

Preparation of Artificial Urushi via an Environmentally Benign Process

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"Artificial urushi" has been developed by laccase-catalyzed curing of new urushiol analogues. The analogues were designed and conveniently synthesized by regioselective acylation of phenol derivatives having a primary alcohol with unsaturated fatty acids using lipase as catalyst. The curing of the catechol derivative having a linolenoyl group proceeded in the presence of acetone powder from Chinese urushi, yielding the crosslinked film ("artificial urushi") with high hardness and gloss surface, which are comparable with those of natural urushi coating. The analogues obtained from vanillyl alcohol were also cured. FT-IR monitoring of the curing showed that the crosslinking mechanism was similar to that of the natural urushi. The curing of the urushiol analogues in the presence of starch–urea phosphate took place to give the artificial urushi consisting exclusively of synthetic compounds.

As "japan" implies the meaning of "a lacquer or varnish giving a hard, glossy finish" and/or "objects decorated and lacquered in the Japanese style", urushi wares have been developed as one of the most typical symbols of Japanese art and many of such wares have also been used for daily needs.[1] Urushi coating exhibits excellent toughness and brilliance for a long period, even longer than one thousand years in some cases; such coating is prepared from sap of Japanese lacquer tree (*Rhus vernicifera*).[2–5] In the early days of this century, pioneering works by Majima revealed the structure of main important components in urushi, "urushiols". Urushiol is a catechol derivative having unsaturated hydrocarbon chains mainly with 1–3 double bonds at 3- or 4-position of catechol.[6–11] Typical urushiols are shown as follows (Chart 1).

Crosslinking of urushiols takes place slowly with laccase catalysis involving sophisticated procedures under air to produce an insoluble polymeric film of urushi, normally taking more than one month for complete crosslinking. The film formation is supposed to be accomplished mainly by a laccase-catalyzed oxidative coupling of the phenol moiety of the urushiol and a subsequent autoxidation of unsaturated alkyl chains.[11,12]

Urushi can be regarded as the sole example of practical natural paints utilizing in vitro enzymatic catalysis for hardening. The film-forming of urushiol proceeds under air at room temperature without organic solvents, and hence, urushi coating system can be regarded as an environmentally benign process, which is more and more required for future coating industry. However, few modeling studies of urushi have been scarcely attempted.[13] This is mainly due to the difficulty in preparation of urushiols.

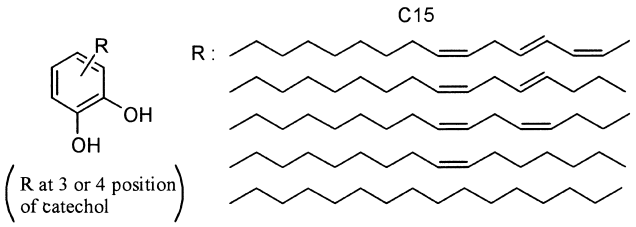

Chart 1.

There has been much interest in polymerizations catalyzed by enzymes ("enzymatic polymerizations") as a new methodology of polymer synthesis.[14–18] Recently, enzymatic synthesis of polyphenols has received much attention as an alternative of conventional phenolic resins (novolaks and resols),[19] since various phenols are enzymatically polymerized under mild reaction conditions without using toxic formaldehyde by convenient procedures to produce a new class of polyphenols consisting of a mixture of phenylene and oxyphenylene units.[20–24] The coupling selectivity (regioselectivity) could be controlled by changing the solvent composition, yielding a DMF-soluble polyphenol from non-substituted phenol.[25,26] In the oxidative polymerization of phenols having an unsaturated polymerizable group, peroxidase catalysis induced the chemoselective polymerization, yielding the polyphenols bearing the polymerizable group in the side chain.[27–29]

Very recently, we have preliminarily reported design, synthesis, and enzymatic curing of new urushiol analogues (**4** and **5**) to produce an "artificial urushi".[30] This modeling is the first example on the single-step synthesis of urushi-like cured film

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from monomeric phenol derivatives (urushiol analogues), which do not possess the rash-causing properties. This study deals with comprehensive results of preparation of the artificial urushi.

Experimental

Materials. Laccase derived from *Pycnoporus coccineus* was purchased from Koken Co. (Tokyo). *Pseudomonas cepacia* lipase was purchased from Amano Pharmaceutical Co. (Aichi). The so-called "acetone powder" (AP) was obtained by pouring Chinese urushi sap into a large amount of acetone.[31] The resulting powder had no laccase activity. Starch-urea phosphate was provided from Nippi Inc. (Tokyo). Vanillyl alcohol (**2**), unsaturated fatty acids (**3**), other reagents, and solvents were commercially available and were used without further purifications.

Synthesis of 4-(Hydroxymethyl)catechol (1). To a dispersion of 3,4-dihydroxybenzaldehyde (15 g, 0.109 mol) in 70 mL of ethanol, was added sodium tetrahydroborate (3.0 g, 0.079 mol) in 120 mL of water at 0 °C. After 3,4-dihydroxybenzaldehyde became completely soluble in the solvent, the reaction mixture was kept at room temperature for 30 min. The solution was adjusted to pH 3–4 by addition of dilute hydrochloric acid and then concentrated under reduced pressure. Sodium chloride was added until the solution became saturated and then the products were extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure and the mixture was subjected to recrystallization using a mixture of diethyl ether/1,2-dichloroethane at −20 °C. The resulting crystal was collected by filtration and dried in vacuo to give 9.9 g of 4-(hydroxymethyl)catechol **1** (yield 65%). ^{1}H NMR (DMSO-d_6) δ 4.3 (2H, d, J = 5.2 Hz, $ArCH_2O$), 4.89 (1H, t, J = 5.6 Hz, $CH_2O\mathit{H}$), 6.52–6.72 (3H, m, Ar), 8.66 (1H, s, ArOH), 8.76 (1H, s, ArOH); FT-IR (KBr) 3369 (O–H), 1606, 1527 (C=C of Ar), 1203, 1159, 1122 cm^{-1} (C–O); mp 123–128 °C (ref. 137 °C).[32]

Enzymatic Synthesis of Urushiol Analogues. A typical procedure was as follows. A mixture of **2** (3.1 g, 20 mmol), **3b** (2.8 g, 10 mmol), and crude lipase (10 g) in a mixture of 90 mL of isopropyl ether and 10 mL of tetrahydrofuran was heated at 60 °C under gentle stirring. After 240 h, the enzyme was removed by filtration and the filtrate was poured into water. The organic layer was separated and further washed twice with water. The organic solution was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. Remaining **2** was removed by recrystallization to give 3.4 g of 2-methoxy-[4-(*cis*,*cis*-9,12-octadecadienoyloxy)methyl]phenol (**5b**) (yield 81%). ^{1}H NMR (DMSO-d_6) δ 0.85 (3H, t, J = 6.9 Hz, CH_3), 1.26 (14H, br, $-CCH_2C-$), 1.52 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.01 (4H, m, $-CH=CHC\mathit{H}_2C-$), 2.29 (2H, t, J = 7.3 Hz, $-C(=O)CH_2C$), 2.73 (2H, m, $-CH=CHC\mathit{H}_2CH=CH-$), 3.75 (3H, s, OCH_3), 4.95 (2H, s, $ArCH_2O$), 5.32 (4H, m, –CH=CH–), 6.73–6.91 (3H, m, Ar), 9.06 (1H, br, ArOH); FT-IR (KBr) 3444 (O–H), 3007, 2925, 2853 (C–H), 1735 (C=O), 1606, 1517, 1460 (C=C of Ar), 1273, 1157, 1035 (C–O), 850, 816, 796, 720 cm^{-1} (C–H of Ar).

Similarly, **4a**–**4c**, **5a**, and **5c** were synthesized. As for **4a**–**4c**, these analogues were purified by silica-gel chromatography (eluent: hexane/ethyl acetate = 77/23 (vol%)). [4-(*cis*-9-Octadecenoyloxy)methyl]catechol (**4a**): Yield = 39%; ^{1}H NMR (DMSO-d_6) δ 0.85 (3H, t, J = 6.8 Hz, CH_3), 1.28 (20H, br, $-CCH_2C-$), 1.50 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.00 (2H, br, $-CH=CHC\mathit{H}_2C-$), 2.17 (2H, t, J = 7.6 Hz, $-C(=O)CH_2C$), 4.90 (2H, s, $ArCH_2O$), 5.32 (2H, m, –CH=CH–), 6.60–6.73 (3H, m, Ar), 8.98 (2H, br, ArOH); FT-IR (KBr) 3373 (O–H), 3004, 2924, 2853 (C–H), 1706 (C=O), 1607, 1519, 1446 (C=C of Ar), 1289, 1190 (C–O), 864, 811, 718 cm^{-1} (C–H of Ar).

[4-(*cis*,*cis*-9,12-Octadecadienoyloxy)methyl]catechol (4b): Yield = 39%; ^{1}H NMR (DMSO-d_6) δ 0.85 (3H, t, J = 7.3 Hz, CH_3), 1.27 (14H, br, $-CCH_2C-$), 1.50 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.01 (4H, br, $-CH=CHC\mathit{H}_2C-$), 2.28 (2H, t, J = 7.3 Hz, $-C(=O)CH_2C$), 2.73 (2H, m, $-CH=CHC\mathit{H}_2CH=CH-$), 4.88 (2H, s, $ArCH_2O$), 5.32 (4H, m, –CH=CH–), 6.60–6.73 (3H, m, Ar), 8.94 (2H, br, ArOH); FT-IR (KBr) 3377 (O–H), 3010, 2928, 2855 (C–H), 1704 (C=O), 1613, 1522, 1448 (C=C of Ar), 1289, 1190 (C–O), 866, 811, 723 cm^{-1} (C–H of Ar).

[4-(*cis*,*cis*,*cis*-9,12,15-Octadecatrienoyloxy)methyl]catechol (4c): Yield = 46%; ^{1}H NMR (DMSO-d_6) δ 0.92 (3H, t, J = 7.3 Hz, CH_3), 1.24 (8H, br, $-CCH_2C-$), 1.51 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.03 (4H, br, $-CH=CHC\mathit{H}_2C-$), 2.28 (2H, t, J = 7.3 Hz, $-C(=O)CH_2C$), 2.77 (4H, m, $-CH=CHC\mathit{H}_2CH=CH-$), 4.88 (2H, s, $ArCH_2O$), 5.32 (6H, m, –CH=CH–), 6.60–6.73 (3H, m, Ar), 8.94 (2H, br, ArOH); FT-IR (KBr) 3386 (O–H), 3008, 2930, 2855 (C–H), 1705 (C=O), 1612, 1523, 1449 (C=C of Ar), 1292, 1190, 1114 (C–O), 856, 813, 725 cm^{-1} (C–H of Ar).

2-Methoxy-[4-(*cis*-9-octadecenoyloxy)methyl]phenol (5a): Yield = 87%; ^{1}H NMR (DMSO-d_6) δ 0.85 (3H, t, J = 7.2 Hz, CH_3), 1.23 (20H, br, $-CCH_2C-$), 1.51 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.01 (2H, br, $-CH=CHC\mathit{H}_2C-$), 2.29 (2H, t, J = 7.3 Hz, $-C(=O)CH_2C$), 3.75 (3H, s, OCH_3), 4.95 (2H, s, $ArCH_2O$), 5.33 (2H, m, –CH=CH–), 6.73–6.91 (3H, m, Ar), 9.06 (1H, br, ArOH); FT-IR (KBr) 3443 (O–H), 3004, 2924, 2853 (C–H), 1732 (C=O), 1606, 1517, 1463 (C=C of Ar), 1275, 1157, 1035 (C–O), 850, 816, 796, 720 cm^{-1} (C–H of Ar).

2-Methoxy-[4-(*cis*,*cis*,*cis*-9,12,15-octadecatrienoyloxy)methyl]phenol (5c): Yield = 80%; ^{1}H NMR (DMSO-d_6) δ 0.92 (3H, t, J = 7.8 Hz, CH_3), 1.29 (8H, br, $-CCH_2C-$), 1.52 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.03 (4H, br, $-CH=CHC\mathit{H}_2C-$), 2.30 (2H, t, J = 7.3 Hz, $-C(=O)CH_2C$), 2.77 (4H, m, $-CH=CHC\mathit{H}_2CH=CH-$), 3.75 (3H, s, OCH_3), 4.95 (2H, s, $ArCH_2O$), 5.33 (6H, m, –CH=CH–), 6.73–6.91 (3H, m, Ar), 9.06 (1H, br, ArOH); FT-IR (KBr) 3446 (O–H), 3009, 2927, 2854 (C–H), 1734 (C=O), 1606, 1517, 1463 (C=C of Ar), 1275, 1229, 1157, 1035 (C–O), 851, 818, 796, 720 cm^{-1} (C–H of Ar).

Enzymatic Curing of Urushiol Analogues. A typical run was as follows. A mixture of an urushiol analogue (0.20 g), laccase solution (0.030 mL, 4.5×10^4 units), and acetone powder (0.15 g) was coated using a film applicator with slit thickness of 50 μm on a glass plate and kept in 80% humidity at 30 °C for 24 h.

Measurements. ^{1}H NMR and IR spectra were recorded on a 300 MHz Varian BB300 and Perkin-Elmer Paragon 1000 spectrometers, respectively. Film hardness was evaluated by a Fischerscope H100VS microhardness tester with test force of 1 mN (Helmut Fischer). Gloss value of films was measured at 60° by a Minolta CM-3610d gloss meter. Pyrolysis GC-MS measurement was carried out using a Frontier Lab PY-2010D vertical micro furnace-type pyrolyzer, a Hewlett-Packard HP 6890 gas chromatograph and a JEOL Automass II spectrometer. The pyrolysis was carried out at 500 °C. The GC analysis was performed using a Frontier Lab PY-1 column kept at 40 °C and subsequently heated at 20 °C/min rate to 330 °C. Dynamic viscoelasticity was measured using a Toyo Baldwin Rheovibron DDV-II-EA with frequency of 3.5 Hz at a heating rate of 1 °C min^{-1}. DSC measurements were made at a 10 °C min^{-1} heating rate under nitrogen using a Mac Science DSC-3200S differential scanning calorimeter

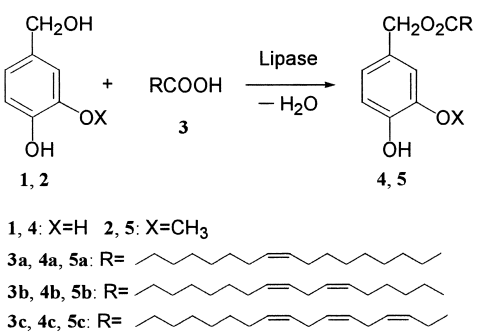
calibrated with an indium reference standard. TG analysis was performed using a Mac Science TG-DTA-2000S apparatus for thermogravimetry/differential thermal analysis at a heating rate of 10 °C min^{-1} in an argon flow rate of 200 mL min^{-1}.

Results and Discussion

Design and Lipase-Catalyzed Synthesis of Urushiol Analogues. Novel urushiol analogues (**4** and **5**), in which the unsaturated group is connected with the phenolic group through an ester linkage, were designed and synthesized via facile procedures (Scheme 1); the analogues were prepared by a lipase-catalyzed esterification of phenols having a primary alcohol (**1** or **2**) with unsaturated fatty acids of different number of double bonds (**3**). In conventional acylations of compounds having more than two kinds of hydroxy groups, it is often difficult to achieve the regioselective esterification.[33] In the case of our new approach, however, the analogues were obtained by one or two reaction steps from commercially available reagents, whereas urushiol synthesis involved multi-step reaction pathways mainly owing to the difficulty of the direct introduction of the unsaturated group onto the phenolic aromatics; protection and deprotection of the phenol moiety are often required.[34–36]

We have paid much attention to selective catalysis of lipase toward acylation between an aliphatic alcohol and a phenolic alcohol and used *Pseudomonas cepacia* lipase as catalyst for the esterification of **1** or **2** with acid **3**. By using an excess of phenolic substrates (**1** or **2**), the acid was quantitatively reacted to give oily products **4** and **5** with purity of ca. 95% in moderate yields (see, experimental). In ^{1}H NMR spectrum of the product, a peak at δ 4.3 due to the methylene protons bonded to the aromatic moiety was completely shifted to one at ca. 4.9, whose integrated area was two-thirds as large as that of the peak at δ 0.9 due to the terminal methyl protons of the higher fatty acids. These data indicate that the primary aliphatic alcohol has been regioselectively acylated to give urushiol analogues (**4** or **5**).

Enzymatic Curing of Urushiol Analogues Using Acetone Powder. In this study, laccase derived from *Pycnoporus coccineus* was used; it was highly active for the oxidative polymerization of 2,6-dimethylphenol and syringic acid to give poly(oxy-1,4-phenylene).[37,38] Laccase belongs to an oxidoreductase having a copper-protein moiety as active site.[14] The laccase-catalyzed curing of **4** and **5** was performed in the presence of acetone powder (AP, containing mainly polysaccharides and glycoproteins) with 80% humidity at 30 °C for 24 h. AP, an acetone-insoluble part of the urushi sap, is a third component of the sap in addition to an urushil and laccase. This third component is believed to act as emulsifier of oily urushiol and aqueous laccase solution. The curing of **4b**, **4c**, **5b**, and **5c**, which possessed more than 2 carbon–carbon double bonds, took place to give a film insoluble in organic solvents and water. On the other hand, **4a** and **5a** were not cured. In the curing without laccase (control experiment), the film formation was not observed. These data indicate that the present curing took place via the enzymatic catalysis and that two or three unsaturated groups in the side chain were required for the hardening. The hardening of **4** proceeded faster than that of **5**. This may be due to the formation of unstable *o*-quinone intermediates from **4**.



Scheme 1.

The curing of **4** was monitored by using a dynamic microhardness tester (Fig. 1). At the initial stage of the curing of **4c**, the curing proceeded very slowly. After two weeks, the hardness value suddenly increased. Later, the value gradually increased to reach ca. 150 N mm^{-2} after 5 weeks. The pencil scratch hardness[39,40] of the sample after 15 days was H, which is hard enough for practical uses. The gloss value of the film surface was more than 100. These data are comparable to those of natural urushi coating, indicating the formation of the brilliant film with the high gloss surface from the urushiol analogues. On the other hand, the curing of **4b** produced a soft film with the hardness less than 5 N mm^{-2} after 6 weeks.

Figure 2 shows FT-IR spectra of the cured films of **4c** with different reaction times. Intensity changes of characteristic

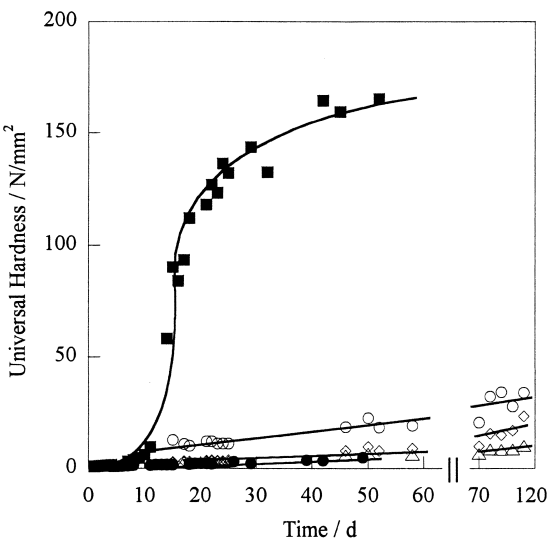


Fig. 1. Time course in hardening of artificial urushi films from **4b** and **4c** by using Fischer microhardness tester: (●) **4b** with 2.3 × 10^5 units of laccase per 1 g of the substrate in the presence of AP; (■) **4c** with 2.3 × 10^5 units of laccase per 1 g of the substrate in the presence of AP; (△) **4b** with 7.5 × 10^4 units of laccase per 1 g of the substrate in the presence of SP; (○) **4b** with 1.5 × 10^5 units of laccase per 1 g of the substrate in the presence of SP; (◇) **4c** with 7.5 × 10^4 units of laccase per 1 g of the substrate in the presence of SP.

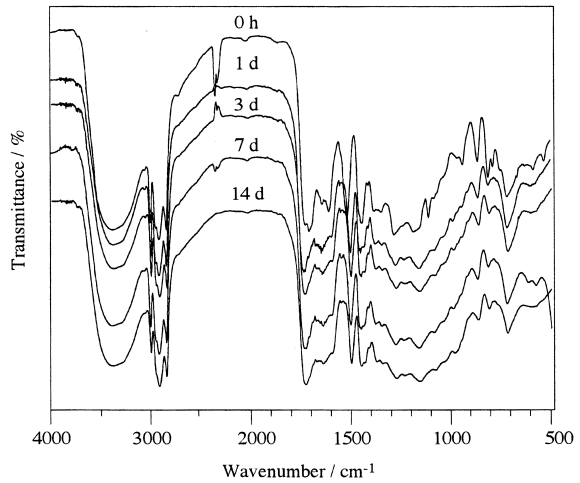


Fig. 2. Monitoring of the enzymatic curing of **4c** in the presence of AP using FT-IR spectroscopy.

peaks using a peak at 2856 cm^{-1} due to C–H vibration of the terminal methyl group as standard are shown in Fig. 3. In the curing of **4c**, a peak at 3010 cm^{-1} ascribed to C–H vibration of the unsaturated group in the side chain rapidly decreased in the period from 10 to 20 days (Fig. 3C); such behaviors might be correlated with those of the hardness (Fig. 1). On the other hand, a slight decrease of the peak was observed in the case of **4b**.

For both **4b** and **4c**, a peak at 990 cm^{-1} due to C–H vibration of the conjugated trans group newly appeared. The intensity rapidly increased at the initial curing stage and afterward became constant (Fig. 3B). Formation of a new peak at 970 cm^{-1} ascribed to that of the non-conjugated trans bond was also observed. In case of **4c**, the peak slightly increased at the initial stage and a sudden increase was seen after 10 days (Fig. 3A). These behaviors were similar to those of hardening of natural urushi. As to **4b**, the peak intensity slightly increased as a function of the time.

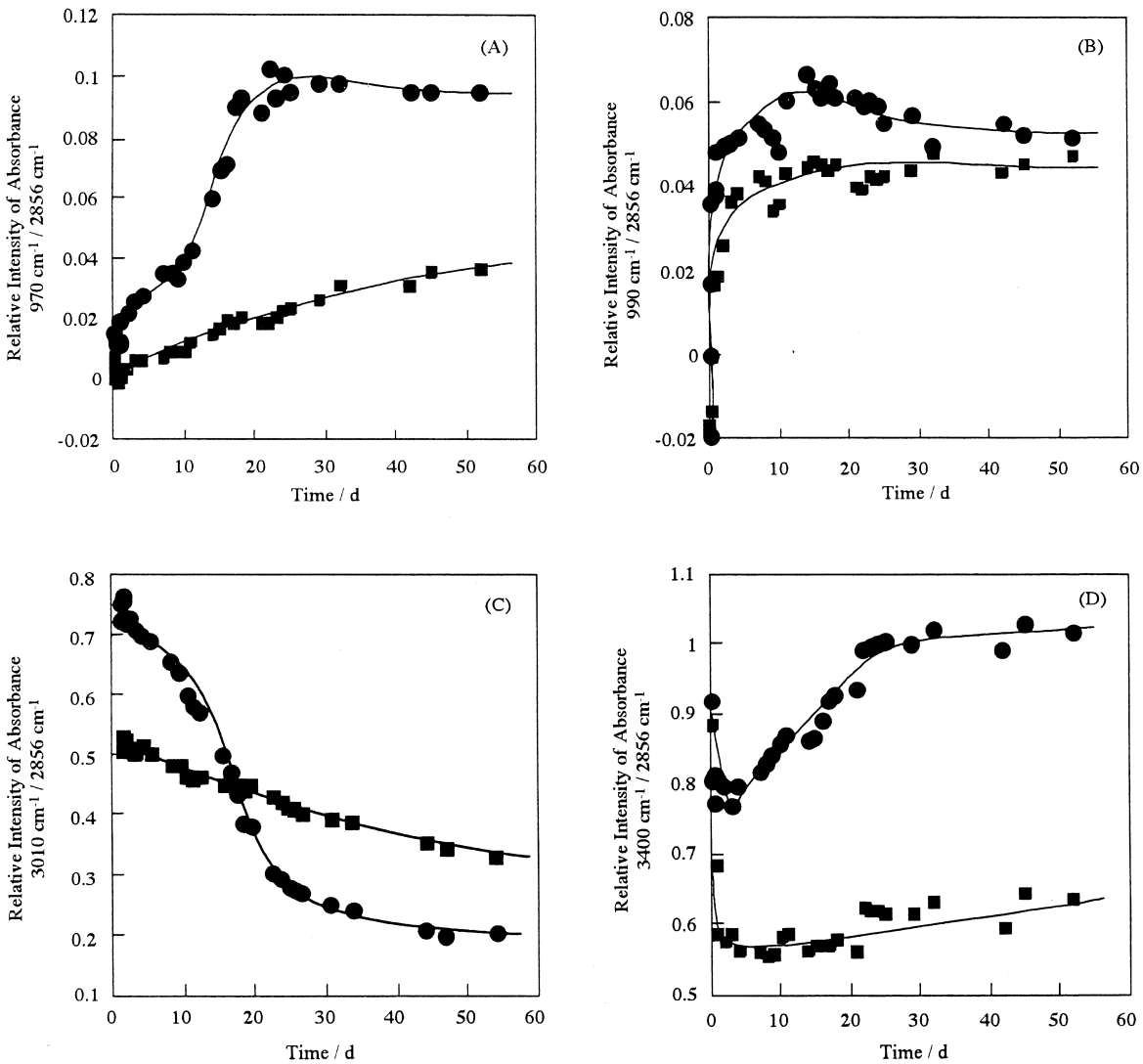


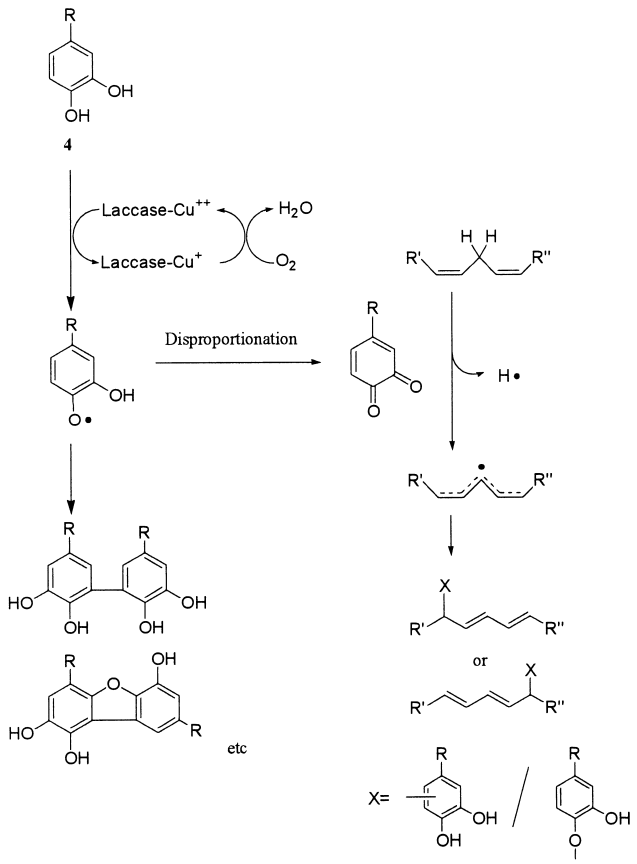
Fig. 3. Time course of relative FT-IR peak intensity in the enzymatic curing of **4b** (■) and **4c** (●) employing AP as a third component with use of intensity of a peak at 2856 cm^{-1} as standard: (A) 970 cm^{-1}; (B) 990 cm^{-1}; (C) 3010 cm^{-1}; (D) 3400 cm^{-1}.

The broad peak at 3400 cm^{-1} due to O–H vibration (Fig. 3D) showed a rapid decrease at the initial stage. This is probably owing to the evaporation of water contained in the enzyme solution and the oxidative coupling of the phenol moiety of **4** (Scheme 2). Afterwards, the peak gradually increased, suggesting that the autoxidation of the unsaturated group in the side chain takes place.[11] The change of the peak intensity of **4c** was much larger than that of **4b**.

Furthermore, the urushiol quinone was detected at the initial curing stage from the appearance of a new peak at 1650 cm^{-1}. Similar behaviors were observed in the curing of natural urushiols, indicating that the present curing of **4** proceeds via the oxidative coupling of the phenol moiety of **4** and the subsequent autoxidation of the unsaturated group in the side chain.[11]

In relation to the laccase catalysis, iron-protoporphyrin-type oxidoreductases, horseradish and soybean peroxidases, were examined for the present system. However, under similar reaction conditions, these peroxidases did not induce the crosslinking of urushiol analogues.

Enzymatic Curing of Urushiol Analogues Using Starch–Urea Phosphate as Third Component. Recently, starch-urea phosphate (SP), a synthetic material, has been reported to be highly effective as the third component for in vitro enzymatic curing of urushiols.[41] Here, the laccase-catalyzed curing of **4** was examined in the presence of SP, which is a substitute of AP, the natural sap component (Fig. 1). In the same enzyme amount, the hardness of the film obtained from **4c** was larger than that from **4b**; however, the hardness was much smaller than that using AP as the third component. The hardness was improved by adding more laccase; the hardness value of the film from **4b** attained 30 N mm^{-2} after 10 weeks. Interestingly, the curing of **4b** in the presence of SP produced the crosslinked film with relatively good hardness; only a soft film was obtained by curing of **4b** in the presence of AP.



Scheme 2.

Characterization of Artificial Urushi. Pyrolysis gas chromatography-mass (GC-MS) is very useful for structural analysis of crosslinked polymers such as phenolic polymers and natural urushi.[28,42–44] Figure 4 shows pyrolysis GC-MS spectra of natural urushi film and the cured product from **4c** obtained by using AP as the third component. The samples were decomposed at 500 °C. In the spectrum of natural urushi at m/z = 108, 10 peaks due to alkylphenols with carbon number of the side chain from 1 to 10 were clearly observed; such alkylphenols are formed by the cleavage of C–O bonds (Chart 2). Although these peaks at m/z = 108 were also observed in

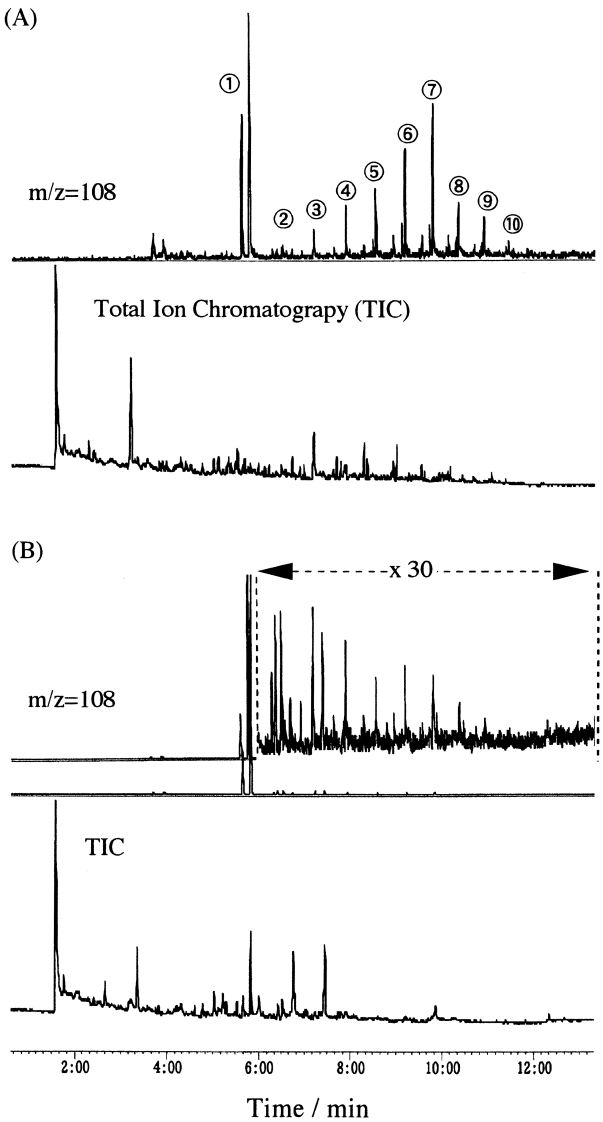


Fig. 4. Pyrolysis GC-MS chromatographs of (A) natural urushi coating and (B) the enzymatically cured products from **4c** obtained in the presence of AP.

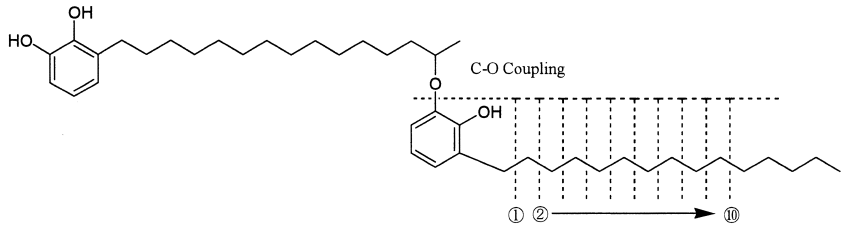


Chart 2.

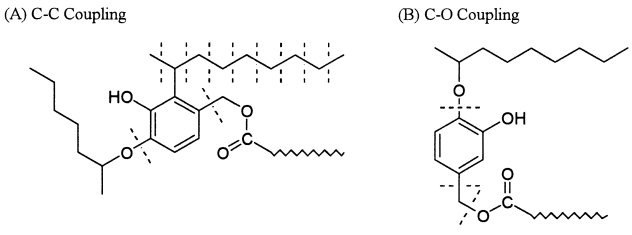


Chart 3.

the spectrum of the artificial urushi, the peak pattern was different from that of the natural urushi and the peak intensity was very small. Considering the structure of **4**, which possesses an ester group connected with phenolic and unsaturated alkyl groups, these peaks are formed by cleavage of the C–C coupling products (Chart 3A); the decomposition of the C–O oligomers does not afford the peaks ascribed to longer alkylphenols (Chart 3B). These data suggest the formation of the coupling units between the aromatics and unsaturated alkyl group in the curing of **4** in a similar manner to that of the natural urushi.

Storage modulus (E') and dissipation factor (tan δ) of the cured films from **4c**, as a function of temperature, are shown in Fig. 5. In case of the sample obtained in the presence of AP after drying for 5 months, the glass transition temperature was observed at 102 °C (Fig. 5A). From the increase of E' in the region of high temperature, it is suggested that the unreacted unsaturated carbon-carbon double bonds remained in the measured sample. The smooth trace of tan δ means the homogeneous structure of the present cured film, suggesting good miscibility between the urushiol analogue and AP. Similar traces were observed in the sample prepared by using SP as the third component (Fig. 5B). These dynamic elastic behaviors of the artificial urushi were very similar to those of natural urushi (Fig. 5C). For both artificial and natural urushi films, there was a small change of E' in the wide range of temperature. These behaviors of the urushi fims were quite characteristic since big change of E' by changing the measured temperature is often observed in the case of industrial coating materials.[3,45–47]

Thermal properties of the cured film from **4c** obtained using AP as the third component were also evaluated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). In the first DSC scan measured under nitrogen, endothermic and exothermic peaks were observed at 67 and 150 °C, respectively. The latter is probably due to the crosslinking of the unreacted unsaturated group in the side chain. In the TG measurement under nitrogen, the cured film gradually decomposed and the temperatures at 5 and 10 wt% loss were 180 and 230 °C, respectively. Similar DSC and TG data were found in the natural urushi film.[48]

Conclusion

In conclusion, "artificial urushi" has been developed by enzymatic crosslinking of new urushiol analogues, which were designed and synthesized by lipase-catalyzed regioselective

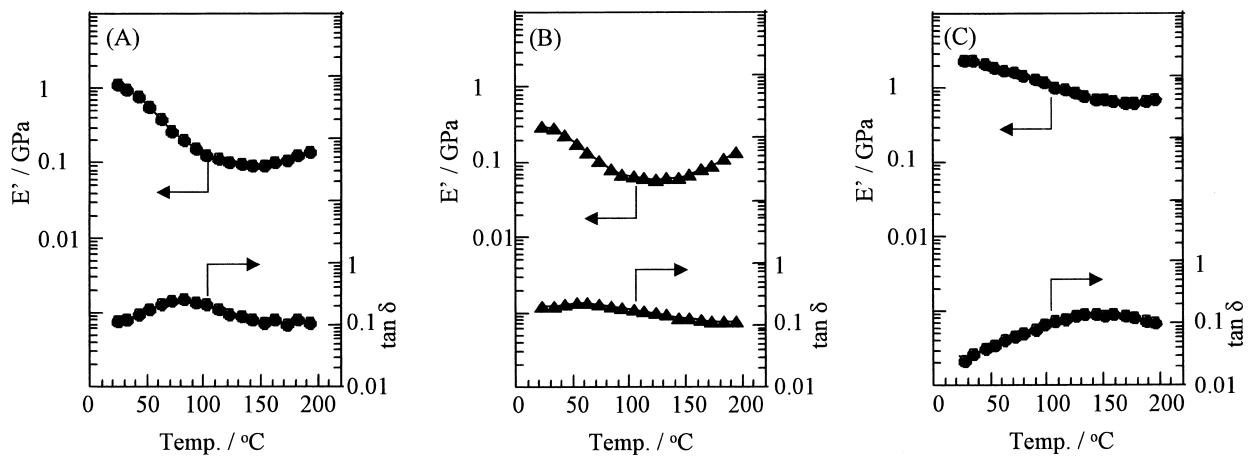


Fig. 5. Dynamic viscoelasticity of (A) artificial urushi obtained from **4c** in the presence of AP; (B) that from **4b** in the presence of SP, and (C) natural urushi.

acylation with facile procedures. These compounds were cured in the presence of commercially available laccase catalyst under mild reaction conditions without use of organic solvents to produce the crosslinked polymeric film with high gloss surface and good elastic properties. In case of the combination of the urushiol analogue and starch–urea phosphate, the artificial urushi was prepared from exclusively synthetic compounds. Therefore, the present method has large potential for a future environmentally-benign process of polymer coating, giving an example system of *green polymer chemistry*.[49–53]

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