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Yasuyuki Matsushita · Takuya Sekiguchi · Ryoichi Ichino
Kazuhiko Fukushima

Electropolymerization of coniferyl alcohol

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Abstract Electropolymerization of coniferyl alcohol was carried out in an aqueous system (0.2 M NaOH) and in an organic solvent system [CH_2Cl_2/methanol (4:1 v/v) in the presence of 0.2 M $LiClO_4$] to produce a dehydrogenation polymer (DHP) – artificial lignin. In both systems, the polymerization of coniferyl alcohol was visually confirmed. In the aqueous system, no dimer was detected in the reaction medium after electropolymerization, suggesting that endwise polymerization occurred on the electrode surface. Thioacidolysis degradation revealed that the obtained polymers had numerous 8-*O*-4′ linkages. The electropolymerization products obtained in the organic solvent system also had numerous 8-*O*-4′ linkages; in particular, the polymers obtained in the initial polymerization stage. This was probably because of the limited area available for reaction and the orientation of coniferyl alcohol on the electrode surface controlled the polymerization.

Key words Electropolymerization · Coniferyl alcohol · Lignin · Dehydrogenation polymers · Thioacidolysis

Introduction

Lignin is biosynthesized in plants and is one of the most abundant organic materials on earth. In lignin biosynthesis, oxidases such as peroxidase and laccase catalyze the dehydrogenation of monolignols such as coniferyl alcohol, sinapyl alcohol, and *p*-coumaryl alcohol.[1–3] The enzymatic dehydrogenation reaction is initiated by electron transfer that results in the formation of resonance-stabilized phenoxy radicals. These radicals are randomly coupled, and the repeated coupling reaction leads to the formation of lignin with mixed linkages between the phenylpropane units (e.g., 8-*O*-4′, 8-5′, and 8-8′ structures). In lignin, the 8-*O*-4′ linkage is the major one; approximately 50% of the linkages in lignin are of this type.

Lignin has multiple functions that are essential for the life of a plant.[1] A decrease in the permeation of water enhances the transportation of water, nutrients, and metabolites. Lignin also increases the rigidity of the cell wall and acts as a permanent bonding agent between cells, thereby generating a composite structure that is outstandingly resistant toward impact, compression, and bending. Furthermore, it assists in resisting attacks by microorganisms by impeding the penetration of destructive enzymes into the cell wall.

Although lignin is a very useful polymer, its isolation from plants without modification is very difficult; this is because lignin is a part of a complex structure, being deposited between polysaccharides in the cell wall. In order to gain a better understanding of the properties of lignin, artificial lignin (dehydrogenation polymer; DHP) was synthesized by a biomimetic method (dehydrogenative polymerization) using an enzyme-catalysis system such as the peroxidase-H_2O_2 system.[4] The polymerization of monolignol in vivo leads to the formation of a controlled structure that is rich in 8-*O*-4′ linkages. However, DHPs prepared in vitro have a relatively random structure that is poor in 8-*O*-4′ linkages.[4] A modified DHP synthesis that yields a DHP similar to native lignin has been previously reported. Tobimatsu et al.[5] attempted the synthesis of DHPs through the dehydrogenative polymerization of monolignol glycosides catalyzed by horseradish peroxidase followed by removal of the glucose unit by enzymatic or chemical degradation. Because lignin is biosynthesized in the presence of polysaccharides, the synthesis of DHPs using polysaccharide templates has been investigated. Higuchi et al.[6] prepared a DHP of coniferyl alcohol in the presence of several polysaccharides. Terashima et al.[7,8] studied the dehydrogenative polymerization of coniferyl alcohol in the presence of pectin

Y. Matsushita (✉) · T. Sekiguchi · K. Fukushima
Graduate School of Bioagricultual Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8601, Japan
Tel. +81-52-789-4160; Fax +81-52-789-4160
e-mail: ysmatsu@agr.nagoya-u.ac.jp

R. Ichino
Ecotopia Science Institute, Nagoya University, Aichi 464-8603, Japan

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as a polysaccharide matrix in a biomimetic system and reported the formation of DHPs rich in 8-*O*-4′ linkages under acidic conditions. Cathala and Monties[9] also used pectin as a template and obtained high molecular weight DHPs. Barakat et al.[10] synthesized DHPs in the presence of xylan. In our previous report,[11] we stated that the synthesis of DHPs in the presence of cyclodextrins leads to the formation of DHPs with an increased number of 8-*O*-4′ linkages.

In this study, the electropolymerization of coniferyl alcohol was carried out. The reactant was expected to oxidize on the surface of the anode and then polymerize. The polymerization proceeds through radical formation, as in the case of enzymatic dehydrogenative polymerization. The electrode area available for electropolymerization is limited and this has an effect on the structure of the resulting polymer. Thus, electropolymerization products may have properties that are different from those of the DHPs prepared by enzymatic dehydrogenative polymerization.

Materials and methods

Apparatus

Electrochemical experiments were carried out by using a potentiostat/galvanostat (HAB-151, Hokuto Denko) connected to a personal computer for data storage. For electropolymerization, a Pt electrode with an area of 4 cm^2 was used as the working electrode. The counter electrode was a Pt mesh electrode (50 × 50 mm, 80 mesh) while a Ag/AgCl electrode was used as the reference electrode. The volume of coniferyl alcohol solution used was 50 ml. For cyclic voltammetry measurements, a Pt disk (diameter 1.6 mm) was used as the working electrode. Prior to the experiment, the working electrode was polished using a slurry containing 0.05-μm alumina particles and then rinsed with distilled water.

Gas chromatography-mass spectrometry (GC-MS) analysis was performed using a Shimadzu GCMS-QP2010 system equipped with a Durabond column (DB-1; 30 m × 0.32 mm i.d.). Before GC-MS analysis, the sample was silylated using *N*,*O*-bis(trimethylsilyl)trifluoroacetamide. The MS spectra were recorded on a JEOL JMD D-100 mass spectrometer.

Electropolymerization

Electropolymerization was carried out in 0.2 M NaOH (aqueous system) and in CH_2Cl_2/methanol (4:1, v/v) in the presence of 0.2 M $LiClO_4$ (organic solvent system).

Analysis of reaction products after electropolymerization

In the aqueous system, the pH of the aqueous reaction mixture was adjusted to pH 3–4 by using 10% aqueous HCl after polymerization and then extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous Na_2SO_4. Then it was evaporated under reduced pressure at 40°C. The extract was separated on a silica gel column using ethyl acetate:*n*-hexane (12:5, v/v) as the eluant to isolate compound **I**. **I**: MS *m/z*: 360 (M^+); ^1H nuclear magnetic resonance (NMR) (methanol-d_4) δ: 1.93 (1 H, m), 2.09 (1 H, m), 3.68 (1 H, dd, J = 10.8, 5.2 Hz), 3.79 (1 H, dd, J = 10.8, 4.8 Hz), 3.84 (3 H, s), 3.84 (3 H, s), 4.61 (1 H, d, J = 7.2 Hz), 5.87 (1 H, ddd, J = 4.8, 5.2, 16.0 Hz), 6.18 (1 H, d, J = 16.0 Hz), 6.68 (1 H, d, J = 8.0 Hz), 6.72 (1 H, dd, J = 8.0, 1.6 Hz), 6.78 (1 H, d, J = 8.0 Hz), 6.81 (1 H, dd, J = 8.0, 1.6 Hz), 6.85 (1 H, d, J = 1.6 Hz), 6.96 (1 H, d, J = 1.6 Hz); ^{13}C NMR (methanol-d_4) δ: 32.6, 49.2, 56.4, 56.4, 63.5, 76.7, 110.1, 111.6, 115.9, 116.1, 120.4, 120.8, 126.8, 131.5, 132.6, 136.5, 146.1, 146.9, 149.0, 149.1.

In the organic solvent system, the organic reaction mixture was concentrated, and the residue was purified on a silica gel column using ethyl acetate:*n*-hexane (12:5, v/v) as the eluant; two compounds were isolated in this case. **II-A**: ^1H NMR (acetone-d_6) δ: 3.17 (3 H, s), 3.23 (1 H, dd, J = 10.8, 4.8 Hz), 3.32 (1 H, ddd, J = 6.4, 4.8, 2.8 Hz), 3.41 (1 H, dd, J = 10.8, 2.8 Hz), 3.43 (3 H, s), 3.84 (3 H, s), 4.18 (1 H, d, J = 6.4 Hz), 6.77 (1 H, dd, J = 2.0, 8.0 Hz), 6.80 (1 H, d, J = 8.0 Hz), 6.93 (1 H, d, 2.0 Hz); ^{13}C NMR (acetone-d_6) δ: 56.0, 56.8, 59.5, 61.5, 84.7, 84.8, 109.3, 114.2, 120.7, 130.2, 145.6, 146.8. **II-B**: ^1H NMR (acetone-d_6) δ: 3.16 (3 H, s), 3.18 (3 H, s), 3.31 (1 H, dd, J = 11.4, 6.0 Hz), 3.57 (1 H, ddd, J = 6.4, 6.0, 4.0 Hz), 3.68 (1 H, dd, J = 11.4, 6.0 Hz), 3.85 (3 H, s), 4.13 (1 H, d, J = 6.4 Hz), 6.79 (1 H, dd, J = 2.0, 8.0 Hz), 6.82 (1 H, d, J = 8.0 Hz), 6.95 (1 H, d, J = 2.0 Hz); ^{13}C NMR (acetone-d_6) δ: 56.4, 56.7, 58.9, 62.3, 84.2, 86.2, 112.0, 115.3, 121.6, 131.8, 147.1, 148.2.

Thioacidolysis

Thioacidolysis was performed according to the procedure reported by Rolando et al.[12] The sample (0.5 mg) was added to 5 ml of the thioacidolysis reagent [$(C_2H_5)_2OBF_3$ in 8.76:1 (v/v) dioxane/ethanthiol] and docosane (internal standard) in a glass tube fitted with a Teflon-lined screw cap. Thioacidolysis was carried out at 100°C in an oil bath for 4 h with occasional shaking. The reaction product was cooled in ice water, and 2.5 ml of 0.4 M $NaHCO_3$ was added to it. After adjusting the pH of the mixture to pH 3–4 with dilute aqueous HCl, the reaction mixture was extracted with CH_2Cl_2. The organic extracts were dried over anhydrous Na_2SO_4 and then evaporated under reduced pressure at 40°C. The final residue was redissolved in approximately 0.5 ml of CH_2Cl_2.

Results and discussion

Electropolymerization in the aqueous system

Figure 1 shows a cyclic voltammogram (CV) obtained during the electropolymerization of 20 mM coniferyl alcohol in 0.2 M NaOH at a scan rate of 100 mV/s. In the first cycle,

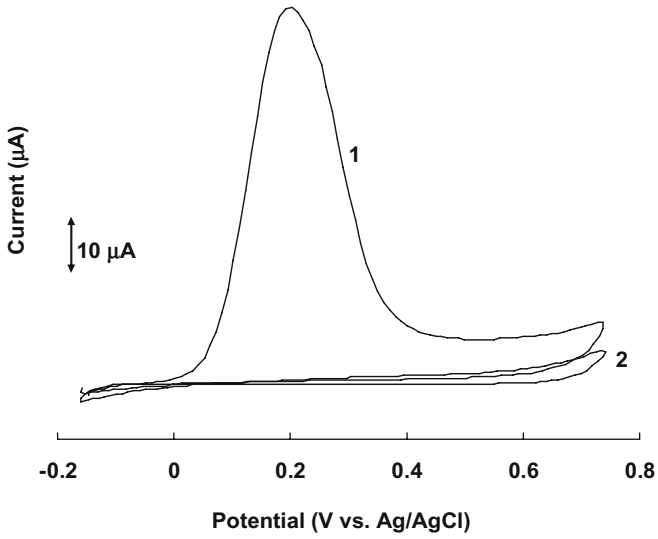

Fig. 1. Successive cyclic voltammograms for the oxidation of coniferyl alcohol in 0.2 M NaOH. Conifery alcohol; 20 mM, scan rate; 100 mV/s. The voltammogram obtained by repeating the cycling more than three times was the same as for the second cycle

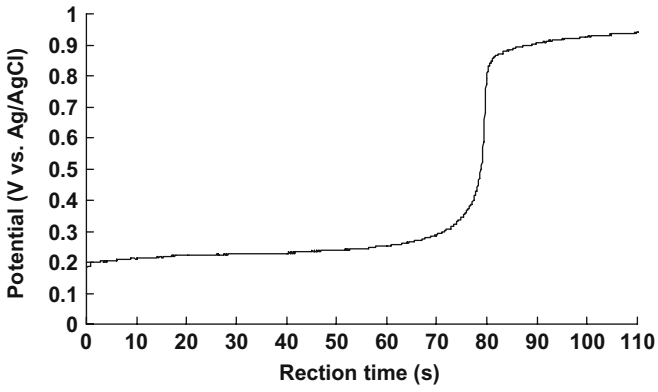

Fig. 2. Transient of electrode potential during the constant current electrolysis of 0.2 M NaOH aqueous solutions of 20 mM coniferyl alcohol. Current density: 0.25 mA/cm^2

the peak appears at a potential of 0.2 V (vs Ag/AgCl). However, by repeating the cycling more than twice, the electrode rapidly passivated, as can be seen in the CV. This phenomenon has been observed in the case of many other phenolics.[13–18] A drastic decrease in the current is observed during the electrooxidation of phenolic compounds because of the formation of a passivation film on the electrode surface. Figure 2 shows the change in the electrode potential with time during the constant-current (1 mA) electrolysis. For ca. 1 min, the electrode potential generally remained constant at 0.2 V, which is the oxidation potential of coniferyl alcohol. After ca. 80 s, the electrode potential drastically increased to ca. 1 V. This result agrees with that obtained from the CV. Coniferyl alcohol was oxidized and polymerized on the electrode surface soon after the reaction commenced, and the electrode became coated with the oxidized film.

The electrode potential stopped increasing after it reached ca. 1 V and remained constant at this value, thereby

Fig. 3. Polymer film synthesized by electropolymerization

implying that the oxidation reaction occurred at the electrode surface. In fact, the formation of the polymer at the electrode surface was visually confirmed. The polymer film was able to be removed from the electrode by ultrasound treatment (Fig. 3). Ciszewski and Milczarek[15] reported similar behavior in the electrolysis of eugenol. Gattrell and Kirk[13,14] suggested that during propagation of the electropolymerization reaction, the polymer film was degraded and ruptured, which led to the possible transfer of the monomer to the electrode surface or that the polymerization proceeded via electron tunneling through the oxidized polymer film.

Table 1 shows the electropolymerization conditions and yields for the polymerization of coniferyl alcohol in the aqueous system. The increase in the reaction time led to an increase in the yield of the polymer.

After electropolymerization, the reaction solution was analyzed by GC-MS. The results showed that the main compound in the solution was coniferyl alcohol, along with a small amount of compound **I**. Compound **I** (Fig. 4) was isolated by silica gel column chromatography and identified by ^{1}H and ^{13}C NMR spectroscopy as 1,5-bis(4-hydroxy-3-methoxyphenyl)-2-hydroxymethyl-4-penten-1-ol. It was expected that diastereomers of compound **I** would be present, but in this case it was unclear if they were present. The formation of this dimer from coniferyl alcohol in alkaline solution at 135°C has been previously reported.[19] In this study, analysis using thin layer chromatography and GC-MS confirmed that compound **I** was generated in the aqueous system by a nonelectrolytic process. Thus, it was confirmed that the dimer was formed by an ionic reaction and not by electrolysis.

Because no dimer was generated during electrolysis, it was suggested that the electropolymerization of coniferyl

Table 1. Reaction conditions and properties of products from electropolymerization of coniferyl alcohol in aqueous system

Entry	Reaction conditions[a]			Electropolymerization materials	
	Current (mA)	Reaction time (min)	Quantity of electricity (F/mol)	Yield (mg)	M1 + M2 in thioacidolysis[b] (mmol/g)
1	1	320	0.20	0.71	1.05
2	1	640	0.40	1.19	0.94
3	1	1280	0.80	1.54	0.87
4	10	320	2.0	1.06	0.91
5	10	640	4.0	2.16	1.18
6	10	960	6.0	1.91	1.04
Milled wood lignin from Japanese red pine				–	1.01

[a] Coniferyl alcohol 180 mg
[b] M1 and M2 are thioethylated monomers, see Fig. 5

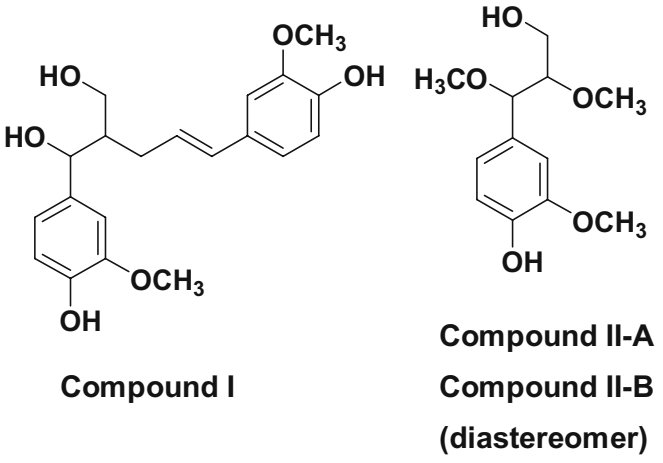

Fig. 4. Chemical structures of compounds **I**, **II-A**, and **II-B** obtained from the reaction solution after electropolymerization in aqueous system (compound **I**) and in organic solvent system (compounds **II-A** and **II-B**)

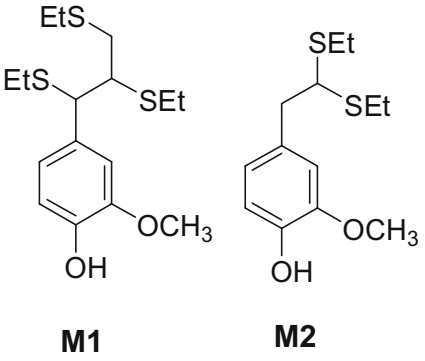

Fig. 5. Thioethylated monomers obtained by thioacidolysis of electropolymerization materials and lignin

alcohol in the aqueous system leads to endwise polymerization. This reaction appeared to be similar to the biosynthesis of lignin in situ and different from enzymatic polymerization in vitro, which predominate the coupling reaction between monomers.[4]

The chemical structure of the polymer obtained by electropolymerization was assumed to be similar to that of native lignin, and the polymer was subjected to thioacidolysis [solvolysis in dioxane/ethanethiol with $(C_2H_5)_2OBF_3$] to characterize the chemical bond between the monomers. The 8-*O*-4′ bonds are efficiently cleaved by thioacidolysis without attendant condensation reactions that result in the formation of new C–C linkages. Quantification of the major monomers formed by degradation of the polymer provides the approximate number of phenylpropane units linked by 8-*O*-4′ bonds. Figure 5 illustrates the thioethylated monomers, and Table 1 shows the distribution of the monomeric thioacidolysis products. Among the thioethylated monomers shown, M1 and M2 were found to be derived from repeating units containing 8-*O*-4′linkages. The total yield of the monomers reflects the number of phenylpropane units involved in the 8-*O*-4′ linkages. As a reference, milled wood lignin (MWL) of red pine, which was extracted with dioxane/water from milled wood, was subjected to thioacidolysis. The yield of monomers from the electropolymerization products was almost identical to that from MWL. This indicated that the electropolymerization products have approximately the same number of 8-*O*-4′ linkages. To the best of our knowledge, DHPs with a large number of 8-*O*-4′ linkages have been synthesized for the first time in this study by electropolymerization of coniferyl alcohol.

The difference in the chemical structure of DHPs obtained from electropolymerization and enzymatic polymerization might be related to the reaction field. In enzymatic polymerization, random coupling of radicals tends to occur because of the large area available for the reaction. Electropolymerization occurs on a very narrow space on the surface of electrode; this leads to the occurrence of a somewhat constrained reaction. Soriaga et al.[20,21] investigated the electrochemistry of aromatic compounds and reported the orientation of adsorbed molecules at solid–liquid interfaces. In this study, specific orientation of coniferyl alcohol seems to have occurred during the electropolymerization and resulted in structures rich in 8-*O*-4′ linkages.

Electropolymerization in the organic solvent system

During electropolymerization in the organic solvent system, the polymer was isolated from the electrode surface as follows: (1) six times every 80 min (entry 7), (2) three times every 160 min (entry 8), and (3) once after 480 min (entry 9). In all cases, the total polymerization time was the same

Table 2. Reaction conditions and properties of products from electropolymerization of coniferyl alcohol in organic solvent system

Entry	Reaction conditions[a]			Electropolymerization materials	
	Current (mA)	Reaction time (min)	Quantity of electricity (F/mol)	Yield (mg)	M1 + M2 in thioacidolysis (mmol/g)
7	10	80 × 6	3.0	2.33	1.91[b] 1.68[c]
8	10	160 × 3	3.0	2.70	1.67[d] 1.35[e]
9	10	480	3.0	2.19	1.44
Milled wood lignin from Japanese red pine				–	1.01

[a] Coniferyl alcohol 180 mg
[b] Part 1 (initial phase: first four polymer samples)
[c] Part 2 (later phase: last two polymer samples)
[d] Part 1 (initial phase: first two polymer samples)
[e] Part 2 (later phase: the third polymer sample)

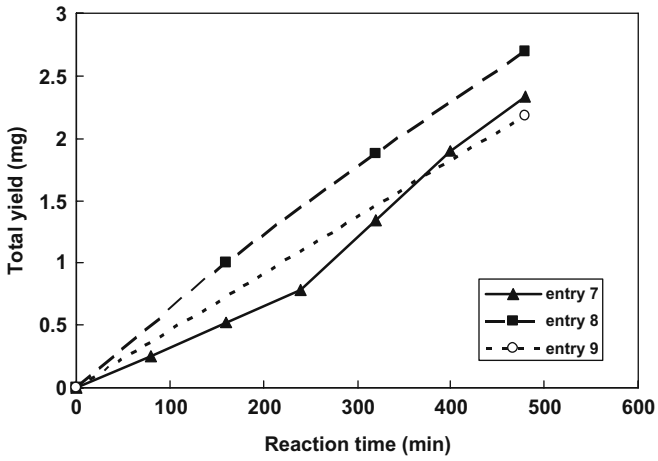

Fig. 6. Total yield of electropolymerized polymer films at the electrode in the organic solution system

(480 min). There was no significant difference between the yields of the polymer film among the abovementioned cases (Fig. 6).

The potential was increased at the start of the electropolymerization and then maintained at approximately 3 V. The formation of the polymer at the electrode surface was visually confirmed.

Thioacidolysis was carried out on two parts of the electropolymerization products to investigate their chemical structures. The polymerization products in part 1 were obtained in the initial phase of electropolymerization; these included the first four polymer samples isolated in entry 7 and the first two polymer samples isolated in entry 8. On the other hand, the polymerization products obtained in the later phase of electropolymerization (part 2) included the last two polymer samples isolated in entry 7 and the third polymer sample isolated in entry 8. The results of thioacidolysis are shown in Table 2. It was found that the yield of thioacidolysis monomers was higher than the yield of those obtained from MWL, suggesting that the former had a large number of 8-*O*-4′ linkages. The phenomenon was similar to that observed in the aqueous system.

In particular, the polymer obtained in the early stages of polymerization had a significantly large number of 8-*O*-4′ linkages. In the initial phase, the orientation of coniferyl alcohol on the surface of the electrode could occur easily; this probably resulted in structures with large numbers of 8-*O*-4′ linkages.

The reaction medium after the electropolymerization was also analyzed. The reaction solution was concentrated and the residue was purified by silica gel column chromatography to give two compounds (**II-A** and **II-B**). The NMR spectra of II-A and II-B revealed that they were diastereomers (Fig. 4). These compounds were generated by two-electron oxidation followed by the addition of methanol. GC-MS analysis revealed that besides coniferyl alcohol, **II-A** and **II-B** were the main compounds in the reaction medium. These results indicated two possible reaction routes in the organic solvent system after the oxidation of coniferyl alcohol at the electrode: (1) polymerization on the electrode and (2) the addition of methanol. Compounds **II-A** and **II-B** could be reoxidized at the electrode and polymerized; however, except when these compounds were introduced at the end of the polymer, they do not generate 8-*O*-4′ linkages in the electropolymerization product because the C7–C8 bond is saturated. Furthermore, the smaller number of 8-*O*-4′ linkages in the polymer obtained in the later stage of polymerization was thought to be related to the participation of **II-A** and **II-B** in the electropolymerization reaction.

Conclusions

Although many researchers have attempted to synthesize artificial lignin, almost all of them have used enzymes that mimic biosynthesis. In this study, electropolymerization of coniferyl alcohol was carried out in aqueous and organic solvent systems. It was found that oxidation of coniferyl alcohol on an electrode surface yields the polymer. In the aqueous system, no dimer was detected in the reaction medium after electropolymerization. This suggested the occurrence of endwise polymerization on the electrode surface. Thioacidolysis degradation revealed that the obtained polymer was rich in 8-*O*-4′ linkages. Furthermore, in the organic solvent system, the formation of the polymer on the electrode surface was visually confirmed. The results

of thioacidolysis suggested the presence of a large number of 8-*O*-4′ linkages in the obtained polymer.

Enzymatic polymerization and electropolymerization are different with respect to the reaction field. In enzymatic polymerization, the ample reaction field results in random coupling. On the other hand, in electropolymerization, the reaction field is very narrow and this leads to a somewhat constrained reaction. Moreover, orientation of the coniferyl alcohol on the surface of electrode was able to occur. The narrowness of the reaction field and orientation of coniferyl alcohol were hypothesized to strongly control the polymerization, resulting in structures with large numbers of 8-*O*-4′ linkages.

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