catalytic active site. This study deals with facile preparative synthesis of poly(2,6-difluoro-1,4-phenylene oxide) (**2**) by the oxidative polymerization of 2,6-difluorophenol (**1**) using the Fe−salen complex as catalyst (Scheme 1). The enzymatically obtained polymer from **1** was amorphous; on the other hand, the present polymer shows crystallinity with T_m of ca. 250 °C.

[†] Joint Research Center for Precision Polymerization−Japan Chemical Innovation Institute.

[‡] Toyo Ink Mfg. Co., Ltd.

[§] Kyoto University.

[⊥] National Institute of Materials and Chemical Research.

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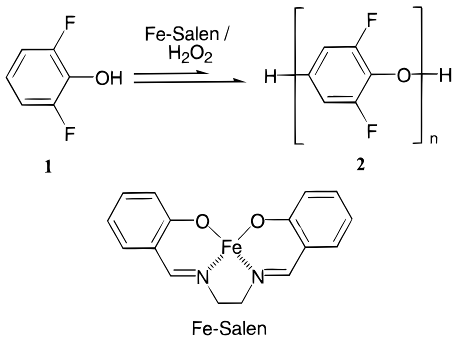
Table 1. Oxidative Polymerization of 1 Using Fe−Salen Complex as Catalyst[a]

	polymerization						polymer			
entry	temp (°C)	solvent	time (h)	cat. amount[b] (%)	pyridine (mL)	H_2O_2 conc (%)	yield[c] (%)	solubility[d]	M_n[e] ($\times 10^{-3}$)	M_w/M_n[e]
1	30	1,4-dioxane	3	1.0	0.20	10	18	+	2.0	1.3
2	60	1,4-dioxane	3	0.50	0.20	10	51	±	2.4	1.4
3	60	1,4-dioxane	3	1.0	0	10	56	+	2.2	1.4
4	60	1,4-dioxane	3	1.0	0	30	21	+	1.7	1.1
5	60	1,4-dioxane	3	1.0	0.20	10	79	−	3.8	1.8
6	60	1,4-dioxane	3	1.0	0.20	30	76	−	3.2	1.7
7	60	1,4-dioxane	3	2.0	0.20	10	78	−	4.4	2.2
8[f]	60	1,4-dioxane	24	1.0	0.20		0			
9	60	1,2-dimethoxyethane	3	1.0	0.20	30	82	−	2.7	1.5
10	60	tetrahydrofuran	3	1.0	0.20	10	30	+	1.7	1.2
11	60	tetrahydrofuran	3	1.0	0.20	30	25	±	1.7	1.2
12	80	1,4-dioxane	3	1.0	0.20	10	51	±	1.8	1.2

[a] Polymerization of 1 (5.0 mmol) using Fe−salen catalyst under air. [b] Mole percent for monomer. [c] Methanol-insoluble part. [d] Solubility toward THF: +, soluble; ±, almost soluble; −, partly soluble. [e] Data of THF-soluble part, determined by SEC. [f] Polymerization without the addition of hydrogen peroxide.

Scheme 1



Results and Discussion

Polymerization Using Fe−Salen Complex as Catalyst. Commercially available Fe(II)−salen was used as catalyst. The polymerization was carried out using hydrogen peroxide as oxidizing agent in 1,4-dioxane. Hydrogen peroxide was added 10 times in each in one-tenth amount. Fe(II)−salen was oxidized by hydrogen peroxide to form Fe(III)−salen, which might be a true catalyst for the present polymerization.

Polymerization results are summarized in Table 1. The polymerization using 10% hydrogen peroxide at 60 °C in 1,4-dioxane produced the polymer in 56% yield (entry 3), which was soluble in tetrahydrofuran (THF), partly soluble in *N*,*N*-dimethylformamide (DMF) and 1,4-dioxane, and insoluble in acetone, benzene, chloroform, ethyl acetate, hexafluorobenzene, hexafluoro-2-propanol, and water. On the other hand, the enzymatically synthesized polymer from **1** was soluble in acetone, benzene, chloroform, DMF, and THF.[13] This is probably due to the structural difference (see part of structural analysis). For reference, PPO from 2,6-dimethylphenol is readily soluble in chloroform and THF. When 30% hydrogen peroxide was used under similar reaction conditions, the yield of **2** greatly decreased (entry 4). This may be because the catalytic activity of the Fe−salen complex was partly inactivated by the high concentration of hydrogen peroxide.

We reported that in the Fe−salen-catalyzed oxidative polymerization of phenols the addition of a small amount of pyridine improved the polymer yield. In the present polymerization, a similar behavior was observed: the yield obtained in the presence of the pyridine was larger (entries 3 and 5); however, the solubility of **2** decreased; the sample of entry 5 was partly soluble in THF (THF soluble part = 56%). In the presence of pyridine, the concentration of hydrogen peroxide hardly affected the polymerization behaviors (entries 5 and 6). Under the reaction conditions of entries 5 and 6, the monomer was quantitatively consumed.

The polymerization at 30 °C produced the soluble polymer in a low yield (entry 1). The yield of **2** obtained at 60 °C was the highest among the examined temperatures (30, 60, and 80 °C) (entries 1, 5, and 12). In the case of a small amount of the catalyst (0.50 mol % for **1**), **2** was almost soluble in THF, whose yield was lower than that of 1.0% catalyst (entry 2). The polymerization results using 1.0% of Fe−salen complex were almost the same as those of 2.0% catalyst (entry 7).

Besides 1,4-dioxane, 1,2-dimethoxyethane and THF were used as solvent. The former produced **2** in a good yield (entry 9); however, the yield was low in using THF (entries 10 and 11). In the polymerization without the addition of hydrogen peroxide for longer reaction time (entry 8), the monomer was recovered unchanged, indicating that Fe−salen/hydrogen peroxide system induced the present polymerization.

Molecular weight was determined by size exclusion chromatography (SEC). When **2** was partly soluble in THF, the THF-soluble part was evaluated. The polymers soluble or almost soluble in THF had the molecular weight of ca. 2000, which was lower than that of the polymers showing low solubility toward THF. The highest molecular weight (4400) was observed in using the high load of the catalyst (entry 7).

Structural Analysis. In the case of oxidative polymerization of halogen-containing phenols, the elimination of halogen atom often took place, leading to the new bond formation at the halogen-substituted position.[16] Our previous study on the enzymatic polymerization of 2,6-fluorophenol showed that fluorine atom was partly eliminated (ca. 15%) to give the polymer with complicated structure.[13] Results of elemental analysis are shown in Table 2. In all cases, the measured fluorine content was very close to that of the calculated value, indicating that the elimination of fluorine atom is negligible.

Figure 1 shows ^{19}F NMR spectra of **1**, **2**, and the enzymatically obtained polymer from **1**. The monomer peak was observed at δ −136 (Figure 1A). The polymer obtained at 80 °C (entry 12) had one large peak at δ −128 and two small peaks at δ −130 and −135 in d_8-THF (Figure 1B). The integrated area of the small peaks

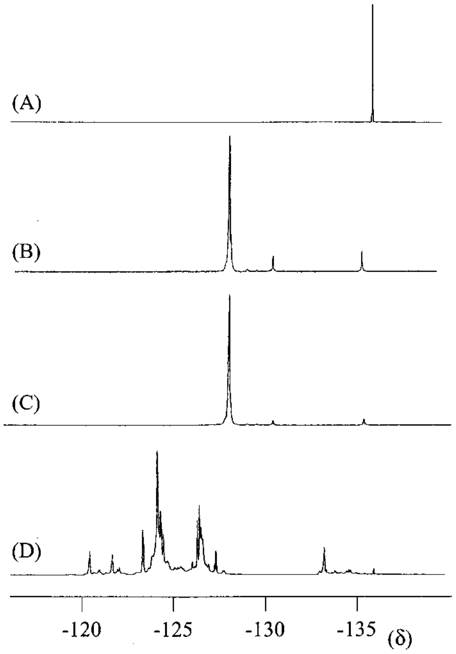


Figure 1. ^{19}F NMR spectra of (A) **1**, (B) **2** (entry 12), (C) **2** (entry 5), and (D) the enzymatically obtained polymer from **1**.

Table 2. Elemental Analysis of Poly(2,6-difluoro-1,4-phenylene oxide)

sample		C	H	F
entry 1	calcd	56.25	1.57	29.68
	found	56.19	1.59	28.49
entry 5	calcd	56.25	1.57	29.68
	found	56.42	1.57	28.84
entry 12	calcd	56.25	1.57	29.68
	found	55.80	1.53	28.80
enzymatically obtained polymer[a]	calcd	56.25	1.57	29.68
	found	56.73	2.23	25.28

[a] Data from ref 13.

was very close to each other, suggesting that these peaks would be ascribed to both terminal units of **2**. On the other hand, the enzymatically obtained polymer from **1** showed a complex pattern of broad peaks (Figure 1D). These data indicate that the polymerization of **1** using Fe–salen catalyst produced the polymer with a well-regulated structure. In the case of the polymer obtained at 60 °C (entry 5), a similar spectrum pattern was observed (Figure 1C), and the intensity ratio of the large peak to the small ones was greater than that at 30 °C (data not shown) or 80 °C, supporting the higher molecular weight of the polymer obtained at 60 °C.

^{1}H and ^{13}C NMR analyses clearly exhibited the formation of poly(2,6-difluoro-1,4-phenylene oxide). In the ^{13}C NMR spectrum of **2** (entry 3), the main four peaks (peaks A, C, I, and K) due to 2,6-difluoro-1,4-oxyphenylene unit are seen at δ 157.8 (dd, $J = 250$ and 5 Hz), 157.4 (dd, $J = 12$ Hz), 127,2 (m), and 102.1 (d, $J = 22$ Hz). The assignment of the other small eight peaks due to the terminal units is shown in Figure 2. A small peak close to peak A may be due to carbon of neighboring unit of the terminal.

The ^{1}H NMR spectrum of **2** is shown in Figure 3. A main doublet peak (peak R) at δ 6.9 with $J = 9.0$ Hz is ascribed to protons of the 2,6-difluoro-1,4-oxyphenylene unit. A small doublet peak (peak S) at δ 6.6 is due to protons of the terminal phenol moiety. Multiplet and doublet–doublet peaks at δ 7.4 and 7.2 (peaks P and Q) are ascribed to protons of another terminal of the polymer. In the 2D NMR (H–H correlation spectroscopy) (data not shown), cross-peaks are observed between peaks P and Q, supporting the above assignment. These spectra data indicate that the present polymer is exclusively of 2,6-difluoro-1,4-oxyphenylene unit. Small peaks at the slightly higher magnetic field of peak R are probably ascribed to protons of the neighboring unit of the polymer end.

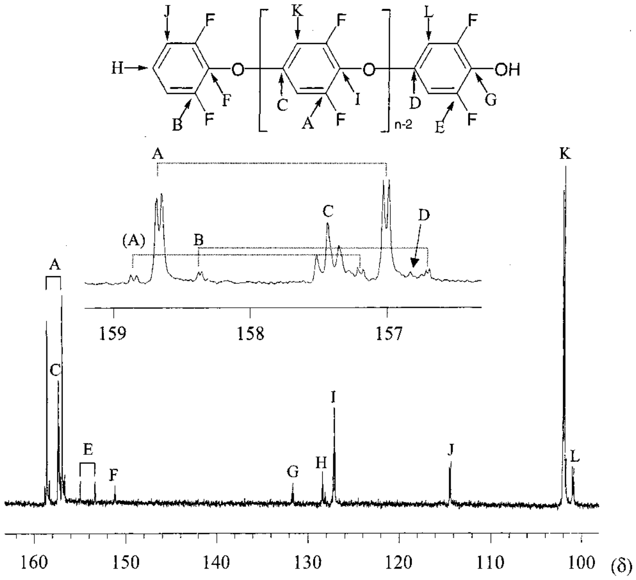


Figure 2. ^{13}C NMR spectrum of **2** (entry 3).

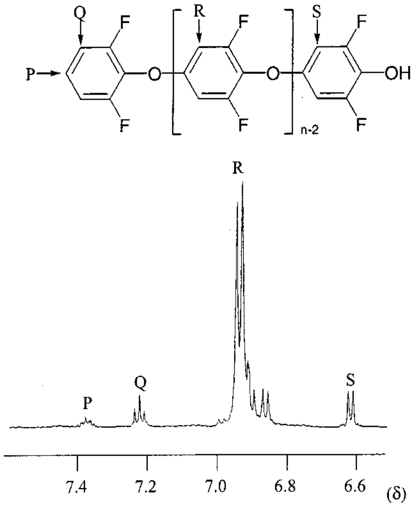


Figure 3. ^{1}H NMR spectrum of **2** (entry 1).

IR analysis supports the structure of the 1,4-oxyphenylene unit. A broad peak centered at 3382 cm^{-1} due to the vibration of O–H linkage of phenolic group became much smaller after the polymerization. A strong peak at 1106 cm^{-1} due to the symmetric vibration of the ether bond newly appeared, which was observed in poly(2,6-difluoro-1,4-phenylene oxide) from the spiro compound.[12] A peak at 767 cm^{-1} due to the out-of-plane vibration of C–H linkage of 1,2,3-trisubstituted benzene disappeared, and a peak at 850 cm^{-1} due to the vibration of C–H linkage of 1,2,3,5-tetrasubstituted benzene was newly observed.

Thermal Properties of Poly(2,6-difluoro-1,4-phenylene oxide). Thermal properties of the polymer were evaluated by using thermogravimetry (TG) and differential scanning calorimetry (DSC). Figure 4 shows

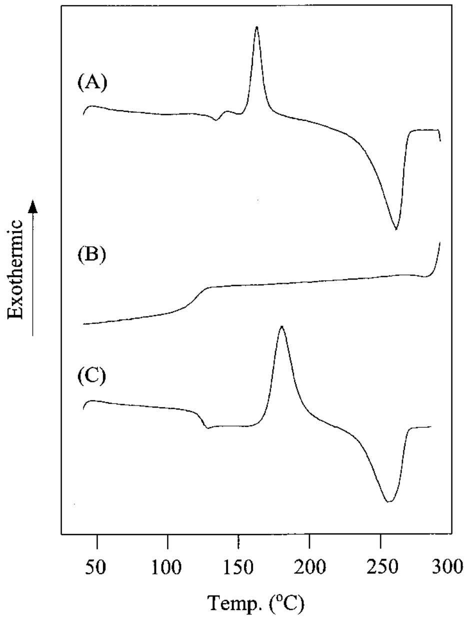


Figure 4. DSC traces of **2** (entry 5) measured under nitrogen: (A) first heating; (B) first cooling; (C) second heating.

DSC traces of **2** (entry 5). The DSC measurement was performed under nitrogen at a heating or cooling rate of 10 °C/min. In the first heating scan, there is an exothermic peak at 157 °C and an endothermic peak at 260 °C, which are due to the crystallization temperature (T_c) and T_m, respectively. Both were also observed in the second heating scan ($T_c = 175$ °C; $T_m = 253$ °C). These data indicate the formation of crystalline polymer from **1** using the Fe–salen complex. T_g was observed at 115 °C in the first cooling and second heating scans.

In the case of **2** having lower molecular weight (entry 3), T_g, T_c, and T_m were observed at 97, 173, and 231 °C, respectively, in the second heating scan. The enthalpies of fusion of **2** of entries 3 and 5 determined in the second heating scan were 17 and 30 J/g, respectively, suggesting that the polymer of higher molecular weight was of higher crystalline. For reference, T_g of the enzymatically obtained polymer from **1** was 79 °C and T_m was not observed. In the case of the polymer synthesized at low temperature (entry 1), only endothermic peaks at 197 and 214 °C due to the melting were observed in the first scan, and there was no melting point in the second scan.

Temperatures at 5 and 10% weight loss of **2** (entry 5) were determined by TG under nitrogen as 400 and 481 °C, respectively. The enzymatically synthesized polymer from **1** was thermally decomposed at a lower temperature (temperatures at 5 and 10% weight loss = 220 and 241 °C). These data indicate that the present polymer is thermally much more stable. This is probably owing to the crystalline property of **2** having a well-defined structure.

Conclusion

We have achieved the first synthesis of a crystalline fluorine-containing PPO derivative by the oxidative polymerization of 2,6-difluorophenol using the Fe–salen complex as catalyst. The solubility of the present polymer was much different from that of the enzymatically synthesized polymer from 2,6-difluorophenol and commercially available PPO. The resulting polymer obtained at 60 °C possessed T_m of 253 °C. TG analysis exhibited that the polymer showed high thermal stability. Further investigations on the oxidative polymerization of phenol derivatives using the Fe–salen catalyst and applications of the present polymer are under way in our laboratory.

Experimental Section

Materials. 2,6-Difluorophenol, Fe(II)–salen (Tokyo Kasei Co.), and other reagents were commercially available and used as received.

Polymerization of 2,6-Difluorophenol Using Fe–salen Complex. The following is a typical procedure for the polymerization (entry 5). Under air, 2,6-difluorophenol (0.65 g, 5.0 mmol) and Fe–salen (17 mg, 50 μmol) in 20 mL of 1,4-dioxane were placed in a 50 mL flask. Hydrogen peroxide (10% aqueous solution, 170 μL, 0.50 mmol) was added to the mixture every 10 min for 10 times at 60 °C under gentle stirring. After 3 h, 1 mL of 5 N HCl aqueous solution was added to the reaction mixture, followed by pouring into a large amount of methanol. The resulting precipitates were collected, followed by drying in vacuo to give 0.51 g of the polymer (yield 79%).

Measurements. Size exclusion chromatographic (SEC) analysis was carried out using a Tosoh SC8020 apparatus with a refractive index (RI) detector under the following conditions: four TSKgel G4000H$_{XL}$, G3000H$_{XL}$, G2500H$_{XL}$, and G2000H$_{XL}$ columns and THF eluent with a flow rate of 1 mL/min at 40 °C. The calibration curves for SEC analysis were obtained using polystyrene standards. NMR spectra were recorded on a JEOL JNM-LA 600 or Bruker DPX-400 spectrometer. IR measurement was carried out with a Perkin-Elmer Paragon 1000. DSC measurement was made at a 10 °C/min heating rate under nitrogen using a Mac Science DSC 3200 differential scanning calorimeter calibrated with an indium reference standard. TG analysis was performed using a Seiko Instruments TG/DTA 220 apparatus for thermogravimetry/differential thermal analysis at a heating rate of 10 °C/min in a nitrogen flow rate of 200 mL/min.

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