Effect of Phenolic Monomer Structure of Precursor Polymers in Oxidative Coupling of Enzymatically Synthesized Polyphenols

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ABSTRACT: We have examined an oxidative coupling of various enzymatically synthesized polyphenols in DMF. Under selected substrate and catalyst concentration, soluble polymers with high molecular weight ($M_n > 10^5$) were obtained without formation of insoluble gels. The oxidative coupling behaviors between the precursor polymers and the corresponding phenolic monomers have been compared. The oxidative coupling of some precursor polymers proceeded more efficiently than the direct polymerization of the corresponding monomers. The structure of the starting monomers had a great influence on the oxidative coupling of the precursor polymers. The polymers from *o*- and *m*-substituted monophenols were subjected to the efficient oxidative coupling to give high molecular weight polymers quantitatively; on the other hand, the oxidative coupling of the polymers from *p*-substituted monophenols scarcely proceeded. Polymers from bisphenol and triphenol were also oxidatively polymerized, leading to the quantitative production of the high molecular weight polyphenols under the appropriate reaction conditions.

Introduction

Phenol−formaldehyde resins using prepolymers such as novolaks and resols are one of the most popular thermosetting polymers widely used in various industrial fields.[1] They show excellent toughness and temperature-resistant properties. However, toxic nature of formaldehyde involves problems in their manufacture and use. Therefore, an alternative process for preparation of phenolic polymers without using formaldehyde is strongly desired.

Oxidative polymerization of phenols is an environmentally benign synthetic process of polymeric materials, owing to excellent economy on atoms (normally, only water as byproduct), no use of toxic formaldehyde, and mild reaction conditions with low energy input. Thus, development of the oxidative coupling for production of phenolic polymers is highly expected to contribute to green polymer chemistry.[2,3] Poly(1,4-phenylene oxide) (PPO) is the representative polymer produced by the oxidative polymerization. PPO is one of the most typical engineering plastics and exhibits excellent properties such as shock resistance, electromagnetic shield performance, and thermal stability.[4] Except for PPO, there are little industrial products prepared by the oxidative polymerization of phenols, which may be because only 2,6-disubstituted phenols afford PPOs with high molecular weight and the polymerization of other phenols often produces insoluble products with uncontrolled structure.[5]

In the past decade, enzymatic syntheses of polyphenols have been investigated extensively.[3,6,7] Peroxidases were often used as catalyst for oxidative polymerization of a variety of phenol derivatives to produce a new class of polyphenols showing high thermal stability.[3,6] The enzymatically synthesized polyphenols are normally composed of a mixture of phenylene (Ph) and oxyphenylene (Ox) units, whose ratio can be precisely controlled by the nature of the reaction solvent and the monomer substituent.[8] This enzymatic process is highly anticipated to be a new synthetic method of phenolic polymers with facile procedures. In most of the polyphenols, however, the molecular weight is in the range of several thousand due to the precipitate formation during the polymerization. These lower molecular weight polymers may limit their applications for structural materials.

We developed a new catalyst for oxidative polymerization of phenols;[9] iron *N*,*N*′-ethylenebis(salicylideneamine) (Fe-salen) efficiently catalyzed the oxidative polymerization of various phenol derivatives, yielding high-performance polymeric materials.[10] Fe-salen can be regarded as a mimic of peroxidases. We found that Fe-salen was also an efficient catalyst for the intermolecular oxidative coupling of phenol-containing polymers.[11−13] A new class of soluble high molecular weight poly(amino acid)s were prepared by the oxidative coupling of poly(glutamine) and poly(asparagine) derivatives having a phenol moiety in the side chain.[11]

Very recently, we have achieved synthesis of ultrahigh molecular weight polyphenols by the oxidative coupling of enzymatically synthesized poly(*m*-cresol) and poly(bisphenol A) using Fe-salen as catalyst.[12] Under selected conditions, the soluble product was quantitatively obtained without the formation of the cross-linked insoluble gels, and the molecular weight reached 6 × 10^6. Light scattering analysis showed that the resulting polymer had a spherical structure with densely branched three-dimensional topology in solution. In this study, we have systematically examined the oxidative coupling behaviors of various precursor polyphenols (Scheme 1) in order to elucidate relationships between the structure of starting phenolic monomers and oxidative coupling behaviors of the precursor polyphenols. The present study provides fundamental data for design of synthesis of soluble high molecular weight polymers by “polymerization of polyfunctional macromolecules”.[11]

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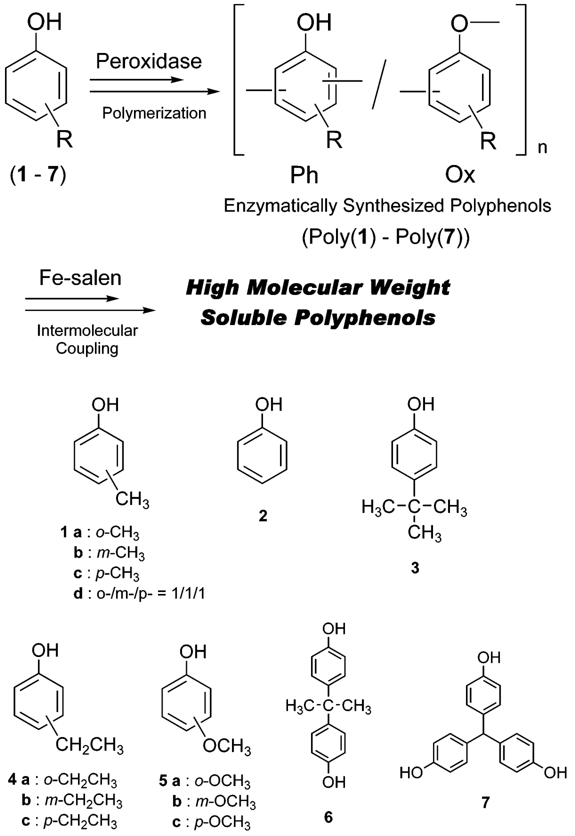
Scheme 1



Results and Discussion

Oxidative Coupling of Poly(cresol)s. Previously, we found the formation of an ultrahigh molecular weight polyphenol by the oxidative coupling of enzymatically synthesized poly(*m*-cresol) using Fe-salen catalyst.[12] In this study, we investigated the effect of the substituted position of cresol for the oxidative coupling of the precursor polyphenol. The precursor polymers were synthesized by the oxidative polymerization of *o*-cresol (**1a**), *m*-cresol (**1b**), *p*-cresol (**1c**), and an industrial product of cresol (**1d**; an almost equimolar mixture of *o*-, *m*-, and *p*-cresols) using horseradish peroxidase (HRP) in an equivolume mixture of methanol and phosphate buffer (pH 7): poly(*o*-cresol) (poly(**1a**); $M_n = 1.7 \times 10^3$, Ph/Ox = 43/57), poly(*m*-cresol) (poly(**1b**); $M_n = 2.5 \times 10^3$, Ph/Ox = 63/37), poly(*p*-cresol) (poly(**1c**); $M_n = 700$, Ph/Ox = 50/50), poly(cresol mixture) (poly(**1d**); $M_n = 1.0 \times 10^3$, Ph/Ox = 54/46). The oxidative coupling of the polyphenols was carried out using hydrogen peroxide as an oxidant in the presence of Fe-salen catalyst in *N*,*N*-dimethylformamide (DMF) at room temperature under air. A small amount of pyridine was added to the mixture for the efficient oxidative coupling.[11,12]

Generally, cross-linking preferentially takes place in polymerization of polyfunctional macromolecules. For example, poly(vinylphenol) was cross-linked by the oxidative coupling using the Fe-salen catalyst to give the insoluble gel.[13] In this study, the reaction conditions for the production of soluble polymers with high molecular weight from poly(cresols)s (poly(**1a**−**d**)) have been first screened. The molecular weight change of the reaction mixture was monitored by size exclusion chromatography (SEC). Table 1 summarizes the effects of the substrate and catalyst amount on the oxidative coupling of poly(**1a**−**d**).[14]

Table 1. Oxidative Coupling of Enzymatically Synthesized Poly(cresol)s[a]

entry	substrate[b]	Fe-salen (μmol)	product $M_n \times 10^{-3}$ [c]	product M_w/M_n [c]
1	poly(**1a**) (0.5)	1.0	2.4	3.6
2	poly(**1a**) (0.5)	2.5	280	1.3
3	poly(**1a**) (0.5)	5.0	*d*	*d*
4	poly(**1a**) (0.5)	5.0	*e*	*e*
5	**1a** (0.5)	5.0	640	1.9
6	**1a** (1.0)	10	*e*	*e*
7	poly(**1b**) (0.5)	1.0	3.0	4.5
8	poly(**1b**) (0.5)	2.5	190	1.8
9	poly(**1b**) (0.5)	5.0	420	1.7
10	poly(**1b**) (1.0)	5.0	*e*	*e*
11	**1b** (0.5)	5.0	5.6	12
12	**1b** (1.0)	10	*e*	*e*
13	poly(**1c**) (0.5)	1.0	1.8	1.3
14	poly(**1c**) (0.5)	2.5	2.7	1.8
15	poly(**1c**) (0.5)	5.0	2.7	2.1
16	poly(**1c**) (1.0)	5.0	3.5	2.4
17	**1c** (0.5)	5.0	0.9	2.3
18	**1c** (1.0)	10	1.1	2.9
19	poly(**1d**) (0.5)	1.0	1.4	2.7
20	poly(**1d**) (0.5)	2.5	4.8	10
21	poly(**1d**) (0.5)	5.0	110	1.7
22	poly(**1d**) (1.0)	5.0	180	1.8
23	**1d** (0.5)	5.0	2.2	3.2
24	**1d** (1.0)	10	4.3	28

[a] Oxidative coupling using Fe-salen complex and hydrogen peroxide (equimolar to phenol unit) as catalyst and oxidizing agent, respectively, in 0.4 vol % pyridine/DMF (2.5 mL) at room temperature under air. [b] In parentheses, phenol unit (mmol). [c] Determined by SEC using DMF as eluent with polystyrene standards. [d] Formation of insoluble product. [e] Gelation took place.

For poly(**1a**), poly(**1b**), and poly(**1d**), the precursor polymer was quantitatively consumed, and the molecular weight of the products increased with increasing the catalyst amount (Figure 1). Gelation took place in the higher substrate concentration of poly(**1a**) and poly(**1b**) (entries 4 and 10 in Table 1). In the case of poly(**1d**), the molecular weight increased as increasing the substrate concentration (entries 21 and 22). These data indicate that the oxidative coupling of the polyphenol takes place more efficiently in the higher concentration of the substrate due to the intermolecular reaction, resulting in the increase of the molecular weight or the gelation. Under selected conditions, the molecular weight reached larger than 10^5. On the other hand, the oxidative coupling of poly(**1c**) hardly took place; a slight increase of the molecular weight was observed (entries 13−16).

The oxidative coupling behavior of poly(**1b**) was monitored by SEC (Figure 2A). With the addition of hydrogen peroxide, poly(**1b**) was quantitatively consumed and the molecular weight of the coupling product gradually increased, supporting that the intermolecular oxidative coupling of poly(**1b**) proceeded efficiently. The FT-IR spectrum of the resulting coupling product was similar to that of poly(**1b**), suggesting that a small fraction of the phenolic moiety in poly(**1b**) was reacted with each other, yielding the high molecular weight polymer.

For comparison, the corresponding monomers **1a**−**d** were directly subjected to oxidative polymerization with Fe-salen catalyst. In all cases examined, the monomer was not quantitatively consumed. Figure 2B shows SEC traces of the oxidative polymerization of **1b** under the similar reaction conditions. The gradual increase of the molecular weight of the resulting polymer was observed; however, the final product contained a significant

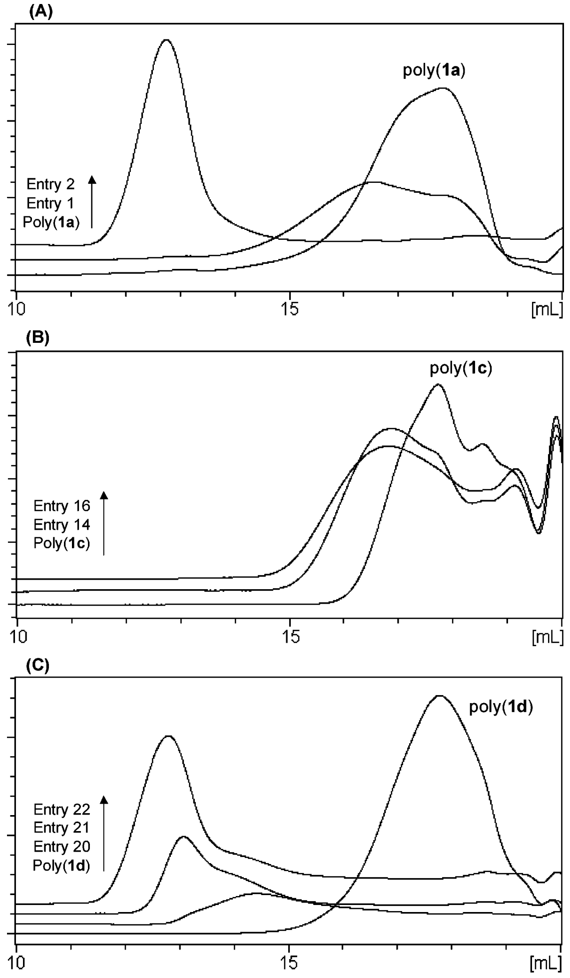


Figure 1. SEC traces of oxidative coupling products of (A) poly(**1a**), (B) poly(**1c**), and (C) poly(**1d**) under different reaction conditions shown in Table 1 with RI detector.

amount of the monomer and possessed very broad molecular weight distribution. These data strongly suggest that the intermolecular oxidative coupling of the enzymatically synthesized polyphenol was superior to the direct polymerization of the corresponding monomer for the production of high molecular weight polymers. For the cresol mixture, the polymer precursor was also suitable for the quantitative synthesis of the high molecular weight polyphenol in comparison with the monomer; on the other hand, the polymerization of **1a** efficiently produced the soluble high molecular weight polyphenol (entry 5). This may be due to the reactivity difference between the monomer and corresponding precursor polyphenol for the oxidative coupling.

Oxidative Coupling of Enzymatically Synthesized Polymers of Phenol and Monosubstituted Phenol Derivatives. Next, we performed the oxidative coupling of a variety of enzymatically synthesized polyphenols obtained from phenol and other monosubstituted phenol monomers. The influences of the monomer substituent and the position of the substituent on the coupling reactivity were investigated.

In the oxidative coupling of enzymatically synthesized poly(phenol) (poly(**2**); M_n = 3000, Ph/Ox = 38/62) obtained from nonsubstituted phenol (**2**), the precursor was quantitatively consumed, and the soluble high molecular weight polyphenol was obtained under the appropriate conditions (entry 2 in Table 2). Gelation was observed in the high concentration of the catalyst and substrate (entries 3 and 4). The oxidative polymerization of phenol proceeded in the high concentration of the catalyst to produce the high molecular weight polyphenol (entry 5).

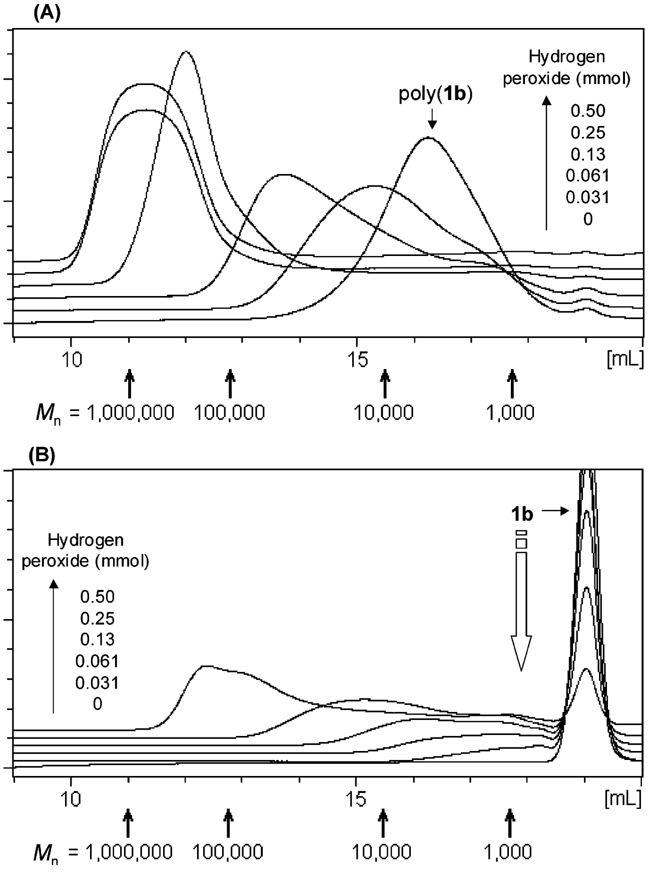


Figure 2. SEC traces of oxidative coupling products of (A) poly(**1b**) (entry 9 in Table 1) and (B) **1b** (entry 11 in Table 1) with RI detector.

In the oxidative coupling of poly(*p*-*tert*-butylphenol) (poly(**3**); M_n = 900, Ph/Ox = 81/19), the coupling hardly proceeded, and the high molecular weight polymer was not obtained even in the large amount of the catalyst (entries 7–9). A similar behavior was observed in the case of poly(**1c**). The soluble high molecular weight polymer was not also obtained from *p*-*tert*-butylphenol (**3**) by the oxidative coupling (entry 10).

Moreover, we prepared the polyphenols from all the isomers of ethylphenols (**4a**–**c**) and methoxyphenols (**5a**–**c**) and examined their oxidative coupling using the Fe-salen catalyst in DMF: poly(*o*-ethylphenol) (poly(**4a**); M_n = 1500, Ph/Ox = 45/55), poly(*m*-ethylphenol) (poly(**4b**); M_n = 2000, Ph/Ox = 72/28), poly(*p*-ethylphenol) (poly(**4c**); M_n = 700, Ph/Ox = 53/47), (poly(*o*-methoxyphenol) (poly(**5a**); M_n = 800, Ph/Ox = 44/56), poly(*m*-methoxyphenol) (poly(**5b**); M_n = 1400, Ph/Ox = 59/41), poly(*p*-methoxyphenol) (poly(**5c**); M_n = 700, Ph/Ox = 38/62). The oxidative coupling of poly(**4a**) was not performed, owing to the very low solubility toward DMF. Poly(**5a**) was quantitatively converted into the high molecular weight polymers by selection of the reaction conditions (entry 25), whereas the formation of the high molecular weight polymer was not found in the oxidative polymerization of **5a** under similar reaction conditions (entry 27). For poly(*m*-substituted phenol)s, the oxidative coupling of poly(**4b**) proceeded efficiently, similarly to that of poly(**1b**). In the oxidative coupling of poly(**5b**), the high molecular weight polymer was formed;

Table 2. Oxidative Coupling of Enzymatically Synthesized Polyphenols of Nonsubstituted and Monosubstituted Phenols[a]

entry	substrate[b]	Fe-salen (μmol)	product $M_n \times 10^{-3}$ [c]	product M_w/M_n [c]
1	poly(**2**) (0.5)	2.5	62	2.0
2	poly(**2**) (0.5)	5.0	120	1.9
3	poly(**2**) (0.5)	10	*d*	*d*
4	poly(**2**) (1.0)	5.0	*d*	*d*
5	**2** (0.5)	10	330	1.9
6	**2** (1.0)	10	*d*	*d*
7	poly(**3**) (1.0)	2.5	1.5	1.4
8	poly(**3**) (1.0)	5.0	2.4	2.3
9	poly(**3**) (1.0)	10	2.8	2.9
10	**3** (0.5)	10	1.8	1.6
11	poly(**4b**) (0.5)	1.0	4.0	2.8
12	poly(**4b**) (0.5)	2.5	6.4	6.3
13	poly(**4b**) (0.5)	5.0	700	2.3
14	poly(**4b**) (1.0)	5.0	*d*	*d*
15	**4b** (0.5)	10	7.3	32
16	**4b** (1.0)	10	*e*	*e*
17	poly(**4c**) (0.5)	1.0	1.4	1.8
18	poly(**4c**) (0.5)	2.5	1.8	2.4
19	poly(**4c**) (0.5)	5.0	2.6	2.5
20	poly(**4c**) (1.0)	5.0	3.5	2.8
21	**4c** (0.5)	10	1.5	2.0
22	**4c** (1.0)	10	1.8	2.8
23	poly(**5a**) (0.5)	1.0	78	3.6
24	poly(**5a**) (0.5)	2.5	170	2.6
25	poly(**5a**) (0.5)	5.0	470	2.6
26	poly(**5a**) (1.0)	5.0	*d*	*d*
27	**5a** (1.0)	10	1.3	7.8
28	poly(**5b**) (0.5)	1.0	2.6	2.3
29	poly(**5b**) (0.5)	2.5	3.7	4.0
30	poly(**5b**) (0.5)	5.0	160	1.8
31	poly(**5b**) (1.0)	5.0	48	4.2
32	poly(**5b**) (1.0)	10	*d*	*d*
33	**5b** (1.0)	10	5.0	28
34	poly(**5c**) (0.5)	1.0	1.0	1.5
35	poly(**5c**) (0.5)	2.5	1.2	1.6
36	poly(**5c**) (0.5)	5.0	0.8	1.9
37	poly(**5c**) (1.0)	5.0	1.2	2.0
38	**5c** (1.0)	10	0.7	1.7

[a] Oxidative coupling using the Fe-salen complex and hydrogen peroxide (equimolar to phenol unit) as catalyst and oxidizing agent, respectively, in 0.4 vol % pyridine/DMF (2.5 mL) at room temperature under air. [b] In parentheses, phenol unit (mmol). [c] Determined by SEC using DMF as eluent with polystyrene standards. [d] Gelation took place. [e] Formation of insoluble product.

however, poly(**5b**) was not quantitatively consumed. The oxidative polymerization behaviors of **4b** and **5b** (entries 15 and 33) were similar to that of **1b**. No significant increase of the molecular weight was observed in the oxidative coupling of poly(*p*-substituted phenol)s (poly(**4c**) and poly(**5c**)) as well as the corresponding *p*-substituted phenolic monomers.

Table 3. Oxidative Coupling of Enzymatically Synthesized Polyphenols of Bisphenol and Triphenol[a]

entry	substrate[b]	Fe-salen (μmol)	product $M_n \times 10^{-3}$ [c]	product M_w/M_n [c]
1	poly(**6**) (0.5)	1.0	11	3.0
2	poly(**6**) (0.5)	2.5	200	1.6
3	poly(**6**) (0.5)	5.0	350	1.6
4	poly(**6**) (1.0)	5.0	*d*	*d*
5	**6** (1.0)	5.0	33	9.2
6	poly(**7**) (1.0)	1.0	7.7	1.5
7	poly(**7**) (1.0)	2.5	18	2.7
8	poly(**7**) (1.0)	5.0	230	2.1
9	poly(**7**) (1.0)	10	*d*	*d*
10	**7** (1.0)	10	31	16

[a] Oxidative coupling using the Fe-salen complex and hydrogen peroxide (equimolar to phenol unit) as catalyst and oxidizing agent, respectively, in 0.4 vol % pyridine/DMF (2.5 mL) at room temperature under air. [b] In parentheses, phenol unit (mmol). [c] Determined by SEC using DMF as eluent with polystyrene standards. [d] Gelation took place.

Oxidative Coupling of Enzymatically Synthesized Poly(bisphenol) and Poly(triphenol). Besides polyphenols enzymatically obtained from nonsubstituted and monosubstituted phenol derivatives, we examined the oxidative coupling of the polyphenols of bisphenol A (**6**) and 4,4′,4″-trihydroxytriphenylmethane (**7**): poly(bisphenol A) (poly(**6**); $M_n = 3.8 \times 10^3$, Ph/Ox = 67/33) and poly(4,4′,4″-trihydroxytriphenylmethane) (poly(**7**); $M_n = 7.4 \times 10^3$, Ph/Ox = 63/37). Both polymers were subjected to the oxidative coupling, and the high molecular weight polyphenols were quantitatively obtained under selected conditions (Table 3). As described above, the oxidative coupling of poly(*p*-substituted phenol)s hardly proceeded; on the other hand, precursor polymers (poly(**6**) and poly(**7**)) obtained from *p*-substituted bisphenol and triphenol showed high reactivity toward the intermolecular oxidative coupling. This is probably because they contained an unreacted phenolic moiety (*p*-monosubstituted phenol), which was readily intermolecularly coupled with each other, yielding the high molecular weight polyphenols. In the direct oxidative polymerization of **6** and **7**, on the other hand, the monomers were not quantitatively consumed, and the molecular weight distribution values of the products were very broad (entries 5 and 10).

Conclusion

The oxidative coupling of various enzymatically synthesized polyphenols has been systematically investigated. The position of the substituent of starting phenol substrates greatly affected the oxidative coupling behaviors of the precursor polyphenol, and little effects of the nature of substituent were significantly observed. Enzymatically synthesized polyphenols from nonsubstituted phenol as well as *o*- and *m*-monosubstituted phenols were subjected to the oxidative coupling using the Fe-salen catalyst in DMF, and soluble polyphenols of high molecular weight ($M_n > 10^5$) were quantitatively obtained by the selection of the reaction conditions. Especially the concentrations of the substrate and catalyst were crucial parameters for the production of the soluble polymers without the gel formation. On the other hand, the polymers of *p*-monosubstituted phenols were not suitable precursors for the oxidative coupling. Interestingly, the intermolecular oxidative coupling of the precursor polymers of *p*-substituted bisphenol and triphenol efficiently proceeded (Figure 3). These data are highly useful for design and synthesis of soluble high molecular weight polyphenols by oxidative coupling. Further studies on development of new functional and useful polymers by oxidative coupling of phenol-containing polymers are under way in our laboratory.

Experimental Section

Materials. HRP and Fe-salen complex were purchased from Wako Pure Chemical Co. and Tokyo Kasei Inc., respectively, and used without further purification. Other reagents and solvents were commercially available and were used as received.

Enzymatic Oxidative Polymerization of Phenol Derivatives. The following is a typical procedure for the HRP-catalyzed oxidative polymerization.[15] Under air condition, *o*-cresol (**1a**) (0.54 g, 5.0 mmol) and HRP (1.0 mg) in a mixture of 12.5 mL of methanol and 12.5 mL of 0.1 M phosphate buffer

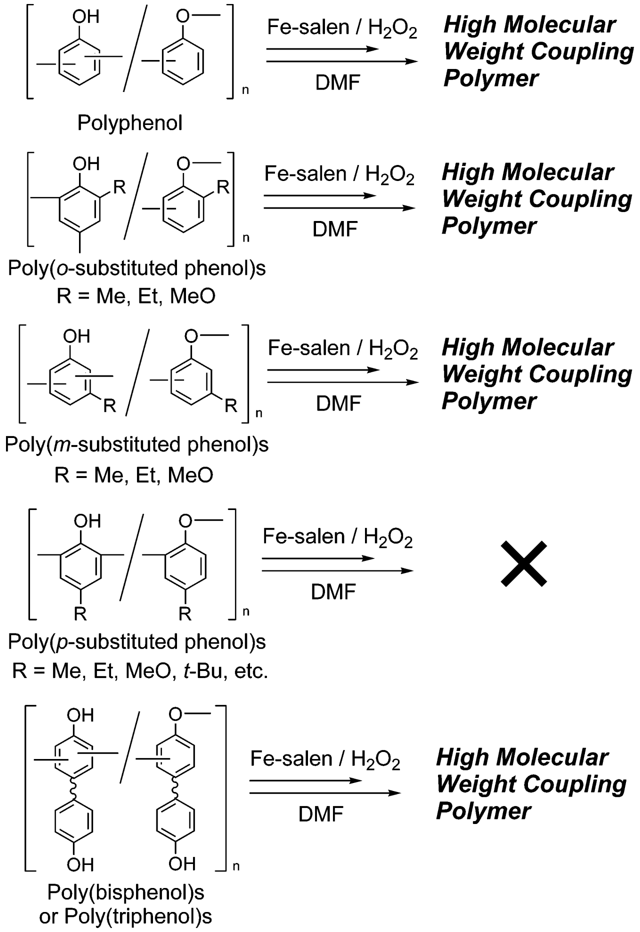


Figure 3. Summary of oxidative coupling of enzymatically synthesized polyphenols.

(pH 7) were placed in a 50 mL flask. Hydrogen peroxide (5% aqueous solution, 3.4 mL, 5.0 mmol) was added dropwise to the mixture for 2 h at room temperature under air. After 3 h, polymer precipitates were collected by centrifugation. The polymer was washed with an aqueous methanol (50:50 vol %), followed by drying in vacuo to give 0.50 g of the polymer (yield 93%). The ratio of phenylene/oxyphenylene units was 43/57, determined by titration of the residual phenolic group.

Oxidative Coupling of Enzymatically Synthesized Polyphenols by Fe-salen Catalysis. The following is a typical procedure for the oxidative coupling of enzymatically synthesized polyphenol (entry 2 in Table 1). A mixture of poly(**1a**) (54 mg, 0.50 mmol of phenol unit) and Fe-salen (0.8 mg, 2.5 μmol) was dissolved in DMF (2.5 mL) containing 10 μL of pyridine. The coupling was initiated by the addition of a quarter mole amount of hydrogen peroxide (30%) for poly(**1a**) under air. The same amount of hydrogen peroxide was further added three times more every 15 min. After 24 h, the reaction mixture was analyzed by SEC without purification.

Measurements. SEC analysis was carried out using a TOSOH GPC-8020 apparatus equipped with refractive index (RI) and UV detectors under the following conditions: TSKgel α-3000 and α-M columns; eluent: DMF containing 0.10 M LiCl; flow rate: 1.0 mL/min; temperature: 60 °C. The calibration curves for SEC analysis were obtained by using polystyrene standards.

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(14) It is to be noted that reproducibility of all reactions in Table 1 was very good; polymerization results of three experiments were close to each other.

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