Enzymatic Synthesis of Soluble Polyphenol

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Enzymatic oxidative polymerization of phenol using peroxidase as catalyst has been carried out in a mixture of alcohol and buffer. Hydrogen peroxide (oxidizing agent) was added dropwise to the reaction mixture. Effects of the reaction parameters have been systematically investigated. The polymer solubility strongly depended on the buffer pH and content, and a polymer soluble in *N,N*-dimethylformamide (DMF) was obtained in good yields under appropriate reaction conditions. The solvent composition also affected the regioselectivity of the polymer. Purity and amount of the enzyme also affected the polymerization behaviors. By changing the concentration and addition rate of hydrogen peroxide, the molecular weight and solubility of the polymer could be controlled. Some solid properties of the resulting polyphenol were evaluated. From thermal analysis, the polymer was found to possess relatively high thermal stability.

An enzyme-catalyzed polymerization ("enzymatic polymerization") has been developed as new methodology of polymer syntheses.[1—4] Characteristic properties of enzyme catalysts afforded novel polymerizations to produce polymeric materials, which are often difficult to synthesize by conventional polymerizations. Chemical synthesis of cellulose was first achieved by the polymerization of β-cellobiosyl fluoride in an aqueous acetonitrile catalyzed by cellulase,[5] which is a hydrolysis enzyme of cellulose in nature. This concept, which utilizes the reverse catalysis of a hydrolase enzyme for polymerization, has been applied to synthesis of natural and non-natural polysaccharides, e.g., xylan,[6] chitin,[7] and cellulose-xylan hybrid polymer.[8] Other hydrolases, lipases and proteases, provided aliphatic polyesters[9—14] and poly(amino acid)s,[15] respectively, via non-biosynthetic pathways.

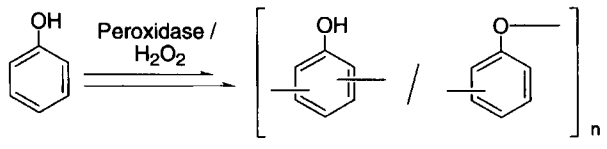
Peroxidases induced oxidative polymerization of phenol derivatives,[16—25] which afforded polyaromatics with novel structure. Furthermore, this process is expected to be an alternative for preparation of conventional phenolic resins without using formaldehyde.[26] We have found that the appropriate solvent composition afforded soluble polyphenols from bisphenol-A and *m*-substituted phenols.[24,25]

Phenol is the simplest and most important phenolic compound in industrial fields. The molecular weight and structural controls of the phenol polymerization had been very difficult since it has multi-reaction sites. For example, copper(I) chloride/amine catalyst, which was first used for the polymerization of 2,6-dimethylphenol to poly(oxy-1,4-phenylene),[27] gave only a black tarry material.[28] The oxidative polymerization in an aqueous 1,4-dioxane catalyzed by horseradish peroxidase (HRP) produced a new class of powdery polyphenols consisting of phenylene and oxyphenylene units in good yields (Scheme 1).[18,19] However, the solubility of the resulting polymer was low: only partly soluble in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Very recently, we have found that a mixed solvent of methanol and buffer afforded a polyphenol soluble in DMF from *unsubstituted phenol*.[29] The present paper describes comprehensive results of the soluble polyphenol synthesis.

Results and Discussion

Enzymatic Polymerization Using Crude Horseradish Peroxidase. In this study, peroxidase and hydrogen peroxide were used as a catalyst and an oxidizing agent, respectively. At first, the enzymatic oxidative polymerization of phenol was performed by using crude HRP (HRP-C) catalyst (10 unit per mg) in a mixture of methanol and phosphate buffer (pH 7) for 30 h at room temperature under air. Hydrogen peroxide (6%) was added dropwise to the reaction mixture for 25 h. Effects of enzyme amount and methanol content of the mixed solvent were systematically investigated (Fig. 1).

In all cases examined, powdery polymeric precipitates were formed during the polymerization. When the methanol content was 25 or 50%, the polymer yield increased as the enzyme amount increased. The quantitative polymer formation was achieved by the polymerization using 50 mg



Scheme 1.

Joint Research Center for Precision Polymerization (JRCPP) - Japan Chemical Innovation Institute (JCII), Higashi 1-1, Tsukuba 305-8565.

National Institute of Materials and Chemical Research (NIMC), Higashi 1-1, Tsukuba 305-8565, Japan.

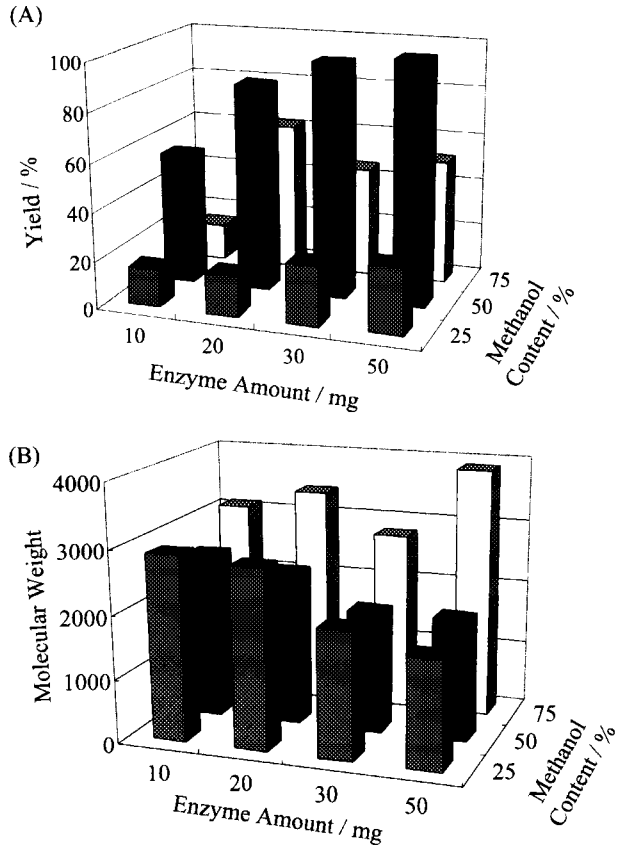


Fig. 1. Effects of reaction parameters on (A) polymer yield and (B) molecular weight in the oxidative polymerization of phenol catalyzed by HRP-C in a mixture of methanol and phosphate buffer (pH 7). The polymerization was performed using phenol (10.6 mmol) monomer at room temperature for 30 h under air.

of HRP-C in 50% methanol. In a series of the polymerizations in 75% methanol, 20 mg of HRP-C afforded the highest yield. The solubility of the resulting polymer toward DMF was dependent on the enzyme amount as well as on the methanol content. In using 25% methanol, the product was not completely soluble in DMF, whereas the polymerization in 75% methanol gave the soluble polymer. In case of 50% methanol, a small enzyme amount (10 or 20 mg) afforded the soluble polymer, and the formation of a small amount of DMF-insoluble part was found when a large amount of the enzyme (30 or 50 mg) was used. No structural difference between the soluble and insoluble polymers was found by FT-IR analysis. The formation of the insoluble polymer was probably due to the slight crosslinking,[19] which was not detected by FT-IR.

The molecular weight of the polymer was determined by size exclusion chromatography (SEC). When the sample was not completely soluble in DMF, the DMF-soluble part was used for SEC analysis. In most cases, a unimodal broad peak was observed. The number-average molecular weight was in the range of several thousands. When the methanol content was 25%, the molecular weight decreased as a function of the enzyme amount.

Results of the polymerization in a mixture of methanol and other buffers (pH 4, 5, and 8) are summarized in Fig. 2. The yield of the polymer obtained by using 50 mg of HRP-C was higher than that by using 10 mg of the enzyme. In most cases, the yield in 50% methanol was higher than that in 25 or 75% methanol. The polymerization in a mixture of methanol and buffer of pH 4 produced the polymer in lower yields than those obtained by using other buffers. The formation of the soluble polymer was observed in an equivolume mixture of methanol and buffer of pH 4, whereas a small amount of the insoluble polymer was obtained in 25 or 75% methanol.

In the case of the buffer of pH 5, 75% methanol produced the soluble polymer. The polymerization using 50 mg of HRP-C in 75% methanol quantitatively produced the polymer. When buffer pH was 8, the polymerization in the presence of the small amount of HRP-C (10 mg) gave the soluble polymer. The quantitative polymer formation was observed in the solvent of 50% methanol using 50 mg of HRP-C as catalyst, however, the resulting polymer contained a small amount of DMF-insoluble part. The polymerization in the presence of 50 mg of HRP-C in 75% methanol produced the soluble polymer. These data show that the polymer yield, molecular weight, and solubility strongly depended on the

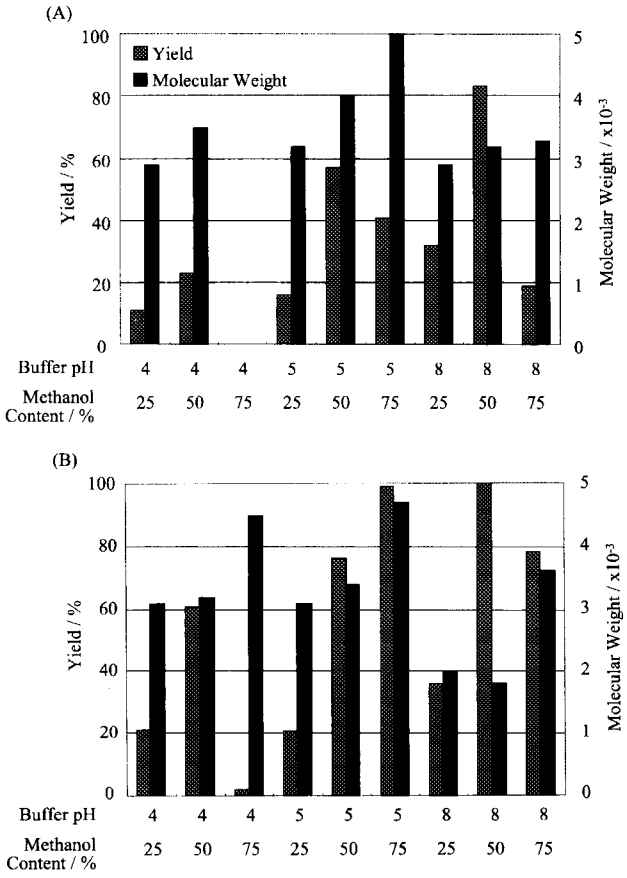


Fig. 2. Effects of buffer pH in the oxidative polymerization of phenol using HRP-C of (A) 10 mg and (B) 50 mg. The polymerization was performed using phenol (10.6 mmol) monomer in an aqueous methanol at room temperature for 30 h under air.

solvent composition. This might be because the solvent composition affected the formation of the monomer clusters[30] and/or the catalytic activity of HRP.

Figure 3 shows results of the polymerization in a mixture of methanol and distilled water (50 : 50 vol%). The polymer yield increased as the enzyme amount increased. The soluble polymer was obtained by using 10 mg of HRP-C; on the other hand, a small amount of DMF-insoluble part was formed in the enzyme amount of more than 20 mg. In all cases, the number-average molecular weight was approximately 3000. These data suggest that distilled water could be used as cosolvent, however, the buffer of pH 7 or 8 was superior to distilled water for the production of the soluble polyphenol.

The polymerization in a mixture of other water-miscible organic solvents and buffer (pH 7) (50 : 50 vol%) has been carried out by using 30 mg of HRP-C catalyst. Acetone, 1,4-dioxane, and tetrahydrofuran were used as organic solvents. In all cases, the polymer was quantitatively obtained; however, its solubility toward DMF was low (solubility of less than 30%). These data indicate that the enzyme amount and the solvent composition greatly affected the yield, molecular weight, and solubility of the polymer.

In the above experiments, hydrogen peroxide (6%) was added very slowly (25 h). Then, the drop time was shortened to 5 h (Fig. 4). The concentration of hydrogen peroxide was 6 or 30%. In using the low concentration of hydrogen peroxide, the polymerization results were almost the same as those obtained for the long drop time (Figs. 1 and 2). The polymerization using 30% of hydrogen peroxide under the similar reaction conditions also produced the polymer in good yields, furthermore, the high concentration of hydrogen peroxide improved the polymer solubility.

The resulting polymer was reported to be of a mixture of phenylene and oxyphenylene units.[18,19] In order to determine the unit ratio, the polymer was acetylated with acetic anhydride in the presence of excess pyridine.[29] The unit ratio was calculated from the ratio of the integrated areas of the peaks of acetyl and aromatic protons. The polymers obtained in

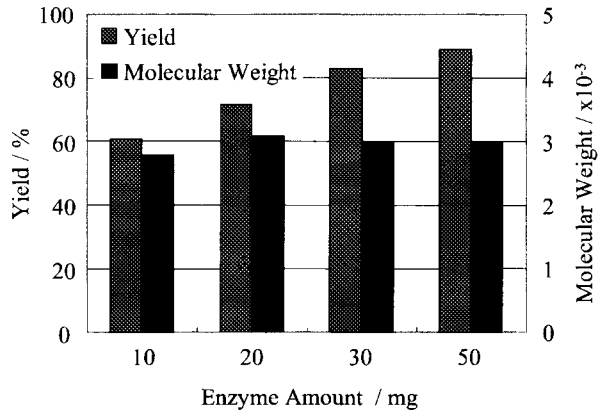


Fig. 3. Polymerization results using distilled water as cosolvent. The polymerization was performed using phenol (10.6 mmol) monomer in the presence of HRP-C catalyst in a mixture of methanol and distilled water at room temperature for 30 h under air.

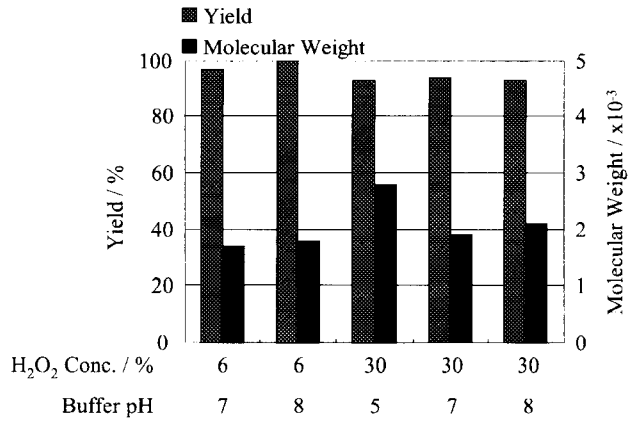


Fig. 4. Polymerization results for short reaction time. The polymerization was performed using phenol (10.6 mmol) monomer in the presence of HRP-C catalyst (50 mg) in an aqueous methanol at room temperature for 6 h under air.

a mixture of methanol and universal buffer were analyzed (Fig. 5).

In methanol/pH 6.9 buffer, the number of oxyphenylene units increased as a function of methanol content, varying in the range from 39 to 65%. A similar behavior was observed in pH 5.1 buffer. The effect of the buffer pH was relatively small; the number of oxyphenylene units slightly increased with increase of the pH value.

Enzymatic Polymerization Using Purified Horseradish Peroxidase. HRP-C used in the above experiments is of industrial grade; its catalytic activity is low (10 unit per mg). On the other hand, purified HRP (HRP-P), which we previously used as catalyst for the oxidative polymerization of phenol derivatives,[18,19] has high activity (220 unit per mg). Next, HRP-P was used as catalyst for preparation of the

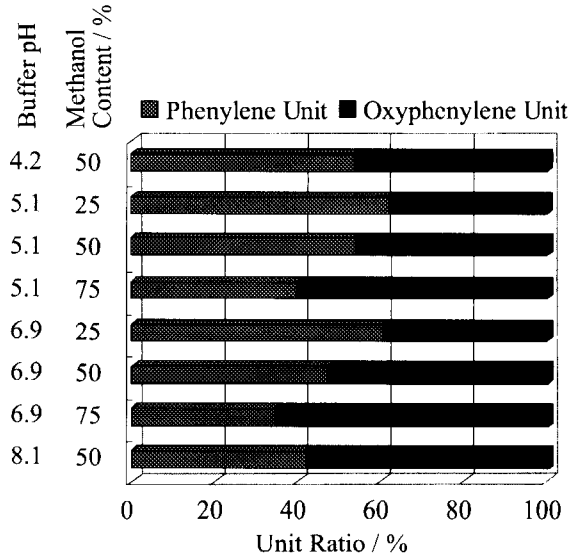


Fig. 5. Effects of solvent composition on the polymer structure. The polymerization was performed using phenol (10.6 mmol) monomer in the presence of HRP-C catalyst (50 mg) in a mixture of methanol and universal buffer at room temperature for 6 h under air.

soluble polyphenol (Fig. 6). The polymerization was carried out in an equivolume mixture of methanol and buffer.

In the polymerization catalyzed by HRP-P under the similar reaction conditions of Fig. 1, the polymer yield increased in comparison with that using the crude enzyme. For example, the polymer was quantitatively obtained by using 10 mg of HRP-P in a mixture of methanol and phosphate buffer (pH 7), however, the polymer solubility was very low. Therefore, the amount of HRP-P was reduced to 0.5 or 1.0 mg based on the catalytic activity. In the polymerization using 6% of hydrogen peroxide for 30 h in methanol/buffer (pH 7), the polymer was obtained in good yields and the lower enzyme amount (0.5 mg) afforded the soluble polymer.

Under the reaction conditions of the fast addition of hydrogen peroxide (5 h) as shown in Fig. 4, the polymerization using HRP-P catalyst also proceeded to give the phenolic polymer. The polymerization results using the low concentration of hydrogen peroxide (6%) in a mixture of methanol and buffer of pH 7 were almost the same as those obtained by the slow addition of hydrogen peroxide. When the buffer of pH 8 was used, the solubility of the resulting polymer became lower.

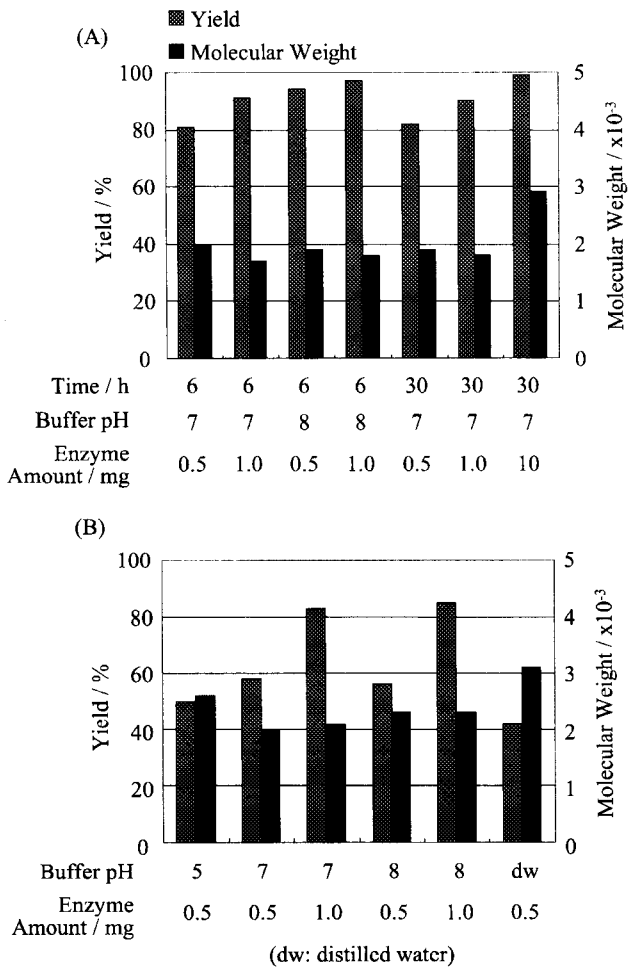


Fig. 6. Polymerization results by HRP-P catalyst using hydrogen peroxides of (A) 6% and (B) 30%. The polymerization was performed using phenol (10.6 mmol) monomer in the presence of HRP-P catalyst in an equivolume mixture of methanol and buffer at room temperature under air.

Next, the polymerization was carried out by using the high concentration of hydrogen peroxide for the short polymerization time. Buffers of pH 5, 7, and 8 as well as distilled water were used as cosolvent. It is to be noted that the soluble polymer was obtained in all cases; the soluble polymer was not obtained by using HRP-C catalyst in an equivolume mixture of methanol and acetate buffer of pH 5 under the slow addition of hydrogen peroxide. These data show that in some cases the purified enzyme was superior to the crude one for production of the soluble polyphenol, although cheaper HRP-C is more suitable for industrial applications.

Enzymatic Polymerization Using Soybean Peroxidase. Soybean peroxidase (SBP) was also reported to show high catalytic activity toward oxidative polymerization of various phenols.[22,24,25,31] In this study, the SBP-catalyzed polymerization was performed in a mixture of alcohol and buffer by using the high concentration of hydrogen peroxide for the short polymerization time. The catalytic activity of SBP was 52 unit per mg. The used unit amount of SBP was close to that of HRP shown in Figs. 1, 2, 3, 4, 5, and 6. Polymerization results are summarized in Fig. 7.

The polymerization in an equivolume mixture of methanol and buffer of pH 5 or 7 produced the soluble polymer. However, the yield was very low; most of the phenol remained unreacted. In the case of the polymerization using a mixed solvent of methanol and pH 7 phosphate buffer, the methanol content of 25 or 50% afforded the soluble polymer in low yields and 75% methanol did not afford the polymeric materials. These data mean that the catalytic activity of SBP in the aqueous methanol was much lower than that of HRP, although SBP catalysis also afforded the soluble polyphenol.

Instead of methanol, ethanol, and 2-propanol were used as cosolvent. It is to be noted that the equivolume mixture of these alcohols and the buffer of pH 7 produced the soluble polymer; under the similar reaction, HRP catalysis did not produce the polymer completely soluble in DMF (data not shown). This may be because of the difference of the catalytic activity between HRP and SBP in these aqueous alcohols. Molecular weight (8.0×10^3) was the highest when using the aqueous 2-propanol. The polymerization in 25% alcohol produced the polymer showing low solubility. In the 75% alcohol solution or use of pH 8 buffer, the SBP catalysis for the present polymerization was very low.

Polymerization Profile. As described above in Figs. 1 and 2, the alcohol content greatly affected the polymerization results; the maximum yield was observed in the equivolume mixture of alcohol and buffer. In order to examine such characteristic behaviors in detail, the polymerization using HRP-C catalyst in a mixture of methanol and a pH 7 phosphate buffer was monitored by using HPLC and SEC. Hydrogen peroxide (30%) was added for 5 h.

Figure 8 shows time-conversion curves in the methanol contents of 0, 25, 50, and 75%. The initial rates of the monomer consumption were not so different from each other. In 50% methanol, the conversion gradually increased as a

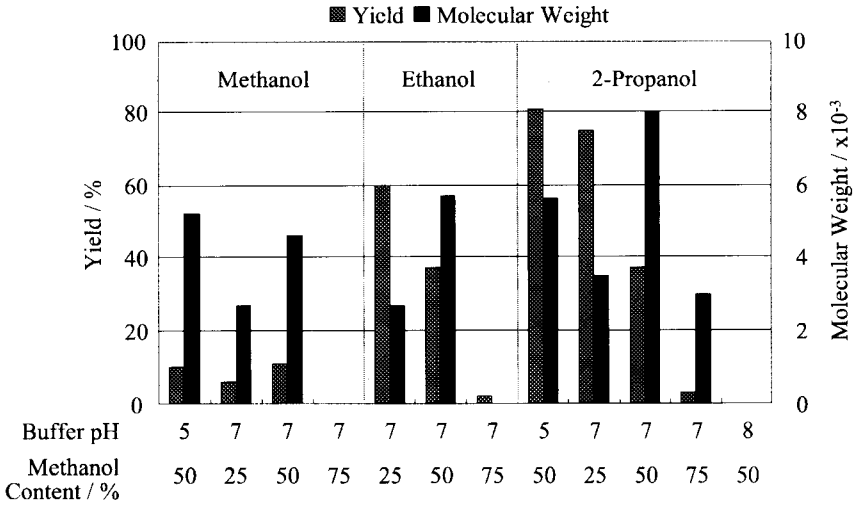


Fig. 7. Polymerization resuls using SBP catalyst. The polymerization was performed using phenol (10.6 mmol) monomer in the presence of SBP catalyst (5 mg) in a mixture of alcohol and buffer at room temperature for 6 h under air.

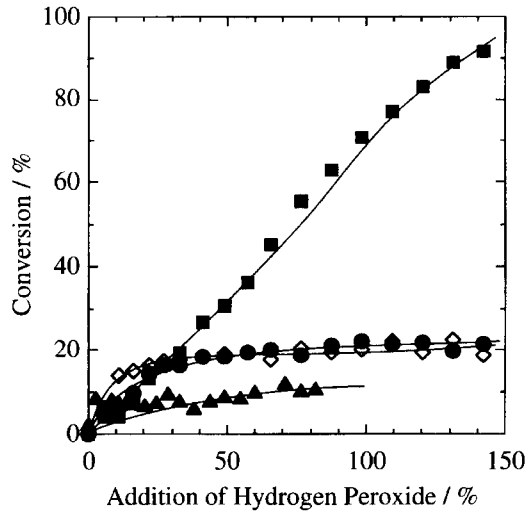


Fig. 8. Addition of hydrogen peroxide (in molar % toward phenol) – conversion curves in the HRP-catalyzed polymerization of phenol in the aqueous methanol solvent with different methanol contents: (▲) 0%; (●) 25%; (■) 50%; (◇) 75%. The polymerization of phenol (1.0 g) was carried out by using HRP-C (30 mg) catalyst in a mixture of methanol and pH 7 phosphate buffer at room temperature under air. Hydrogen peroxide (30%) was added dropwise to the reaction mixture for 5 h.

function of the added volume of hydrogen peroxide, whereas the monomer hardly reacted after the addition of hydrogen peroxide was beyond 30% in 25 or 75% methanol. In the sole use of the phosphate buffer, the monomer conversion did not increase after the initial stage of the polymerization (less than 10% hydrogen peroxide). Interestingly, it was reported that the catalytic activity of HRP in the buffer of pH 7 was much larger than that in the aqueous organic solvents.[32] This specific tendency of the reaction profiles in different solvent compositions agrees with the tendency of the polymerization results under the similar reaction conditions (Fig. 1).

Relationships between the monomer conversion and the polymer molecular weight in the equivolume mixture of methanol and pH 7 phosphate buffer are shown in Fig. 9. The molecular weight was almost constant during the polymerization. The monomer conversion was very close to the polymer yield (data not shown). These data indicate that there were few oligomers soluble in the reaction medium during the polymerization, which was confirmed by HPLC analysis. This may be explained as follows: The resulting soluble dimer and oligomers reacted much faster than the monomer and the precipitated polymer was not reacted any more during the polymerization. A similar behavior was observed in the HRP-catalyzed polymerization of *m*-cresol in an aqueous methanol solvent.[25]

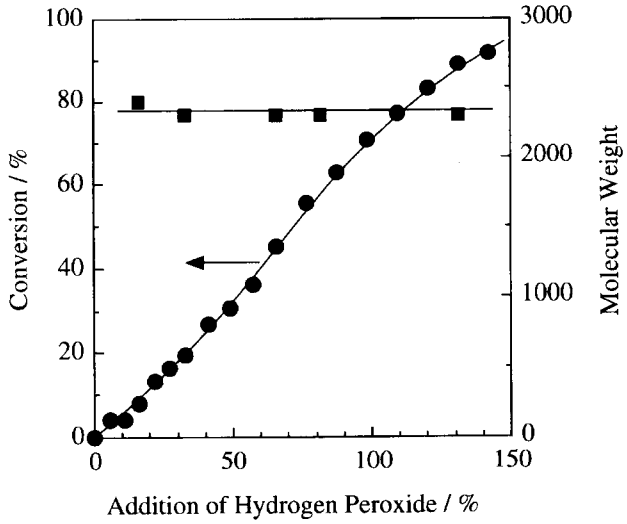


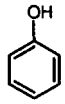
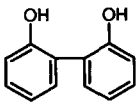
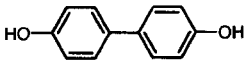
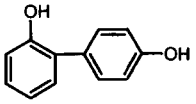
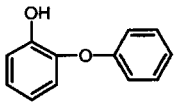
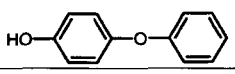
Fig. 9. Addition of hydrogen peroxide (in molar percent toward phenol) versus (●) monomer conversion and (■) polymer molecular weight. The polymerization of phenol (1.0 g) was carried out by using HRP-C (30 mg) catalyst in an equivolume mixture of methanol and pH 7 phosphate buffer at room temperature under air. Hydrogen peroxide (30%) was added dropwise to the reaction mixture for 5 h.

The oxidation reactivity of phenol and its dimers was estimated by their HOMO levels (Table 1). The HOMO level, which is shown as an indication of reactivity toward the oxidative coupling, was calculated by the Spartan set of programs using the AM1 programs. Based on the polymer structure, five dimers were postulated: carbon–carbon linked dimers and carbon–oxygen linked dimers. All dimers were detected by HPLC analysis of the initial reaction mixture. All the dimers calculated showed the higher HOMO level than phenol, supporting the higher reactivity of the dimers toward the oxidation polymerization than that of the monomer, resulting in the specific behaviors of the molecular weight change during the polymerization shown in Fig. 9.

Properties of Polyphenol. For evaluation of properties of the present polyphenol, preparative preparation was performed using HRP-P catalyst (1 mg for 1 g of phenol) with 30% hydrogen peroxide in an equivolume mixture of methanol and phosphate buffer (pH 7) to give the soluble polymer with a molecular weight of 2900.

Thermal properties of the enzymatically synthesized polyphenol were evaluated by using thermogravimetry (TG) and differential scanning calorimetry (DSC). Figure 10 shows the TG trace of the polyphenol. The measurement was performed under argon. In the first step, a slight gradual weight loss of the polymer (less than 10% of the weight loss) was observed below 160 °C. This may be due to the evaporation and/or evolution of low molecular compounds. Temperature at 10% weight loss of the polymer was 345 °C, which was somewhat lower than that obtained in a mixture of 1,4-dioxane and phosphate buffer (80 : 20 vol%).[19] The yield of the carbonized polymer at 1000 °C (50%) was larger than that obtained in the aqueous 1,4-dioxane.[19] The TG trace of the present soluble polymer was similar to that of the cured product of conventional phenolic resins (data not shown). These data indicate that the present polyphenol possessed relatively high thermal stability.

Table 1. HOMO Level of Phenol and Its Dimers[a)]

Compound	HOMO/eV
	−9.11
	−8.76
	−8.53
	−8.81
	−9.03
	−8.80

a) Calculated by the Spartan set of programs using the AM1 method.

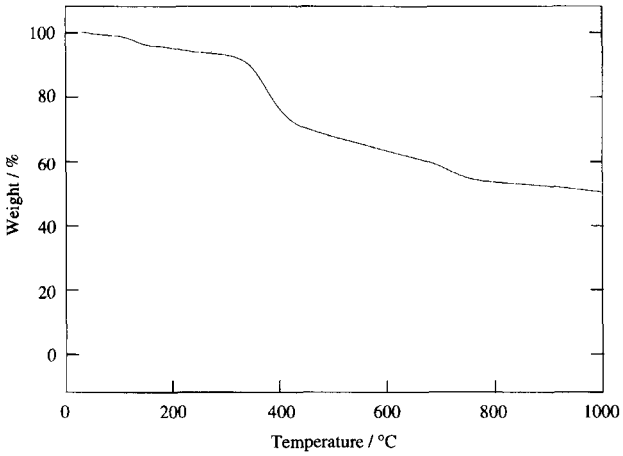


Fig. 10. TG trace of polyphenol measured under argon.

Figure 11 shows the DSC chart measured under nitrogen. In the chart of the first scan, an exothermic peak was observed at 206 °C, probably due to the crosslinking and/or branching of the polymer. There was no defined peak in the charts of the second scan. These data indicate that the present polyphenol exhibited no clear glass transition temperature (T_g) or melting point below 300 °C. A similar phenomenon was observed in the polyphenol obtained in the aqueous 1,4-dioxane.[19] As to conventional phenol resins, T_g of liquid resoles is below room temperature and that of lightly crosslinked phenolics is in the range from 150 to 225 °C.[26] Therefore, the absence of T_g may be one of the characteristic properties of the enzymatically synthesized phenolic resin.

Table 2 summarizes other solid properties of the polyphenol. The obtained values are close to those of commercially available phenol resins (novolak and resol resins).[33] The volume resistivity of the present polyphenol was much smaller than that of poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) or polyethylene (> 10^{14}), whereas the reverse tendency was observed in dielectric constant and dissipation factor (ε' and

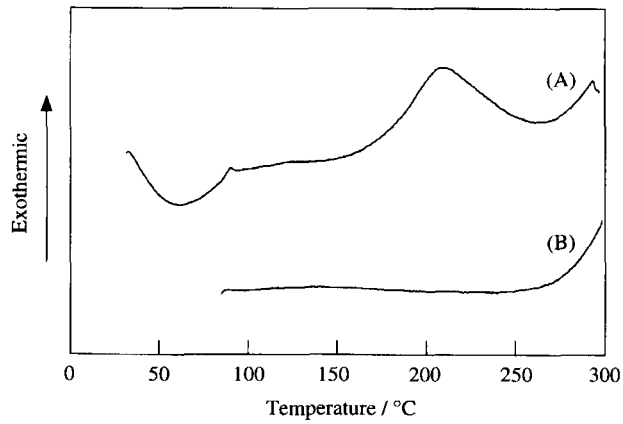


Fig. 11. DSC traces of polyphenol: (A) first scan; (B) second scan.

Table 2. Properties of Polyphenol[a)]

Property	Condition	Value	Method
Specific gravity	23 °C	1.24 ($g\,cm^{-3}$)	JIS K7112
Specific heat		1.14 ($J\,g^{-1}$)	
Thermal diffusivity	20 °C, 1.3 Torr	1.42×10^{-3}($cm^2\,s^{-1}$)	
Thermal conductivity		2.01×10^{-3}($J\,cm^{-1}\,s^{-1}\,°C^{-1}$)	
Coefficient of linear expansion	30 °C → 120 °C	5.0×10^{-5}($°C^{-1}$)	JIS K7197
	150 °C → 200 °C	3.6×10^{-5}($°C^{-1}$)	
	250 °C → 300 °C	1.8×10^{-4}($°C^{-1}$)	
	150 °C → 30 °C	4.2×10^{-5}($°C^{-1}$)	
	250 °C → 150 °C	6.7×10^{-5}($°C^{-1}$)	
	350 °C → 250 °C	1.1×10^{-4}($°C^{-1}$)	
	400 °C → 350 °C	1.3×10^{-4}($°C^{-1}$)	
Dielectric constant (ε')	22 °C, 1.0×10^6 Hz	4.71	JIS K6911
Dissipation factor (tan δ)	22 °C, 1.0×10^6 Hz	1.91×10^{-2}	JIS K6911
Volume resistivity	22 °C, DC500 V	1.9×10^{13}(Ω cm)	ASTM D257

a) Polyphenol was synthesized by HRP-catalyzed polymerization in the equivolume mixture of methanol and pH 7 phosphate buffer.

tan δ of PPO are 2.6 and 9.0×10^{-4}, respectively).[33]

Conclusion

A soluble polyphenol was synthesized by peroxidase-catalyzed polymerization of phenol in an aqueous alcohol. The molecular weight of the polymer was controlled in the range of several thousands. The polymerization parameters, enzyme origin, buffer pH, mixed ratio of alcohol and buffer, purity and amount of HRP, and concentration and addition rate of hydrogen peroxide, strongly affected the molecular weight and solubility of the polymer. TG analysis showed the relatively high thermal stability of the soluble polyphenol. The present polyphenol was obtained only from phenol, and hence, is regarded truly as a "phenolic resin". Furthermore, the production of the polyphenol is an environmentally benign process (mild reaction conditions and no use of toxic reagents), giving an example system of *green polymer chemistry*.[34] Studies on detailed structural analysis and control of the enzymatically obtained polyphenols are under way in our laboratory.

Experimental

Materials. HRP-P and SBP were purchased from Wako Pure Chemical Co. and Sigma Chemical Co., respectively. HRP-C was obtained from Toyobo Co. These enzymes were used without further purification. Other reagents and solvents were commercially available and were used as received.

Enzymatic Polymerization. A typical run was as follows. Phenol (1.00 g, 10.6 mmol) and HRP-C (20 mg) in a mixture of 10 mL of methanol and 10 mL of 0.05 M phosphate buffer (pH 7) were placed in a 50 mL of flask. To the mixture, 6.2 mL of 6% hydrogen peroxide (10.6 mmol) was added dropwise for 25 h. The mixture was stirred at room temperature under air. After 5 h, the precipitated materials were collected by filtration and washed with water, followed by drying in vacuo to give 0.86 g of the polymer (yield 86%).

Measurements. For SEC and HPLC measurement, a Tosoh SC8020 apparatus was used. SEC analysis was carried out by using a refractive index (RI) detector at 60 °C under the following conditions: two TSKgel α-M columns and DMF containing 0.09 M LiCl eluent (1 M = 1 mol dm^{-3}) at a flow rate of 1.0 mL min^{-1}. The calibration curves were obtained using polystyrene standards. HPLC analysis was performed using a UV monitor (278 nm) under the following conditions: YMC-Pack ODS AM-312 column and methanol/water eluent at a flow rate of 1.8 mL min^{-1}. ^{1}H NMR spectra were recorded on a JEOL JNM-LA 600 spectrometer. FT-IR measurements were carried out with a Perkin–Elmer Paragon 1000 spectrometer. DSC measurement was made at a 10 °C min^{-1} heating rate under nitrogen using a Seiko Instruments DSC 22 differential scanning calorimeter calibrated with an indium reference standard. TG analysis was performed using a Mac Science TG-DTA 2000S apparatus for thermogravimetry/differential thermal analysis at a heating rate of 10 °C min^{-1} in a gas flow rate of 200 mL min^{-1}. Specific gravity was measured by using a Mettler AE-240 meter. Specific heat was determined by using a TA Instrument 2910M DSC calibrated with alumina under nitrogen. Thermal diffusivity was measured by using a Rigaku LF/TCM FA8510B laser flash thermal constants analyzer equipped with normal oscillation type ruby laser of 2.5 kV voltage under vacuum (1.3 Torr, 1 Torr = 133.322 Pa). Measurement of the coefficient of linear expansion was carried out with a Seiko Instruments TMA 120C thermomechanical analyzer. Dielectric properties were evaluated by using a Hewlett Packard HP-4284A precision LCR meter with frequency of 1.0×10^6 Hz at 22 °C under 60% humidity. Volume resistivity was measured with a Hewlett Packard 4140B DC source/pA meter with DC 500 V at 22 °C under 60% humidity.

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