Synthesis and Curing of Crosslinkable Polyphenols from Urushiol Analogues

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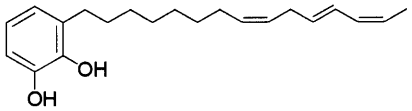
New crosslinkable polyphenols were designed on the basis of model “urushi” and synthesized by oxidative polymerization of urushiol analogues, phenol derivatives bearing an unsaturated group. The polyphenols were readily cured to give crosslinked polymeric films with high gloss surface.

Urushi is a typical Japanese traditional coating showing excellent toughness and brilliance for a long period, which is prepared from the sap of the Japanese lacquer tree.[1,2] Main important components of urushi are urushiols having a catechol structure with unsaturated hydrocarbon chains consisting of a mixture of monoenes, dienes, and trienes at the 3- or 4-position of catechol.[3,4] A crosslinking of urushiols takes place in the presence of a laccase catalyst under air to produce an insoluble polymeric film.[5,6] A typical urushiol is shown as follows.



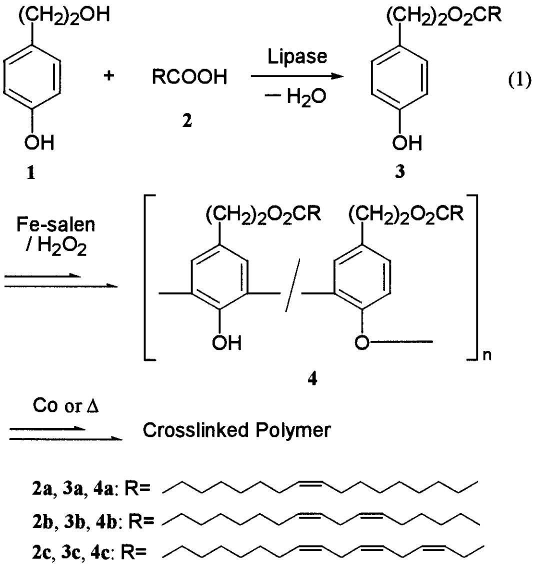
urushiol of *R. vernicifera*

So far, many studies on total synthesis of urushiol have been extensively investigated, which involve elaborative and time-consuming procedures.[7]

Worldwide potential demands for replacing petroleum-derived raw materials with renewable plant-based ones in production of polymeric materials are quite significant in the social and environmental viewpoints. Using such plant-based raw materials contributes to global sustainability without depletion of scarce important resources. Furthermore, these materials are often cheaper than petrochemicals. We have recently achieved synthesis of new prepolymers for coating materials from renewable resources. An oxidative polymerization of cardanol, a phenol derivative having the meta substituent of a C15 unsaturated hydrocarbon chain mainly with 1–3 double bonds, by iron(II)-*N*,*N*′-ethylenebis(salicylideneamine) (Fe-salen) or peroxidase catalyst produced the polyphenol containing unsaturated alkyl groups in the side chain. The resulting polymer was cured by cobalt naphthenate catalyst or thermal treatment, yielding the crosslinked polymeric materials.[8–11] Cardanol is a main component obtained by thermal treatment of cashew nut shell liquid, and development of its applications has been strongly desired.

We have achieved preparation of “artificial urushi” from new urushiol analogues via laccase catalysis under mild reaction conditions without using organic solvents.[12] The resulting cured film possessed good hardness and high gloss surface comparable with those of natural urushi. This study deals with design, synthesis, and polymerization of other urushiol analogues (**3**) based on plant oils

Urushiol analogues **3** were produced from commercially available reagents by a single-step, facile procedure; *Pseudomonas cepacia* lipase catalyzed the regioselective acylation of 4-hydroxyphenethyl alcohol (**1**) with unsaturated fatty acids (**2**) to give **3** in good yields (eq 1).[12,13]



Polymerization of **3** was carried out using hydrogen peroxide as oxidizing agent in tetrahydrofuran (THF).[14] The polymer was isolated by pouring the reaction mixture into a large amount of methanol. In all cases, an oily polymer (**4**) was obtained. Polymerization results are summarized in Table 1. Molecular weight of **4** was estimated by size exclusion chromatography (SEC).

Table 1. Oxidative polymerization of urushiol analogues (**3**)[a]

Entry	Monomer	Catalyst /mol%	Polymer			
			Code	Yield[b] /%	M_n[c] /x10^{-3}	M_w/M_n[c]
1	**3a**	0.3	**4a**	45	5.5	1.4
2	**3a**	0.5	**4a**	84	9.0	1.6
3	**3a**	0.7	**4a**	83	9.1	1.7
4	**3b**	0.5	**4b**	86	16	5.4
5	**3b**	0.7	**4b**	82	16	4.8
6	**3c**	0.3	**4c**	64	13	5.0
7	**3c**	0.5	**4c**	82	8.4[d]	2.2[d]

[a]Polymerization of **3** (3.0 mmol) using Fe-salen catalyst in THF (10 mL) at room temperature for 2 h. [b]Methanol-insoluble part. [c]Determined by SEC using THF eluent. [d]Data of THF-soluble part.

Polymerization of **3a** produced soluble polymer **4a** with molecular weight of several thousands, whose index was relatively small (< 2). On the other hand, polymers **4b** and **4c** possessed larger molecular weight and molecular weight distribution than those of **4a**. Furthermore, **4c** became partly insoluble in the high loading of the catalyst. These data imply that the crosslinking between the unsaturated groups in the side chain of **4b** or **4c** partly took place, resulting in the increase of the molecular weight distribution value and/or the formation of the insoluble products.

The structure of the soluble polymer was confirmed by ^{1}H NMR spectroscopy.[15] In the ^{1}H NMR spectrum of **4**, the peaks' pattern was similar to that of **3**, although all the peaks became broader. The ratio of the integrated area of peaks due to unsaturated groups toward peaks ascribed to aliphatic hydrocarbon moiety was not changed before and after the polymerization, indicating no reaction of the unsaturated moiety during the polymerization.

The curing was examined by two methods: catalysis of cobalt naphthenate (3 wt % for **4**) and thermal treatment (150 °C for 2 h).[9] The sample film was prepared on a glass slide by using applicator for 50 μm thickness and stood at 25 °C under the humidity of 70%. In both methods, **4b** and **4c** were cured within 1 h to give yellow transparent films, however, crosslinking of **4a** did not take place. These data indicate **4b** and **4c** were good crosslinkable prepolymers and 2 or 3 unsaturated groups in the side chain were required for the hardening. Thereafter, the curing of **4b** and **4c** has been examined.

The film hardness was evaluated by using a dynamic microhardness tester. The hardness of the thermally cured film reached nearly 100 N/mm^2 after 3 days, whereas the film hardness by using the cobalt catalyst was less than 30 N/mm^2 after 1 week, suggesting that the thermal treatment was suitable for the production of hard film. The gloss value of the film surface was about 100 for both cured samples. The hardness and gloss value of the present cured film are comparable to those of natural urushi, indicating that the brilliant film with the high gloss surface was obtained by the curing of **4**.

In conclusion, novel urushiol analogues **3** were conveniently synthesized by using regioselective catalysis of lipase and their oxidative polymerization produced a new class of crosslinkable polyphenols **4** having unsaturated alkyl group in the side chain. The resulting polymer was cured by cobalt naphthenate or thermal treatment to give the brilliant film with high gloss surface. The present prepolymer is synthesized from renewable plant-based materials. In the curing stage, the crosslinked polymeric film is obtained in the absence of organic solvents at an ambient temperature under air. Therefore, the present method is expected as an environmentally benign process of polymer coating, giving an example system of green polymer chemistry.[9,16–19] Further investigations on the production of crosslinkable polymers from renewable resources are under way in our laboratory.

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13 A mixture of **1** (3.1 g, 23 mmol), **2b** (2.8 g, 10 mmol), and *Pseudomonas cepacia* lipase (3.0 g) in a mixture of 90 mL of isopropyl ether and 10 mL of tetrahydrofuran were 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 the solvent was evaporated under reduced pressure to give 3.8 g of **3b** (yield 94%). ^{1}H NMR δ 0.91 (3H, t, CH_3), 1.30 (14H, br, $-CCH_2C-$), 1.59 (2H, m, $-C(=O)CH_2C\mathit{H}_2C-$), 2.06 (4H, m, $-CH{=}CHC\mathit{H}_2C-$), 2.31 (2H, t, $-C(=O)CH_2C$), 2.87 (2H, m, $-CH{=}CHC\mathit{H}_2CH{=}CH-$), 4.26 (4H, m, $ArCH_2$ and $-C(=O)OCH_2$), 5.38 (4H, m, $-CH{=}CH-$), 6.77, 7.10 (4H, d, Ar), 9.22 (1H, br, ArOH). Similarly, **3a** and **3c** were obtained in 96 and 97% yields, respectively.
14 The following is a typical procedure for the polymerization (entry 4). Under air, **3b** (1.2 g, 3.0 mmol) and Fe-salen (4.8 mg, 0.015 mmol) in 10 mL of THF were placed in a 50 mL flask. Hydrogen peroxide (30% aq solution, 68 μL, 0.6 mmol) was added to the mixture every 15 min for 5 times at room temperature under gentle stirring. After 2 h, the reaction mixture was poured into a large amount of methanol. The oily precipitates were separated by centrifugation, followed by drying in vacuo to give 1.0 g of polymer (yield 86%).
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