

Synthesis of a soluble polyphenol by oxidative polymerization of bisphenol-A using iron-salen complex as catalyst

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Summary

A soluble polyphenol was synthesized by oxidative polymerization of bisphenol-A using iron(III)-salen and hydrogen peroxide as catalyst and oxidizing agent, respectively. The addition of pyridine increased the yield and molecular weight of the polymer. NMR and IR analysis showed that the polymer was composed of a mixture of phenylene and oxyphenylene units. The iron-salen also induced the polymerization of phenol, m-cresol, and p-t-butylphenol.

Introduction

Enzymatic syntheses of polyaromatics using oxidoreductase as catalyst have been extensively developed for the last decade (1-4). Peroxidases induced an oxidative polymerization of various phenol derivatives (5-10), yielding a new class of polyphenols showing high thermal stability. Furthermore, this enzymatic process is expected to be an alternative way for preparation of phenol polymers without use of toxic formaldehyde, which is a monomer for production of conventional phenolic resins (phenol-formaldehyde resins). In the peroxidase-catalyzed polymerization of a phenol derivative having methacryloyl group, the phenolic moiety was chemoselectively polymerized to give a polymer having the methacryloyl group in the side chain (11). The enzymatic polymerization of 3,5-dimethoxy-4-hydroxybenzoic acid (syringic acid) involved the elimination of hydrogen and carbon dioxide from the monomer to give poly(1,4-oxyphenylene) having a carboxylic acid group at one end and a phenolic group at the other (12,13). Interestingly, conventional chemical oxidation catalysts did not induce the polymerization of syringic acid.

The biocatalytically synthesized polyphenols often showed low solubility toward organic solvents, which restricts their applications as polymeric materials. Recently, the solubility of the polyphenols improved by changing the solvent composition; a phenolic oligomer showing high solubility toward methanol, acetone, DMF, and DMSO was obtained by using an aqueous methanol solvent in the peroxidase-catalyzed polymerization of bisphenol-A and m-substituted phenols (14,15). The resulting polymers consisted of a mixture of phenylene and oxyphenylene units.

Very recently, we have found that iron - N,N'-ethylenebis(salicylideneamine)

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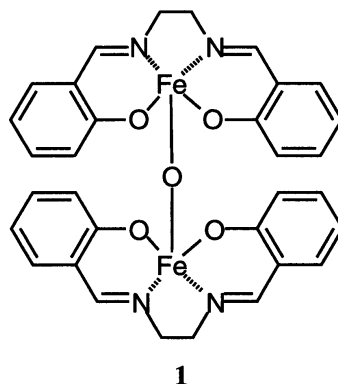
(salen) complex (**1**, Fe-salen complex) efficiently catalyzed an oxidative polymerization of 2,6-dimethylphenol to give poly(phenylene oxide) (16). We regarded **1** as model complex of peroxidase having a heme as catalytic active site. This study deals with the oxidative polymerization of bisphenol-A using **1** as catalyst to produce the soluble polyphenol.

Results and discussion

The oxidative polymerization of bisphenol-A was performed by using Fe(III)-salen (**1**) and hydrogen peroxide as catalyst and oxidizing agent, respectively, at room temperature under air. As a polymerization solvent, 1,4-dioxane was used since it shows high solubility toward poly(bisphenol-A) and is miscible with aqueous hydrogen peroxide solution. By the addition of hydrogen peroxide, the reaction solution turned dark-red and the reaction mixture was homogeneous during the polymerization. This is in contrast with our previous study on the peroxidase-catalyzed polymerization of bisphenol-A; the polymer precipitates were formed in the initial stage of the polymerization since the product polymer was insoluble in the reaction medium (a mixed solvent of buffer and water-miscible organic solvents such as methanol, acetone, and 1,4-dioxane) (14). After 3 h, the products were isolated by pouring the reaction mixture into a large amount of aqueous methanol (water/methanol = 50/50 (vol %)) to give the powdery polymer (yield 45 %). The polymer was soluble in polar organic solvents, i.e., chloroform, tetrahydrofuran (THF), methanol, acetone, and N,N-dimethylformamide. The polymer molecular weight and its index estimated by size exclusion chromatographic (SEC) analysis using THF eluent were 2700 and 2.4, respectively.

It is reported that the oxidative polymerization of 2,6-dimethylphenol catalyzed by **1** afforded poly(phenylene oxide) along with a byproduct dimer of 3,5,3',5'-tetramethyl-4,4'-diphenylquinone, and the addition of pyridine efficiently suppressed the formation of the dimer and greatly improved the polymer yields (16). Thus, the polymerization of bisphenol-A by **1** was performed in the presence of small amount of pyridine (0.020 mL per 1.0 mmol of the monomer) to give the polymer with molecular weight of 3400 in 69 %. These data indicate that the yield and molecular weight increased by the addition of pyridine. The role of the pyridine may be explained as follows. Bisphenol-A is neutralized in situ by pyridine to produce a phenoxy anion having higher reactivity for oxidative couplings, which polymerizes by **1** to give the polymer in a higher yield.

Polymerization results are summarized in Table 1. The polymerization also proceeded in dimethoxyethane and THF. In all solvents, the yield and molecular weight values of the polymer obtained in the presence of pyridine were larger than those without pyridine. In using 1,4-dioxane, both values were the largest, indicating that 1,4-dioxane was the most suitable for the oxidative polymerization of bisphenol-A by **1**. In this study, a very small amount of the catalyst (0.10 mol % for the monomer) afforded the polymer in moderate yields, showing the efficient catalysis of **1** for the bisphenol-A



polymerization.

Table 1. Oxidative polymerization of bisphenol-A catalyzed by **1**^a

Entry	Solvent	Pyridine (mL)	Yield (%)	Mn ^b	Mw/Mn ^b
1	Dimethoxyethane	0	18	2400	2.0
2	Dimethoxyethane	0.10	42	2800	2.1
3	1,4-Dioxane	0	45	2700	2.4
4	1,4-Dioxane	0.10	69	3400	2.9
5	THF	0	36	1800	1.7
6	THF	0.10	45	2200	1.8

^a Polymerization of bisphenol-A (5.0 mmol) catalyzed by **1** (5.0 μmol) using hydrogen peroxide (5.0 mmol) in organic solvent (10 mL) at room temperature for 3 h under air. ^b Determined by SEC using THF eluent.

Polymer structure was confirmed by ¹H NMR and IR spectroscopies. In the ¹H NMR spectrum, there were four broad peaks: δ 1.5 due to the methyl protons, δ 6.5 ascribed to the aromatic protons of ortho position, δ 6.9 due to the meta aromatic protons, and δ 9.1 due to the phenolic protons. Figure 1(A) shows IR spectrum of the polymer (entry 4). Observed were a broad peak centered at 3400 cm⁻¹ due to the vibration of O-H linkage of phenolic group, peaks at 1218 and 1177 cm⁻¹ ascribed to the asymmetric vibrations of the C-O-C linkage and to the C-OH vibration, and a peak at 1115 cm⁻¹ due to the symmetric vibration of the ether. The spectrum pattern of the resulting polymer was similar to that obtained by using soybean peroxidase catalyst (Figure 1(B)). These data show that the present polymer is composed of a mixture of phenylene and oxyphenylene units.

Fe-salen catalyst induced the polymerization of p-t-butylphenol in 1,4-dioxane in the presence of pyridine to give the soluble polymer with molecular weight of 2200 in 83 %

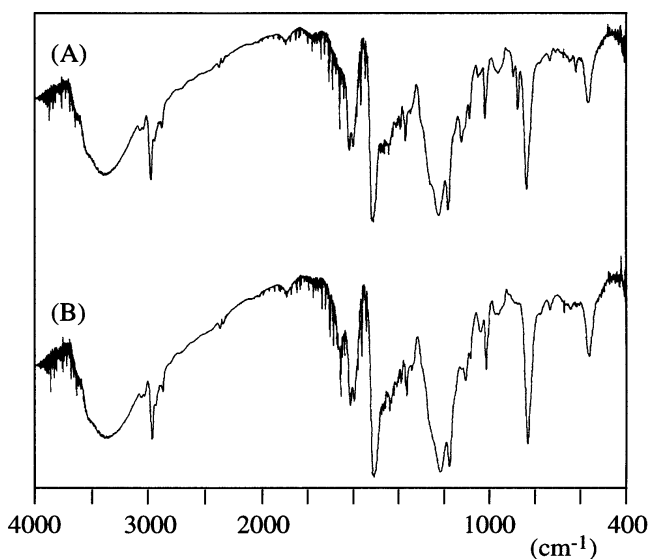


Figure 1 IR spectra of poly(bisphenol-A) prepared by using (A) **1** and (B) soybean peroxidase as catalyst.

yield. Phenol and m-cresol were also polymerized under the similar reaction conditions to give the polymer showing low solubility toward organic solvents.

In conclusion, Fe-salen complex was found to be an efficient catalyst for the synthesis of soluble poly(bisphenol-A) consisting of a mixture of phenylene and oxyphenylene units. The addition of pyridine increased the polymer yield and molecular weight. Further investigations on the oxidative polymerizations of various phenol derivatives by metal-salen complexes are under way in our laboratory.

Experimental part

Materials

Fe-salen complex (**1**) was synthesized according to the literature (17). Other reagents and solvents were commercially available and used as received.

Oxidative polymerization of bisphenol-A

A typical run was as follows (entry 4 in Table 1). Bisphenol-A (1.14 g, 5.0 mmol), **1** (3.3 mg, 5.0 μ mol) and pyridine (0.10 mL) in 10 mL of 1,4-dioxane were placed in a 50 mL of flask. 5.0 % Hydrogen peroxide (3.4 mL, 5.0 mmol) was added dropwise for 1 h at room temperature. The mixture was stirred under air. After 3 h, the reaction mixture was poured into a large amount of an equivolume mixture of methanol and water. The precipitates were separated by centrifugation and washed with the aqueous methanol, following by drying in vacuo to give the polymer (0.79 g, 69 % yield).

Measurements

Size exclusion chromatographic (SEC) analysis was carried out using a Tosoh SC8010 apparatus with a refractive index (RI) detector under the following conditions: TSKgel G3000H_{HR} column and tetrahydrofuran (THF) eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards. NMR spectra were recorded on a 400MHz Bruker DPX-400 spectrometer. IR spectra were recorded on a Horiba FT720 spectrometer.

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