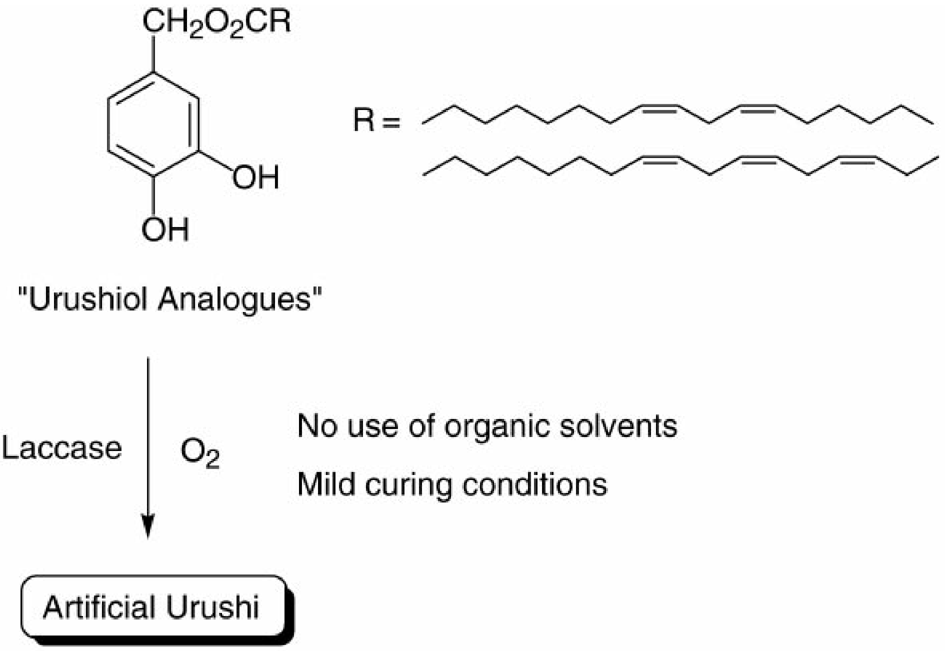
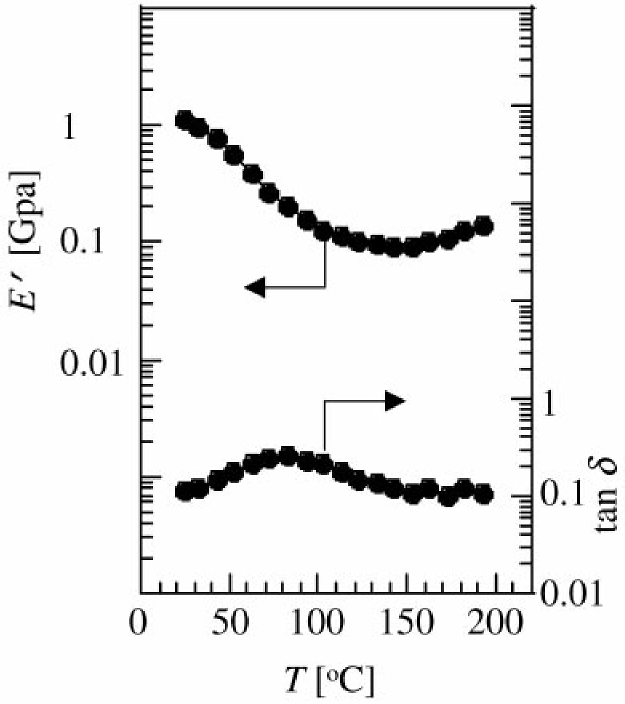


A national treasure, a small box coated with urushi



"Urushi" is a traditional natural coating, which is formed by curing "urushiols" from Japanese urushi trees with laccase catalysis in air. This system has been mimicked to develop "artificial urushi" by curing new urushiol analogues also by using a laccase catalyst in air. The curing proceeded without use of organic solvents under mild reaction conditions. The present method may provide with a future environmentally benign process of coatings.

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Artificial Urushi

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Abstract: A new concept for the design and laccase-catalyzed preparation of "artificial urushi" from new urushiol analogues is described. The curing proceeded under mild reaction conditions to produce the very hard cross-linked film (artificial urushi) with a high gloss surface. A new cross-linkable polyphenol was synthesized by oxidative polymerization of cardanol, a phenol derivative from cashew-nut-shell liquid, by enzyme-related catalysts. The polyphenol was readily cured to produce the film (also artificial urushi) showing excellent dynamic viscoelasticity.

Keywords: artificial urushi • enzyme catalysis • polymerization • renewable resource • urushiol analogues

Introduction

As "japan" means "a lacquer or varnish giving a hard, glossy finish" and/or "objects decorated and lacquered in the Japanese style",[1] urushi wares are regarded as one of the most typical symbols of Japanese art. Oriental lacquer (urushi) from Japan and China is a natural resinous sap of the *Rhus vernicifera* tree (Figure 1).[2] The use of urushi as a protective and later decorative coating originated in China, most likely prior to the fifth century B.C. In the 6th century, urushi spread to Japan with Buddhism. Urushi coating is hard enough to give a brilliant polish, is highly durable (it will last for more than a thousand years under the right conditions), and solvent resistant in comparison with synthetic coatings. The Japanese have fully developed the techniques of utilizing urushi for living wares as well as decorative arts over many years. Outstanding art examples in Japan are found on small boxes (Figure 2).

Figure 1. Harvesting sap from an urushi tree.

Figure 2. Japanese national treasure: urushi-ware box made by Kohrin Ogata in the 17th century.

Majima's pioneering work in the early days of 20th century revealed that main important components of urushi are "urushiols", whose structure is that of a catechol derivative with unsaturated hydrocarbon chains consisting of a mixture of monoenes, dienes, and trienes at the 3 or 4 position of the

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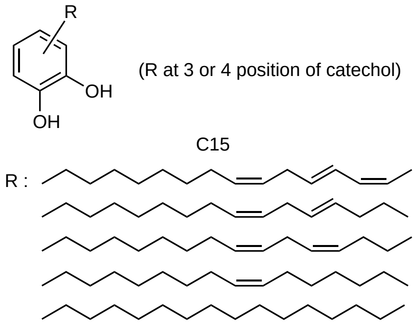
catechol.[3] The average number of olefinic groups in the side chain is 2.0–2.5. Typical urushiols are shown in Scheme 1. The composition of the raw urushi sap in Japan and China is typically about 65% urushiol, 8% plant gum, 2% glycoprotein, less than 1% laccase, and 25% water.[1]



Scheme 1. Structure of typical urushiols.

Within these components, the plant gum is a mixture of highly branched, water-soluble polysaccharides with molecular weights of 8.4×10^4 and 2.8×10^4 Da. The main sugar units are L-rhamnose, L-arabinose, 4-*O*-methyl-D-glucuronic acid, and D-galactose. The gum exists in a salt form with a counter cation of Ca^{2+}, Mg^{2+}, or Na^+. The glycoprotein is water-insoluble and its structure is not clearly known. Laccase is present in very small quantities; however, it is vitally important for the curing process. Laccase is a copper glycoprotein and contains four copper atoms with molecular weight of 1.2×10^5 Da.

Cross-linking of the urushiol 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 in air.[1] At first, laccase catalyzes the oxidation of the catechol unit of the urushiol to give the semiquinone radical (see Scheme 3 below), which is subjected to the reaction by a number of competing pathways, yielding a mixture of dimers and oligomers with complicated structures. Model studies with 3-pentadecylcatechol show that the semiquinone radical intermediate disproportionates to the corresponding *o*-benzoquinone species.

Urushi can be regarded as the only example of a practical natural paint that utilizes in vitro enzymatic catalysis for hardening. Urushi can be cured in air at room temperature without organic solvents, and hence, urushi seems a very desirable coating system from an environmental standpoint. However, modeling studies of urushi were limited to only one paper[4] before our new approach of "artificial urushi". This is mainly due to the difficulty in preparation of the urushiol.

Enzymatic Polymerization

Enzyme-catalyzed polymerization ("enzymatic polymerization") has been of increasing importance as a new trend in macromolecular science.[5] Enzyme catalysis has provided new synthetic strategies for useful polymers, most of which are difficult to produce by conventional chemical catalysts. In vitro enzymatic syntheses of polymers by nonbiosynthetic (nonmetabolic) pathways are therefore recognized as a new area of precision polymer synthesis. Enzymatic polymerization also affords a great opportunity for using nonpetrochemical, renewable resources as starting substrates for functional polymeric materials; this would contribute a lot to global sustainability without the depletion of scarce resources. In enzymatic polymerizations, the product polymers can be obtained under mild reaction conditions (normally at an ambient temperature, under ordinary pressure, at neutral pH, and in water) without using toxic reagents. Thus, enzymatic polymerization has great potential as an environmentally friendly synthetic process for polymeric materials and provides a good way to achieve "green polymer chemistry".[6]

The main target macromolecules for enzymatic polymerization have been polysaccharides, polyesters, and polyaromatics.[5] The former two classes of polymers are synthesized by using hydrolases as catalyst. A hydrolase is an enzyme that catalyzes the hydrolysis of polysaccharides or fats (triglycerides). However, the enzyme has been found to also act as catalyst of the reverse reaction, by appropriate design of a substrate monomer and selecting the reaction conditions, leading to polymer production. As for the polyaromatics, the enzymatic synthesis of polyanilines and polyphenols has been reported.

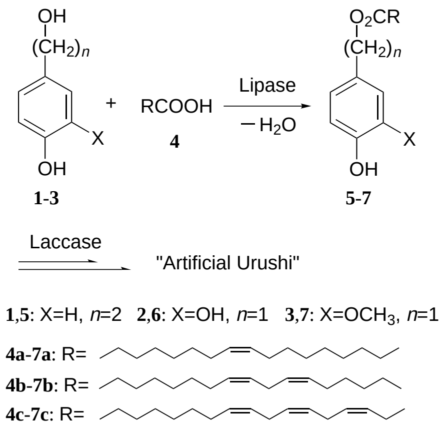
Phenol-formaldehyde resins from prepolymers such as novolaks and resols are widely used in industrial fields. These resins have excellent toughness and temperature-resistant properties. However, the toxic nature of formaldehyde causes problems in their manufacture and use. Therefore, an alternative process for the preparation of phenol polymers without using formaldehyde has been strongly desired.

For the last decades, a new class of polyphenols has been synthesized by using oxidoreductase as catalyst.[5, 7] Some advantages for the enzymatic synthesis of polyphenols are as follows: i) the oxidative polymerization of phenols proceeds under mild reaction conditions without the use of toxic reagents (environmentally benign process); ii) enzymes catalyze the polymerization of a variety of phenol monomers; iii) the structure and solubility of the polymer can be controlled by changing the reaction conditions; iv) the procedures of the polymerization as well as the polymer isolation are very convenient. We found that the peroxidase-catalyzed polymerization of phenol in aqueous methanol produced a soluble polymer with a controlled structure.[8] Furthermore, the enzyme catalysis enabled the production of various functional and high-performance polymers.[7]

We have enzymatically synthesized artificial urushi, new cross-linked polymeric films, on the basis of the design of new urushiol analogues (phenols that have an unsaturated group in the side chain).[9–12] This new concept has expanded the scope of the enzyme catalysis to the environmentally benign production of functional coating materials. The present article gives an overview of our new synthetic methodology of artificial urushi. In a strict sense, "artificial urushi" may be defined as the cross-linked film prepared by in vitro laccase-catalyzed oxidation of urushiol (or urushiol analogue) monomers. Here, we use "artificial urushi" in a broader sense; normally, it denotes the cured polymer film derived from urushiol analogues, which are phenol- or catechol-type monomers that have unsaturated reactive groups, in which the curing obeys a similar oxidation process to the natural system.

Laccase-Catalyzed Curing of Urushiol Analogues

The reason why the synthesis of natural urushiols involves multistep, tedious procedures is that the reactive unsaturated group can not be directly introduced into the catechol moiety; protection and deprotection of the catechol moiety is required.[13] Thus, we designed new urushiol analogues (**5**–**7**), in which the unsaturated group is connected with the phenolic group through an ester linkage.[9, 12] The analogues were synthesized by a lipase-catalyzed esterification of phenols having a primary alcohol (**1**–**3**) with unsaturated fatty acids having different numbers of double bonds (**4**) (Scheme 2). The primary aliphatic hydroxy group in **1**–**3** was regioselectively acylated by *Pseudomonas cepacia* lipase to produce oily urushiol analogues. In our new approach, the analogues were obtained in one or two steps by facile procedures from commercially available reagents. Furthermore, it is to be noted that the urushiol analogues showed no dermatitis-causing activity.



Scheme 2. Production of artificial urushi.

The curing was performed by using laccase, derived from *Pycnoporus coccineus*, as catalyst in the presence of acetone powder (AP, an acetone-insoluble part of the urushi sap containing mainly polysaccharides and glycoproteins) in air with 80 % humidity at 30 °C for 24 h. AP, a third component of the sap in addition to an urushiol and laccase, acts as emulsifier of oily urushiol and aqueous laccase solution. The sample film was prepared on a glass slide with an applicator for 50 μm thickness. The film formation was observed for four urushiol analogues **6b**, **6c**, **7b**, and **7c**; however, the other urushiol analogues (**5a**, **5b**, **5c**, **6a**, and **7a**) were not cured. The cross-linking did not occur in the curing without laccase (control experiment). These data indicate that the curing took place through enzymatic catalysis and that a catechol or 2-methoxyphenol moiety having two or three unsaturated groups in the side chain was required for the hardening. The cross-linking rate of **6** was greater than that of **7**.

The curing of **6b** and **6c** was monitored by using a dynamic microhardness tester. At the initial stage of the curing of **6c**, the curing proceeded very slowly (Figure 3). After two weeks, the hardness value suddenly increased. Later, the value gradually increased to reach about 150 N mm^{-2} after five weeks. The pencil-scratch hardness 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. The hardness and gloss values of the present cured film are comparable to those of natural urushi coating; the curing of the urushiol analogues produced a brilliant film with the high gloss surface. On the other hand, the resulting film from **6b** showed low hardness—less than 5 N mm^{-2} after six weeks (Figure 3).

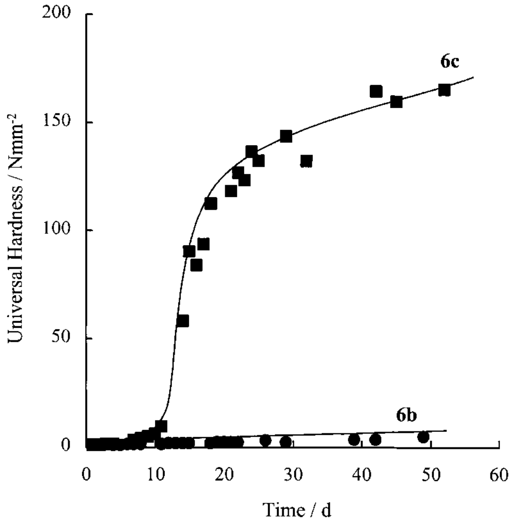
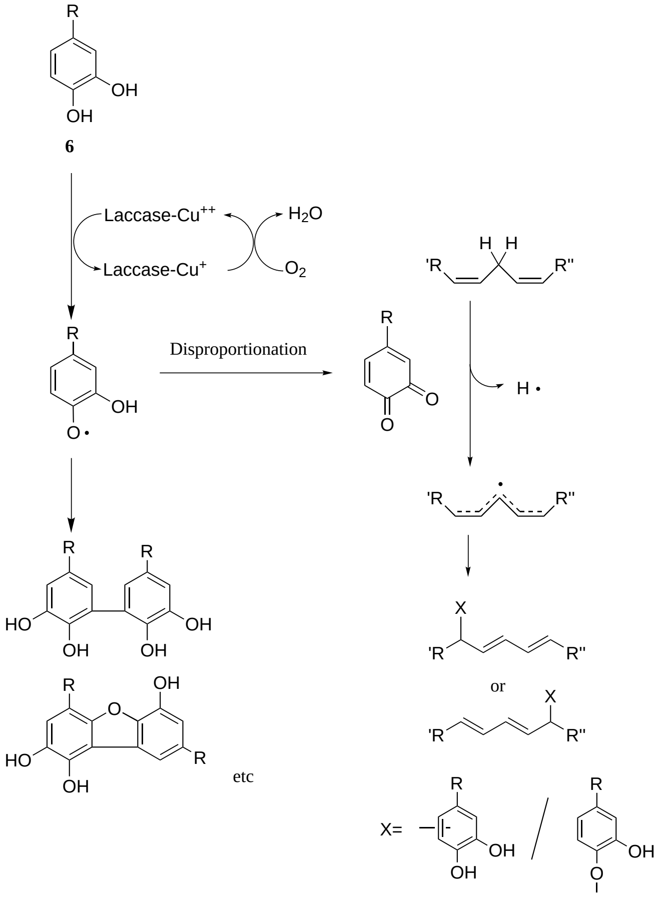


Figure 3. Time course in hardening of artificial urushi films from **6b** and **6c** as measured by using a Fischer microhardness tester.

It was reported that starch urea phosphate (SP), a synthetic material, was available as an AP substitute for in vitro enzymatic curing of urushiols.[14] For **6c**, curing took place in the presence of SP; however, the film hardness was much less than that obtained in the presence of AP. The use of SP as the third component allowed the artificial urushi to be provided from exclusively synthetic compounds.

The curing was monitored by FT-IR, which showed that the cross-linking mechanism is similar to that of natural urushiols; the curing of **6** proceeds by the oxidative coupling of the phenol moiety of **6** and the subsequent autoxidation of the unsaturated group in the side chain (Scheme 3).

The storage modulus (E′) and dissipation factor (tan δ) of the cured films from **6c**, as a function of temperature, are shown in Figure 4. In the case of the sample obtained in the presence of AP after drying for 5 months, the glass transition temperature was observed at 102 °C (Figure 4a). The increase of E′ in the high-temperature region indicates that unreacted unsaturated C=C double bonds remained in the sample measured. The smooth trace of tan δ indicates the homogeneous structure of the cured film; this suggests good miscibility between the urushiol analogue and AP. The



Scheme 3. Postulated curing mechanism of urushiol analogues **6**.

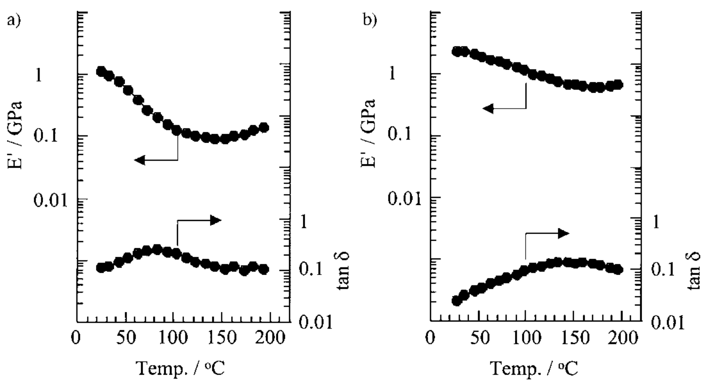
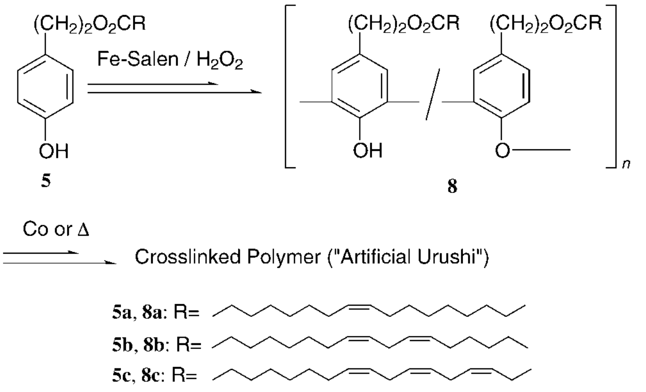


Figure 4. Dynamic viscoelasticity of a) artificial urushi obtained from **6c** in the presence of AP and b) natural urushi.

dynamic elastic behavior of the artificial urushi was very similar to that of natural urushi (Figure 4b).[15]

Preparation of Cross-Linkable Polyphenols from Urushiol Analogues

As described above, the laccase-catalyzed curing of urushiol analogue **5** did not occur. Therefore, we examined the preparation of another artificial urushi by an oxidative polymerization of **5** with iron-*N*,*N*'-ethylenebis(salicylideneamine) (Fe-salen) as catalyst, followed by curing of cross-linkable polyphenols (**8**) (Scheme 4).[10, 12]



Scheme 4. Synthesis and curing of cross-linkable polyphenols.

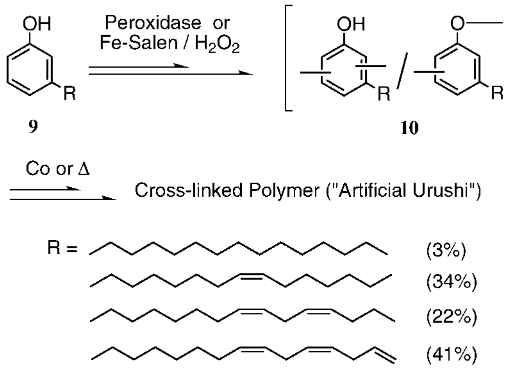
Fe-salen can be regarded as a model complex for peroxidase. We showed high catalytic activity of Fe-salen for the oxidative polymerization of phenols.[16] Fe-salen catalyzed an oxidative polymerization of *para-tert*-butylphenol and bisphenol-A, which yielded soluble polyphenols. 2,6-Dimethyl- and 2,6-difluorophenols were polymerized by Fe-salen to give poly(phenylene oxide) derivatives. The latter polymer showed crystallinity with a melting point higher than 250 °C.

The polymerization of **5** catalyzed by Fe-salen was performed with hydrogen peroxide as oxidizing agent in tetrahydrofuran at room temperature under air and yielded an oily polymeric precipitate. From ^{1}H NMR analysis of **8**, it was found that the unsaturated moiety did not react during the polymerization. The curing of the product polymer was examined by two methods: oxidation catalyzed by cobalt naphthenate (3 wt% for **8**) in air and thermal treatment (150 °C for 2 h). The sample film prepared on a glass slide stood at 25 °C and 70% humidity. Polymers having two or three unsaturated groups in the side chain (**8b** and **8c**) were cured by both methods, and the resulting film obtained by thermal treatment was extremely hard. The formation of the cured film from **8a**, however, was not observed.

Preparation of Cross-Linked Polymeric Film from Cardanol

Cardanol (**9**), a main component obtained by thermal treatment of cashew-nut-shell liquid (CNSL), is a phenol derivative having as meta substituent a C15 unsaturated hydrocarbon chain, mainly with 1–3 double bonds. Since CNSL is nearly the one third of the total nut weight, a large amount of CNSL is formed as a by-product from the mechanical processing of cashew nuts for food use. Only a small part of **9** obtained during the production of cashew kernels is used in the industrial field, although it has potential industrial utilizations in various ways such as resins, friction lining materials, and surface coatings.[17] Therefore, new uses for **9** are very attractive.

Phenolic resins from **9** and formaldehyde are industrially produced as prepolymers of coating materials with a high gloss surface mainly for indoor use.[17] However, there is a lot of concern about the toxic nature of formaldehyde in the manufacture and use of these resins. We have examined the synthesis and curing of polymer **10** obtained by oxidative polymerization of **9** with peroxidase or its model complex as catalyst (Scheme 5).[11, 12] This curing reaction is regarded as a new formaldehyde-free coating system for **9**.



Scheme 5. Synthesis and curing of poly(cardanol).

Fe-salen catalyzed the polymerization of **9** in organic solvents. The polymerization proceeded in 1,4-dioxane to give soluble polymer **10** with a molecular weight of several thousand daltons in good yields; the addition of pyridine improved the polymer yield and molecular weight. NMR and FT-IR analyses of the polymer indicate no reaction of the unsaturated group during the polymerization. Soybean peroxidase also induced polymerization in an aqueous isopropanol; however, the yield was much lower than with the Fe-salen catalyst.

The curing of **10** was examined by a similar method to that of **8**: catalysis of cobalt naphthenate (3 wt% for **10**) and thermal treatment (150 °C for 30 min). In the curing of the sample obtained by Fe-salen catalysis, yellowish transparent films (also artificial urushi) were obtained within 1 h by both methods. On the other hand, such a quick hardening was not observed for monomer **9**. These data indicate that **10** was a good cross-linkable prepolymer. The resulting cross-linked film exhibited good elastic properties comparable to cardanol-formaldehyde coating materials (Figure 5). From FT-IR monitoring of the curing of **10**, it was found that the cross-linking mechanism is similar to that of the oil autoxidation.

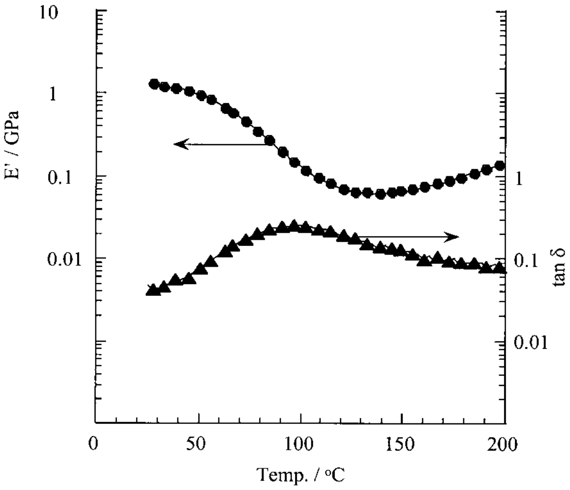


Figure 5. Dynamic viscoelasticity of a cross-linked film of poly(cardanol).

Conclusion

In this article, our new synthetic methodology for polymeric coating materials is described. New urushiol analogues, catechol derivatives having two or three unsaturated groups in the higher alkyl side chain, were cross-linked by laccase catalysis under mild reaction conditions without the use of organic solvents; this led to the production of "artificial urushi" with a high gloss surface and good elastic properties. Other urushiol analogues and cardanol were oxidatively polymerized by enzyme-related catalysts; this yielded new soluble cross-linkable prepolymers. The curing of these two kinds of polyphenols afforded cross-linked films with good hardness. In all three cases, artificial urushi was obtained from cheap plant-based oils, one of the most important renewable resources, without the use of toxic formaldehyde. The curing proceeded in the absence of organic solvents at an ambient temperature in air. Therefore, the present method is expected to have large potential for a future environmentally-benign process of polymer coating.

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[1] a) B. V. Rague, *A History of Japanese Lacquer Work*, University of Toronto Press, Toronto, **1976**; b) J. Kumanotani in *Polymer Application of Renewable Resource Materials* (Eds.: C. E. Carraher, L. H. Sperling), Plenum, New York, **1983**, pp. 225–248; c) D. M. Snyder, *J. Chem. Educ.* **1989**, *66*, 977–980; d) J. Kumanotani in *The Polymeric Materials Encyclopedia* (Ed.: J. C. Salamone), CRC Press, Boca Raton, **1996**, pp. 4835–4842; e) O. Vogl, *J. Polym. Sci. Polym. Chem. Ed.* **2000**, *38*, 4327–4335.

[2] *Webster's New World Dictionary of the American Language* (Ed.: D. B. Guralink), 2nd ed, The World Publishing Co., New York, **1970**, p. 754.

[3] a) R. Majima, *Ber. Dtsch. Chem. Ges. B* **1909**, *42*, 1418–1423; b) R. Majima, *Ber. Dtsch. Chem. Ges. B* **1922**, *55*, 172–191; c) R. Majima, *Ber. Dtsch. Chem. Ges. B.* **1922**, *55*, 191–214.

[4] M. Terada, H. Oyabu, Y. Aso, *J. Jpn. Soc. Colour Mater.* **1994**, *67*, 681–687.

[5] a) S. Kobayashi, S. Shoda, H. Uyama, *Adv. Polym. Sci.* **1995**, *121*, 1–30; b) S. Kobayashi, S. Shoda, H. Uyama in *The Polymeric Materials Encyclopedia* (Ed.: J. C. Salamone), CRC Press, Boca Raton, **1996**, pp. 2102–2107; c) S. Kobayashi, S. Shoda, H. Uyama in *Catalysis in Precision Polymerization* (Ed.: S. Kobayashi), Wiley, Chichester, **1997**, Chapter 8; d) H. Ritter in *Desk Reference of Functional Polymers, Syntheses and Applications* (Ed.: R. Arshady), American Chemical Society, Washington, **1997**, pp. 103–113; e) (Eds.: R. A. Gross, D. L. Kaplan, G. Swift), *ACS Symp. Ser.* **1998**, *684*; f) S. Kobayashi, H. Uyama in *Materials Science and Technology—Synthesis of Polymers* (Ed.: A.-D. Schlüter), Wiley-VCH, Weinheim, **1998**, Chapter 16; g) H. Joo, Y. J. Yoo, J. S. Dordick, *Korean J. Chem. Eng.* **1998**, *15*, 362–374; h) S. Kobayashi, H. Uyama, M. Ohmae, *Bull. Chem. Soc. Jpn.* **2001**, *74*,

613–635; i) S. Kobayashi, H. Uyama in *Encyclopedia of Polymer Science and Technology*, 3rd ed. (Ed.: J. I. Kroschwitz), Wiley, New York, in press; j) S. Kobayashi, H. Uyama, S. Kimura, *Chem. Rev.* in press.

[6] a) S. Kobayashi, *High Polym. Jpn.* **1999**, *48*, 124–127; b) S. Kobayashi, *J. Polym. Sci. Polym. Chem. Ed.* **1999**, *37*, 3041–3056.

[7] a) J. S. Dordick, M. A. Marletta, A. M. Klibanov, *Biotechnol. Bioeng.* **1987**, *30*, 31–36; b) H. Uyama, H. Kurioka, I. Kaneko, S. Kobayashi, *Chem. Lett.* **1994**, 423–426; c) J. A. Akkara, D. L. Kaplan, V. T. John, S. K. Tripathy in *The Polymeric Materials Encyclopedia* (Ed.: J. C. Salamone), CRC Press, Boca Raton, **1996**, pp. 2115–2125; d) M. Ayyagari, J. A. Akkara, D. L. Kaplan, *Acta Polym.* **1996**, *47*, 193–203; e) H. Uyama, C. Lohavisavapanich, R. Ikeda, S. Kobayashi, *Macromolecules* **1998**, *31*, 554–556; f) J. A. Akkara, M. S. R. Ayyagari, F. F. Bruno, *Trends Biotechnol.* **1999**, *17*, 67–73; g) H. Uyama, S. Kobayashi, *CHEMTECH* **1999**, *29(10)*, 22–28; h) H. Tonami, H. Uyama, S. Kobayashi, T. Fujita, Y. Taguchi, K. Osada, *Biomacromolecules* **2000**, *1*, 149–151; i) S. Kobayashi, H. Uyama, H. Tonami, T. Oguchi, H. Higashimura, R. Ikeda, M. Kubota, *Macromol. Symp.*, in press.

[8] a) T. Oguchi, S. Tawaki, H. Uyama, S. Kobayashi, *Macromol. Rapid Commun.* **1999**, *20*, 401–403; b) T. Oguchi, S. Tawaki, H. Uyama, S. Kobayashi, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1389–1396.

[9] a) S. Kobayashi, R. Ikeda, H. Oyabu, H. Tanaka, S. Kobayashi, *Chem. Lett.* **2000**, 1214–1215; b) R. Ikeda, H. Tanaka, H. Oyabu, H. Uyama, S. Kobayashi, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1067–1073.

[10] T. Tsujimoto, R. Ikeda, H. Uyama, S. Kobayashi, *Chem. Lett.* **2000**, 1122–1123.

[11] a) R. Ikeda, H. Tanaka, H. Uyama, S. Kobayashi, *Macromol. Rapid Commun.* **2000**, *21*, 496–499; b) R. Ikeda, H. Tanaka, H. Uyama, S. Kobayashi, *Polym. J.* **2000**, *32*, 589–593; c) H. Uyama, R. Ikeda, S. Yaguchi, S. Kobayashi, *ACS Symp. Ser.* **2000**, *764*, 113–127.

[12] R. Ikeda, T. Tsujimoto, H. Tanaka, H. Oyabu, H. Uyama, S. Kobayashi, *Proc. Acad. Jpn.* **2000**, *76B*, 155–160.

[13] a) Y. Furukawa, Y. Yamagiwa, T. Kamikawa, *J. Chem. Soc. Chem. Commn.* **1986**, 1234–1235; b) A. Jefferson, M. V. Sargent, S. Wangchareontrakul, *Aust. J. Chem.* **1988**, *41*, 19–25; c) M. V. Sargent, S. Wangchareontrakul, *J. Chem. Soc. Perkin Trans. 1.* **1990**, 1429–1934; d) T. Miyakoshi, H. Kobuchi, N. Niiura, Y. Yoshihiro, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2560–2562.

[14] H. Oyabu, M. Terada, Y. Aso, Y. Oda, *J. Jpn. Soc. Colour Mater.* **1995**, *68*, 729–734.

[15] M. Kasamori, M. Sakamoto, K. Awazu, T. Ichikawa, T. Egashira in *The Polymeric Materials Encyclopedia* (Ed.: J. C. Salamone), CRC Press, Boca Raton, **1996**, pp. 3499–3504.

[16] a) H. Tonami, H. Uyama, S. Kobayashi, H. Higashimura, T. Oguchi, *J. Macromol. Sci. Pure Appl. Chem.* **1999**, *A36*, 719–730; b) H. Tonami, H. Uyama, H. Higashimura, T. Oguchi, S. Kobayashi, *Polym. Bull.* **1999**, *42*, 125–129; c) R. Ikeda, H. Tanaka, H. Uyama, S. Kobayashi, *Macromolecules* **2000**, *33*, 6648–6652.

[17] a) A. R. R. Menon, C. K. S. Pillai, J. D. Sudha, A. G. Mathew, *J. Sci. Ind. Res.* **1985**, *44*, 324–338; b) P. H. Gedam, P. S. Sampathkumaran, *Prog. Org. Coat.* **1986**, *14*, 115–157; c) P. L. Nayak, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 1–21.

0947-6539/01/0722-4760 $ 17.50+.50/0