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PEROXIDASE-CATALYZED POLYMERIZATION OF FLUORINE-CONTAINING PHENOLS

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Key Words: Enzymatic Polymerization, Peroxidase, Fluorine-Containing Phenol, Oxidative Polymerization, Polyphenol, Fluoropolymer

ABSTRACT

Peroxidase-catalyzed oxidative polymerization of fluorine-containing phenols has been performed in a mixture of a water-mis-

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cible organic solvent and buffer at room temperature under air. The monomers used were 2,6-difluorophenol, 3- and 4-fluorophenols. In the polymerization of 2,6-difluorophenol catalyzed by horseradish peroxidase (HRP), effects of an organic solvent, buffer pH, and their mixed ratio have been systematically investigated with respect to the polymer yield and molecular weight. The resulting polymer was soluble in common polar organic solvents and showed good water repellent property. From NMR and IR data, it was supposed that the polymer was of mainly 2,6-difluoro-1,4-oxyphenylene unit. Elemental analysis showed that the elimination of a small amount of the fluorine atom took place during the polymerization. HRP catalysis induced the polymerization of 3- and 4-fluorophenols, yielding a new class of fluorine-containing polyphenols.

INTRODUCTION

Recently, enzymatic syntheses of polyphenols have received much attention as an alternative to the preparation of conventional phenolic resins (novolak and resol resins due to no use of toxic formaldehyde, mild reaction conditions (in neutral solvents at room temperature) and facile procedures [1-7]. Peroxidase catalyzed various phenol derivatives, mainly with substituents at m- and p-positions. From non-substituted phenol, a soluble polyphenol was obtained by using horseradish peroxidase (HRP) as catalyst in an aqueous methanol [8]. HRP catalysis induced the chemoselective polymerization of a methacryloyl group-containing phenol derivative to give the polyphenol having the methacryloyl group in the side chain, which was readily thermally and photochemically cured [9].

Fluoropolymer coatings are extensively used in industrial fields [10]. The most well-known coating is TeflonTM, which is based on tetrafluoro-ethylene. TeflonTM possesses excellent chemical and environmental resistance. Vinylidene-based coatings are widely accepted in the building industry due to their low maintenance properties.

Poly(2,6-dimethyl-1,4-oxyphenylene) (poly(phenylene oxide), PPO) is widely used as high-performance engineering plastics, since the polymer has excellent chemical and physical properties, e.g., a high glass transition temperature (ca. 210°C) and mechanically tough property [11]. PPO was first synthesized by an oxidative polymerization of 2,6-dimethylphenol using a copper/amine catalyst [12, 13]. This catalyst is often useful for preparation of PPO derivatives from 2,6-disubstituted phenols. We have reported that the HRP-catalyzed polymerization of 2,6-dimethylphenol produced the polymer consist-

ing of exclusively 1,4-phenylene unit [14]. The enzymatic polymerization of 3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid) gave a PPO derivative [15, 16]. During the polymerization, hydrogen and carbon dioxide were eliminated from the monomer.

Phenolic polymers containing fluorine atoms have much potential as new functional materials since they have excellent performances due to their thermally-stable polyphenol backbone bearing together with unique properties of fluorine substituents. However, there has been no report on an oxidative polymerization of fluorine-containing phenols so far probably due to the low reactivity toward oxidative catalysts. This study deals with peroxidase-catalyzed polymerization of 2,6-difluorophenol (**1**), 3- and 4-fluorophenols (**2** and **3**, respectively) (Chart 1). This is the first example of oxidative polymerization of fluorine-containing phenols. In relevant to this study, a fluorine-containing PPO derivative, poly(2,6-difluoro-1,4-fluorophenylene oxide), was recently synthesized by anionic polymerization of 5,7-difluoro-1-oxaspiro[2.5]octa-4,7-dien-6-one [17], whose synthesis needs tedious multi-step procedures.

EXPERIMENTAL

Materials

Fluorine-containing phenols were commercially available and used as received. HRP and SBP were purchased from Wako Pure Chemical Co. and Sigma Chemical Co., respectively. These enzymes were used without further purification.

Enzymatic Oxidative Polymerization of Fluorophenols

The following is a typical procedure for the polymerization (entry 3 in Table 1). Under air, 2,6-difluorophenol (0.65 g, 5.0 mmol) and HRP (10 mg) in

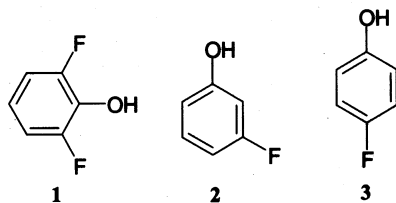


Chart 1.

TABLE 1. Peroxidase-Catalyzed Oxidative Polymerization of 2,6-Difluorophenol^a

Entry	Enzyme ^b	Solvent		Polymer		
		Organic Solvent	Buffer pH	Yield (%)	Mn ^c	Mw/Mn ^c
1	HRP (1)	Acetone	5	20	1000	2.5
2	HRP (10)	Acetone	3	26	1100	2.4
3	HRP (10)	Acetone	5	42	1500	2.1
4	HRP (10)	Acetone	7	31	1000	3.0
5	HRP (10)	Acetone	9	37	1100	2.7
6	HRP (10)	Acetone	11	33	1000	2.9
7	HRP (10)	Acetonitrile	5	33	1300	3.8
8	HRP (10)	2-Butanone	5	3	1100	1.9
9	HRP (10)	1,4-Dioxane	5	25	1200	2.3
10	HRP (10)	Ethanol	5	20	900	2.4
11	HRP (10)	Methanol	5	19	900	2.1
12	HRP (10)	Tetrahydrofuran	5	18	800	2.4
13	SBP (1)	Acetone	5	8	800	2.0
14	SBP (10)	Acetone	5	34	1100	3.1

^a Polymerization of 2,6-difluorophenol (5.0 mmol) using peroxidase catalyst in a mixture of organic solvent and buffer (60:40 vol%) at room temperature for 4 h under air.

^b In parenthesis, catalyst amount (mg).

^c Determined by SEC using THF eluent.

a mixture of 15 mL of acetone and 10 mL of 0.1 M acetate buffer (pH 5) were placed in a 50 mL flask. Hydrogen peroxide (10 % aq. solution, 1.7 mL, 5.0 mmol) was added dropwise to the mixture for 2 hours at room temperature under air. After 4 hours, the solvents were evaporated under reduced pressure and water (20 mL) was added to the residue. The water-insoluble part was collected by filtration and dried in vacuo. The obtained materials were dissolved in a small amount of THF and the solution was poured into a large amount of hexane to give 0.28 g of the polymer (yield 42%).

Measurements

Size exclusion chromatographic (SEC) analysis was carried out using a Tosoh SC8010 apparatus with a refractive index (RI) detector under the following conditions: two TSK gel α -M columns and DMF containing 0.09 M LiCl eluent with a flow rate of 1.0 mL/min at 60°C or TSKgel G3000HHR column and tetrahydrofuran (THF) eluent with a flow rate of 1.0 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 or Horiba FT-720 spectrometer. Contact angle was measured by a Kyowa Interface Science CA-A goniometer. DSC measurement was made at a 10°C/min heating rate under argon or nitrogen using a Mac Science DSC 3200 or Seiko SSC/5200 differential scanning calorimeter calibrated with an indium reference standard.

RESULTS AND DISCUSSION

Peroxidase-Catalyzed Oxidative Polymerization of 2,6-Difluorophenol

At first, the polymerization of 2,6-difluorophenol (**1**) was carried out using HRP catalyst (10 mg) in a mixture of acetone and pH 5 acetate buffer (60:40 vol%) for 4 hours at room temperature under air. During the polymerization, polymeric precipitates were formed. After the polymerization, water-insoluble part was isolated (84% yield), which was a mixture of orange and pale-yellow powders. In the chart of size exclusion chromatography (SEC), a bimodal peak was observed and the peak-top molecular weight of the low molecular weight part (17% of total peak area) was 194. By reprecipitation procedure using tetrahydrofuran (THF) and hexane as good and poor solvents, respectively, the pale-yellow polymer was isolated in 42% yield, during which the low molecular weight polymer soluble in hexane might be lost. The number-average molecular

weight and its index were 1500 and 2.1, respectively. The polymer was soluble in acetone, benzene, chloroform, N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and THF, partly soluble in methanol, and insoluble in hexane and water. The low molecular weight compound may be a diphenoquinone derivative, which is the para-para coupled product from **1**. In the HRP-catalyzed polymerization of 2,6-dimethylphenol, a diphenoquinone was also formed as by-product [14].

Figure 1(A) shows the buffer content versus polymer yield and molecular weight in a mixture of acetone and pH 5 acetate buffer. The polymer yield depended on the mixed ratio, although in all cases the water-insoluble product was formed in ca. 80% yield. In 40% buffer, the yield was the highest. The mixed ratio little affected the molecular weight. In a mixture of THF and the buffer (Figure 1(B)), the yield and molecular weight increased as a function of the buffer content. These data show that the polymerization behaviors in a mixture of acetone and the buffer were different with those in the aqueous THF. This might be because the solvent composition affected the HRP activity and coupling selectivity.

Polymerization results are summarized in Table 1. The effect of the buffer pH was examined in a mixture of acetone and buffer (60:40 vol%). In using the pH 5 buffer, the yield and molecular weight were the largest (entries 2-6). Interestingly, the mixture of acetone and pH 3 buffer produced the polymer

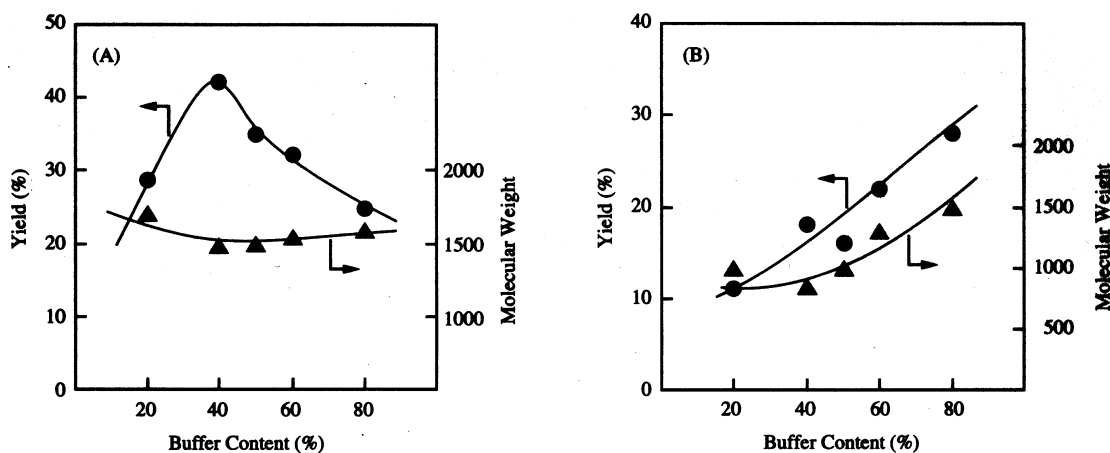


Figure 1. Buffer content versus polymer yield and molecular weight in HRP-catalyzed polymerization of 2,6-difluorophenol in a mixture of pH 5 acetate buffer and (A) acetone and (B) THF.

(entry 2); no polymer formation was observed from 2,6-dimethylphenol under the similar reaction conditions [14].

The polymerization proceeded in a mixture of various organic solvents and pH 5 acetate buffer (60:40 vol%). Among the solvents examined, acetone afforded the polymer of the highest molecular weight in the highest yield (entry 3). The polymerization in aqueous alcohols produced the polymer with lower molecular weight (entries 10 and 11). 2-Butanone was not suitable as cosolvent for the present polymerization (entry 8).

In using a smaller amount of HRP (1 mg), the yield and molecular weight decreased (entry 1). Besides HRP, soybean peroxidase (SBP) induced the polymerization of **1**, however, the catalytic activity for the polymerization was lower than that of HRP (entries 13 and 14). The polymerization did not take place by *Pycnoporus coccineus* laccase catalyst, which was reported to be active for the PPO synthesis from 2,6-dimethylphenol [14].

Enzymatic Polymerization of Fluorophenols

Next, the HRP-catalyzed oxidative polymerization of 3- and 4-fluorophenols (**2** and **3**, respectively) has been examined in an aqueous organic solvent. During the polymerization, observed was the formation of the polymeric precipitates, which were collected by centrifugation. The resulting polymers from **2** and **3** were soluble in chloroform, DMF, DMSO, and THF, and insoluble in hexane and water. In case of the polymerization of **2** or **3**, diphenoquinone derivatives were not formed. Polymerization results are summarized in Table 2. In the polymerization using 1 mg of HRP in an equivolume mixture of methanol and pH 7 phosphate buffer, the polymer was obtained in low yields (entries 1 and 7). Under similar conditions, 3-methylphenol (m-cresol) produced the polymer quantitatively and the yield of the polymer from 3-chloro or bromophenol was larger than that from **2** or **3** (entries 9-11) [18].

In the case of **2**, the polymer yield greatly improved by using 5 mg of HRP (entry 4). On the other hand, the slight increase of the yield was observed in the polymerization of **3** under the similar reaction conditions. The effect of the solvent composition was examined in the polymerization of **2** using 5.0 mg of HRP as catalyst. When the methanol content was 30 or 70%, the polymer yield decreased enormously (entries 3 and 5). In an equivolume mixture of acetone or isopropanol and the buffer, the polymer was formed in high yields, however, the polymer was partly insoluble in THF (entries 2 and 6).

In order to explore the effects of the substituent of 3-substituted phenols on the enzymatic polymerizability, HOMO level of the monomer was calculated

TABLE 2. Peroxidase-Catalyzed Oxidative Polymerization of Fluorophenols^a

Entry	Monomer	HRP Amount (mg)	Solvent		Polymer		
			Organic Solvent	Buffer Content (%)	Yield (%)	Mn ^b	Mw/Mn ^b
1	2	1	Methanol	50	16	860	1.4
2	2	5	Acetone	50	91	870 ^c	1.7 ^c
3	2	5	Methanol	30	7	980 ^c	1.7 ^c
4	2	5	Methanol	50	90	940	1.5
5	2	5	Methanol	70	20	830 ^c	1.5 ^c
6	2	5	Isopropanol	50	100	950 ^c	2.3 ^c
7	3	1	Methanol	50	25	700	2.6
8	3	5	Methanol	50	37	640	2.6
9 ^d	3-Chlorophenol	1	Methanol	50	58	1200	1.4
10 ^d	3-Bromophenol	1	Methanol	50	51	990	1.5
11 ^d	3-Methylphenol	1	Methanol	50	97	1500	2.3

^a Polymerization of phenol derivative (5.0 mmol) using HRP catalyst in a mixture of organic solvent and pH 7 phosphate buffer at room temperature for 3 h under air.

^b Determined by SEC using THF eluent.

^c Data of THF-soluble part.

^d Data from ref. 18.

by MOPAC - AM1 programs (Table 3). The HOMO level is considered to be strongly correlated with the oxidizing reactivity. The HOMO level of **2** is close to 3-chloro or bromophenol and larger than that of 3-methylphenol, the tendency of which agrees with that of the oxidative polymerizability of these monomers (Table 2); the calculation results show that the phenol monomer having electron-drawing group had a lower polymerizability due to the low HOMO level (high oxidation-reduction potential) [18].

Structural Analysis

It was reported that the new bond formation between the monomers took place at the halogen-substituted position involving the elimination of the halogen substituent in the oxidative polymerization of phenol derivatives using the copper/amine catalyst. For example, 4-bromo-2,6-dimethylphenol was subjected to the oxidative coupling by this catalyst to give PPO [19].

The elemental analysis results of the polymers are shown in Table 4. In all cases, the observed fluorine content was smaller than the calculated one. In particular, elimination of fluorine extensively occurred in the polymerization of **3**. Matrix-assisted laser desorption/ionization - time of flight mass (MALDI-TOF MS) spectroscopic analysis of poly(**1**) supports the elimination of fluorine atom (data not shown).

TABLE 3. HOMO Level of 3-Substituted Phenols

compound	HOMO (eV)
2	-9.32
3-chlorophenol	-9.30
3-bromophenol	-9.34
3-methylphenol	-9.03

^a Calculated by MOPAC program using the AM1 method.

TABLE 4. Elemental Analysis of Polyphenols

Sample		C	H	F ^a
Poly(1) (entry 3 in Table 1)	Calcd	56.25	1.57	29.68
	Found	56.73	2.23	25.28 (85 %)
Poly(2) (entry 4 in Table 2)	Calcd	65.46	2.75	17.26
	Found	62.37	2.54	14.83 (86 %)
Poly(3) (entry 8 in Table 2)	Calcd	65.46	2.75	17.26
	Found	68.70	3.54	7.86 (46 %)

^a In parenthesis, the residual ratio of fluorine atom based on the calculated value.

Polymer structure was examined by using IR and NMR spectroscopies. Figure 2 shows IR spectra of **1** and poly(**1**). A broad peak centered at 3400 cm⁻¹ due to the vibration of O-H linkage of phenolic group became much smaller after the polymerization. A strong peaks at 1108 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 [17]. Intensity of a peak at 767 cm⁻¹ due to the out-of-plane vibration of C-H linkage of 1,2,3-trisubstituted benzene greatly decreased and a new peak at 849 cm⁻¹ due to the vibration of C-H linkage of 1,2,3,5-tetrasubstituted benzene appeared. These data suggest that the polymer was mainly of 2,6-difluoro-1,4-oxyphenylene unit.

¹³C NMR of poly(**1**) exhibited complex peak patterns; main peaks were seen at δ 100, 112, 127, 156, and 158. These peaks except the peak at δ 112 are ascribed to carbons of poly(2,6-difluoro-1,4-phenylene oxide) [17]. In the ¹H NMR spectrum of poly(**1**), multiplet peaks were observed in δ 6.6-7.8. From these data, it was suggested that beside 1,4-oxyphenylene unit, other units with complex structure are contained in the polymer, which might be formed by elimination of fluorine atom. In the case of poly(**2**) and poly(**3**), their IR spectra were similar to those of polyphenols from other m- and p-substituted derivatives, indi-

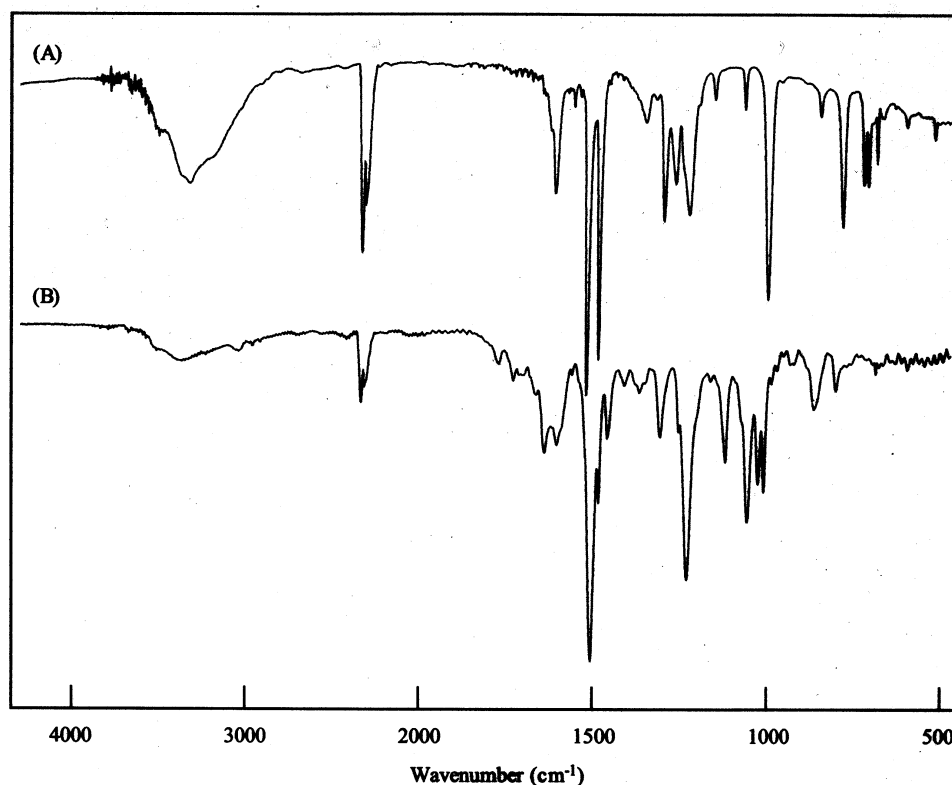


Figure 2. FT-IR spectra of **1** and poly(**1**).

cating that the polymers were of a mixture of phenylene and oxyphenylene units [18, 20].

Water Repellent and Thermal Properties

The contact angle of a water droplet on the film was measured by the means of a goniometer. The film was prepared by solvent casting on glass plate. In the case of poly(**1**) obtained by using HRP catalyst in an equivolume mixture of acetone and pH 5 acetate buffer, the contact angle was 101° , indicating the good water repellent property of poly(**1**). From poly(**2**) and poly(**3**), the film formation was not achieved.

Glass transition temperature (T_g) and melting point (T_m) were determined by differential scanning calorimetry (DSC) under argon or nitrogen. In the second scan of DSC, T_g was observed at 79 and 192°C for poly(**1**) obtained by HRP in a mixture of acetone and pH 5 acetate buffer (40:60 vol%) and for

poly(2) (entry 4 in Table 2), respectively, whereas poly(3) possessed no clear T_g below 250°C. In all polymers, T_m was not detected.

CONCLUSION

Peroxidase catalysis has achieved the oxidative polymerization of fluorine-containing phenols having low oxidative reactivity for the first time to give a new class of fluoropolymers. During the polymerization, fluorine atom was partly eliminated. In the polymerization of 2,6-difluorophenol, the resulting polymer mainly consisted of 2,6-difluoro-1,4-oxyphenylene unit and showed good water repellent property. The polymer from 3- or 4-fluorophenol was of a mixture of phenylene and oxyphenylene units. Further investigations on coating applications of the present fluorine-containing polyphenols are under way in our laboratory.

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