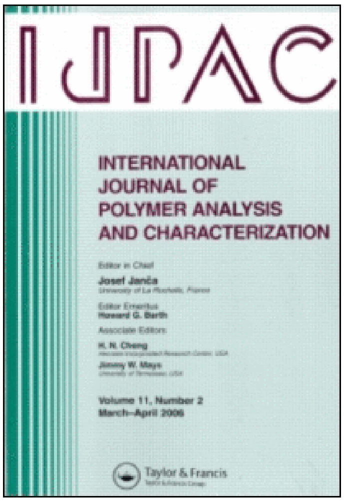

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Structural Studies and Polymerization Mechanisms of Synthesized Lacquer Films Using Two-stage Pyrolysis-Gas Chromatography/Mass Spectrometry

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Two kinds of synthesized lacquer films were investigated and compared with a natural lacquer film using two-stage pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Monoenyl and saturated urushiol were detected from the synthesized lacquer film by pyrolysis at 400°C, as well as from the natural lacquer film. These are attributed to the terminal groups of the synthesized lacquer film. In addition, alkenylphenols, alkylphenols, alkenes and alkanes were detected by pyrolysis at 500°C after pyrolysis at 400°C, as well as in the natural lacquer film. Some alkenes and alkanes have longer carbon chains than the side chains of synthesized urushiol. The alkenylphenols and alkylphenols are the pyrolysis products of the nucleus-side chain C-O coupling synthesized urushiol polymers, and the alkenes and alkanes, whose carbon chains are longer than the side chains of synthesized urushiol, are the pyrolysis products of autoxidative side chain-side chain C-C coupling synthesized urushiol polymer.

Based on these results, it was found that the synthesized lacquer films are terminated with the monoenyl and saturated urushiol, and the polymerization of synthesized urushiol proceeds through the laccase-catalyzed nucleus-side chain C-O coupling and the autoxidative side chain-side chain C-C coupling like the natural lacquer film. Since the structure and polymerization mechanisms of the synthesized lacquer films are very similar to those of the natural lacquer film, these lacquer films must be tough and brilliant enough to be used as preservative surface coating materials like the natural lacquer film.

Keywords: Py-GC/MS, synthesized lacquer film, lac tree sap, urushiol, polymerization mechanisms

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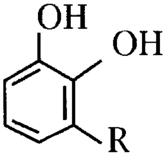
*Corresponding author.

INTRODUCTION

Sap exuded from *Rhus vernicifera* lac tree dries into a hard and brilliant film. It has been used as a coating material for thousands of years in the Orient.[1] These saps are latex that are composed of urushiol (60–65 %), water (20–25 %), plant gum (5–7 %), glycoprotein (2–5 %), and laccase enzyme (1%).[2–5] The components of urushiol are shown in Table I. The lacquer film is the urushiol polymer including plant gum and glycoprotein. The dimerization of urushiol proceeds through the laccase-catalyzed C-C coupling. The detailed mechanism has been reported as follows.[6] At the first step of dimerization, a semiquinone radical is produced from urushiol by oxidation through the Enz-Cu^{++} to Enz-Cu^{+} reaction. During the cooking process of sap, significant foaming occurs due to the presence of plant gum, resulting in an air and sap mixture during treatment and the acceleration of the oxidation of Cu^{+} by oxygen to Cu^{++} in laccase. The reformed Enz-Cu^{++} takes part in the repeated oxidation of urushiol. The formed semiquinone radical undergoes a C-C coupling reaction to produce biphenyl and dibenzofuran dimers, and the urushiol quinone formed through the disproportionation reaction undergoes H^{+} abstraction from the triene side chain of urushiol to yield a nucleus-side chain C-C coupling dimer. From the above mechanism of dimerization, it is considered that the urushiol nucleus in the formed dimers is certainly oxidized to the corresponding semiquinone radicals in the same way, followed by the subsequent poly-

TABLE I The Components of Urushiol



R =	%
$C_{15}H_{31}$	4.5
$C_7H_{14}CH{=}CHC_6H_{13}$	15.0
$C_9H_{18}CH{=}CHC_4H_9$	1.5
$C_7H_{14}CH{=}CHCH_2CH{=}CHC_3H_7$	6.5
$C_7H_{14}CH{=}CHCH_2CH{=}CHC_3H_7$	4.4
$C_7H_{14}CH{=}CHCH_2CH{=}CHCH{=}CHCH_3$	57.2
$C_7H_{14}CH{=}CHCH_2CH{=}CHCH_2CH{=}CH_2$	1.5
$C_7H_{14}CH{=}CHCH_2CH{=}CHC_5H_{11}$	1.8

merization as urushiol. The polymerization probably proceeds through these types of coupling, and finally a tough film is produced.

Presently, many kinds of new coating materials such as plastics have been developed. However, the lacquer film, which is a classical coating material, is still valued highly, because it can maintain its beauty without any degradation for thousands of years.

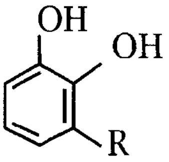
Planting lac trees and collecting their sap are hard work, and thus lacquer is very expensive. This is a problem in the lacquer industry and in conservation and restoration studies. Therefore, the synthesis of urushiol at low cost has been studied.[7,8] In this work, the lacquer films, which were synthesized from drying oil by alkylation and intramolecular cyclization, were investigated using a two-stage pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) method and the results were compared with the characteristics of natural lacquer film.

EXPERIMENTAL

Synthesized Lacquer Films

Synthesized Urushiol A. Synthesized urushiol A was produced from linseed oil by alkylation and intramolecular cyclization.[8] Its components are shown in Table II.

TABLE II The Components of Synthesized Urushiol A



R =	%
$C_{14}H_{29}$, $C_{16}H_{33}$	4–9
$C_{18}H_{37}$	2–8
$C_8H_{16}CH{=}CHC_8H_{17}$	13–37.6
$C_8H_{16}CH{=}CHCH_2CH{=}CHC_5H_{11}$	4.5–29.1
$C_8H_{16}CH{=}CHCH_2CH{=}CHCH_2CH{=}CHC_2H_5$	25.8–53
$C_{20}H_{41}$	0.2–1

Synthesized Urushiol B. Synthesized urushiol B was produced from tung oil in the same way as the synthesized urushiol A. Its components are shown in Table III.

The respective urushiols were added to an acetone powder, which was separated as acetone insoluble material from the sap of lac tree contained non-oily parts, that is, plant gum, glycoprotein and laccase enzyme, in water-isopropyl alcohol and stirred. The mixture had a viscosity suitable for coating, and after coating on a glass plate, it was dried in a humidity-controlled chamber filled (80% relative humidity) at 25–30°C for 10 h. The respective lacquer films were removed from the chamber and placed in air for 3 years.

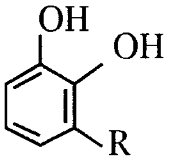
Natural Lacquer Film

Fluid sap exuded from *Rhus vernicifera* lac tree was treated using the traditional Kurome and Nayashi methods[9] and coated on a glass plate followed by hardening in a humidity-controlled chamber (80% relative humidity) at 25–30°C for 10 h. It was then removed from the chamber and placed in air for 30 years.

Py-GC/MS Conditions

Py-GC/MS measurements were carried out using a PY-2010D (Frontier Lab.) vertical microfurnace-type pyrolyzer, a HP5890 series II (HP, Ltd.) gas chromatograph, and a JMS-AMII (JEOL, Ltd.) mass spectrometer. A

TABLE III The Components of Synthesized Urushiol B



R =	%
C_nH_{2n+1} (n = 12–20)	3.5– 8.0
$C_8H_{16}CH{=}CHC_8H_{17}$	4.0–15.8
$C_8H_{16}CH{=}CHCH{=}CHC_6H_{13}$	8.7–10.8
$C_8H_{16}CH{=}CHCH{=}CHCH{=}CHC_4H_9$	77–81.8

stainless-steel capillary column (0.25-mm i.d. × 30 m) coated with 0.5 μm of Ultra Alloy PY-2 (100% methyl silicone) was used for separation. A 50 mL/min He carrier gas flow to the pyrolyzer was reduced to 1mL/min at the capillary column by using a splitter. The sample (0.5 mg) was placed in a platinum sample cup on the top of the pyrolyzer at a near ambient temperature. The sample cup was introduced into a furnace kept at 400°C, and temperature programming of the GC oven was then started. The GC oven was programmed at a constant temperature increase of 20°C/min from 40° to 330°C. After the sample cup was held in the furnace for 30 min, it was retracted to the initial position. The furnace was then reset to 500°C. After the first pyrogram was recorded, the sample cup was dropped into the furnace at 500°C, and the temperature program of the GC oven was restarted. All pyrolysis products were identified by mass spectrometry. The mass spectrometer ionization energy was 70 eV (EI-MS).

RESULTS AND DISCUSSION

Pyrolysis at 400°C

The synthesized lacquer films and the natural lacquer films were pyrolyzed at 400°C. The total ion chromatograms (TIC) and the mass chromatograms (m/z 334, 360, 362) of the synthesized lacquer films are shown in Figure 1. Each mass chromatogram shows peak 1 at a retention time of 14 min, 2–3 s, peak 2 at 14 min 42–43 s, and peak 3 at 14 min 46–47 s. They were identified with the synthesized urushiol components, that is, 3-hexadecylcatechol (MW 334), 3-octadecenylcatechol (MW 360), and 3-octadecylcatechol (MW 362) based on the mass spectra shown in Figure 2. The TIC and the mass chromatograms (m/z 318, 320) of the natural lacquer film are shown in Figure 3. Each mass chromatogram shows peak 1 at a retention time of 13 min 29 s and peak 2 at 13 min 33 s. They were identified with the natural urushiol components, that is, 3-pentadecenylcatechol (MW 318) and 3-pentadecylcatechol (MW 320) based on the mass spectra shown in Figure 4.

As shown above, monoenyl and saturated urushiol components were detected from the synthesized lacquer films, as well as from the natural lacquer film. These urushiol materials are mainly observed as thermally

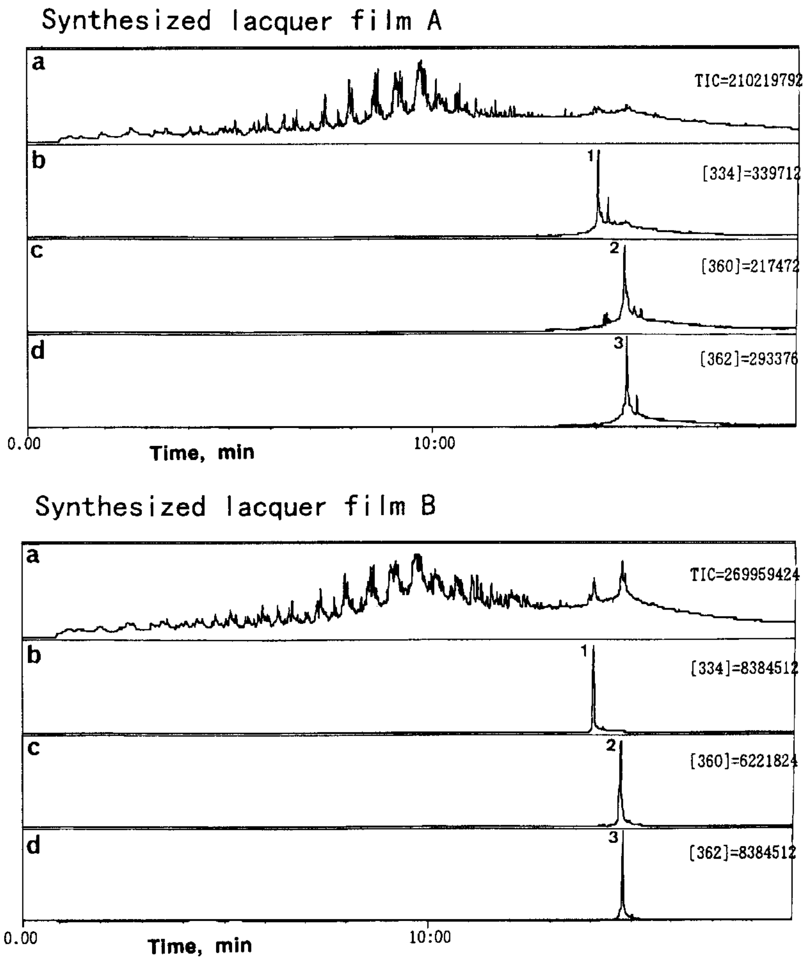


FIGURE 1 TIC and mass chromatograms of the synthesized lacquer film A and B obtained by pyrolysis at 400°C. a) TIC; b) Mass chromatogram (m/z 334), peak 1 : 3-hexadecylcatechol (MW 334); c) Mass chromatogram (m/z 360), peak 2 : 3-octadecenylcatechol (MW 360); d) Mass chromatogram (m/z 362), peak 3 : 3-octadecylcaechol (MW 362).

decomposed components from the terminal alkyl- and alkenylcatechol-side chains of the respective lacquer films. Therefore, the synthesized lacquer films are terminated with monoenyl and saturated urushiol components the same as natural lacquer film.

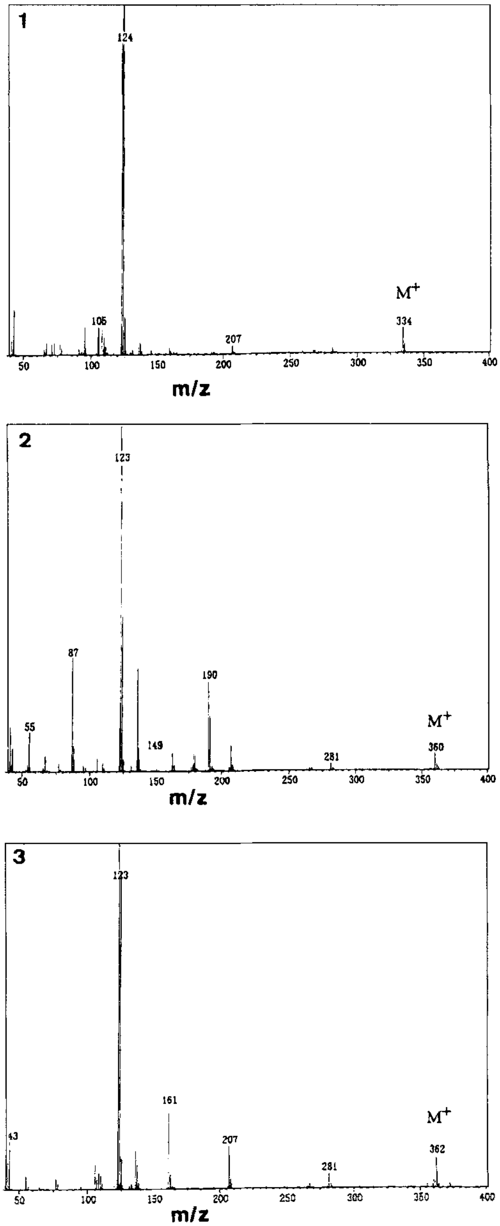


FIGURE 2 Mass spectra of peaks 1, 2, 3 shown in Figure 1. peak 1: 3-hexadecylcatechol (MW 334); peak 2: 3-octadecenylcatechol (MW 360); peak 3: 3-octadecylcaechol (MW 362).

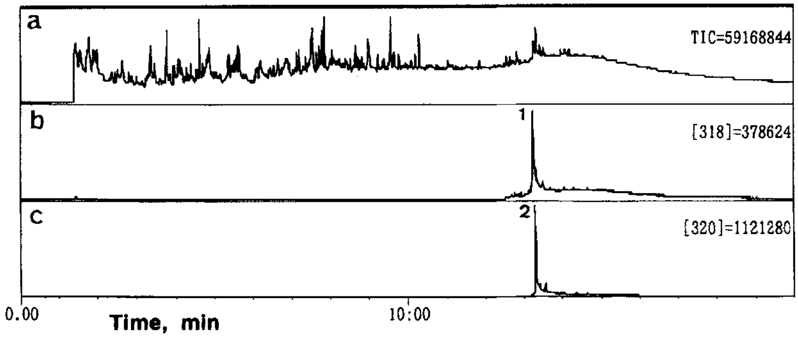


FIGURE 3 TIC and mass chromatogram of natural lacquer film obtained by pyrolysis at 400°C. a) TIC; b) Mass chromatogram (m/z 318), peak 1 : 3-pentadecenylcatechol (MW 318); c) Mass chromatogram (m/z 320); peak 2 : 3-pentadecylcatechol (MW 320).

Pyrolysis at 500°C

The synthesized lacquer films and the natural lacquer films were pyrolyzed at 500°C after pyrolysis at 400°C. The TIC and mass chromatograms of natural lacquer films are shown in Figure 5. Peak pairs of alkenylphenols (much smaller peaks on the left side) and alkylphenols (larger peaks on the right side) were detected in the mass chromatogram (m/z 108) as shown in Figure 5b. Additionally, the alkenylphenols and alkylphenols having the longest side chain are shown to be pentadecenylphnols and pentadecylphenols. These alkenylphenols and alkylphenols are the pyrolysis products of the nucleus-side chain C-O coupling urushiol polymers, because it has been inferred that dimerization of urushiol proceeds through the laccase-catalyzed nucleus-side chain C-O coupling as well as the C-C coupling.[10] Furthermore, since the C-O coupling polymers should mainly terminate with alkyl- and monoenylcatechol, pentadecenylphenols and pentadecylphenols are formed from such terminal groups.

The TIC and mass chromatograms of the synthesized lacquer films are shown in Figure 6. Peak pairs of alkenylphenols and alkylphenols were detected in the respective mass chromatograms (m/z 108) as shown in Figure 6b as well as in the natural lacquer film. In these lacquer films, the alkenylphenols and alkylphenols having the longest side chain are octadecenylphenols, octadecylphenols, eicosenylphenols, and eicosylphenols. These alkenylphenols and alkylphenols must be the pyrolysis products of the nucleus-side chain C-O coupling synthesized urushiol polymers, and

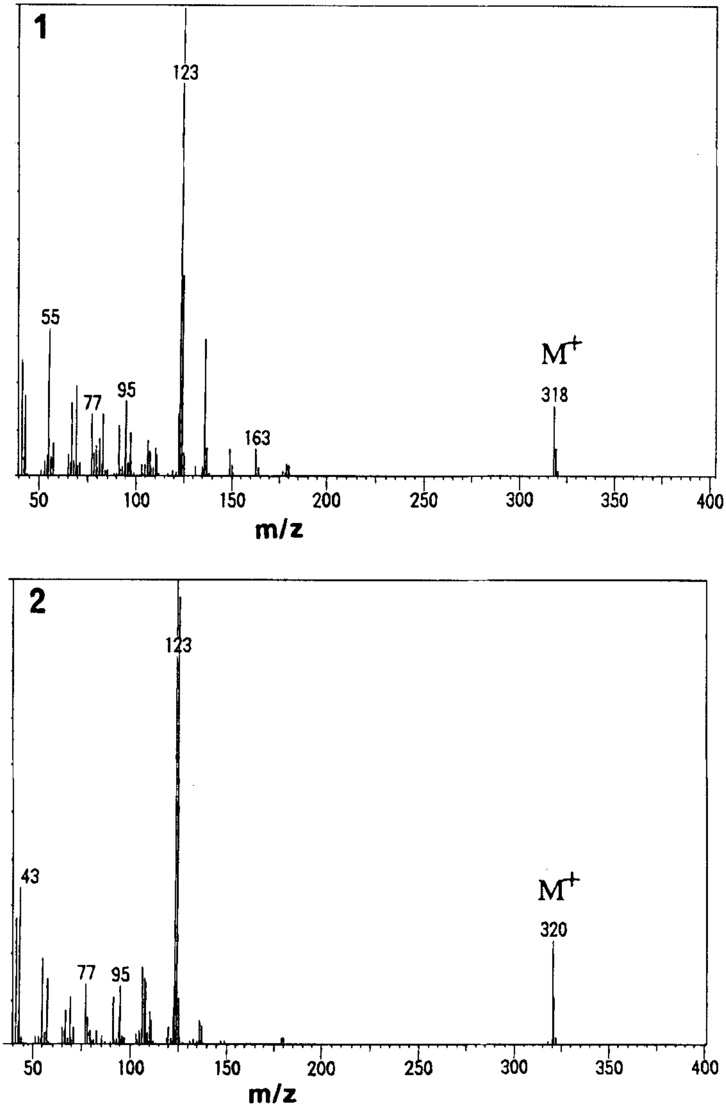


FIGURE 4 Mass spectra of peak 1 and 2 shown in Figure 3. peak 1 : 3-pentadecenylcatechol (MW 318); peak 2 : 3-pentadecylcatechol (MW 320).

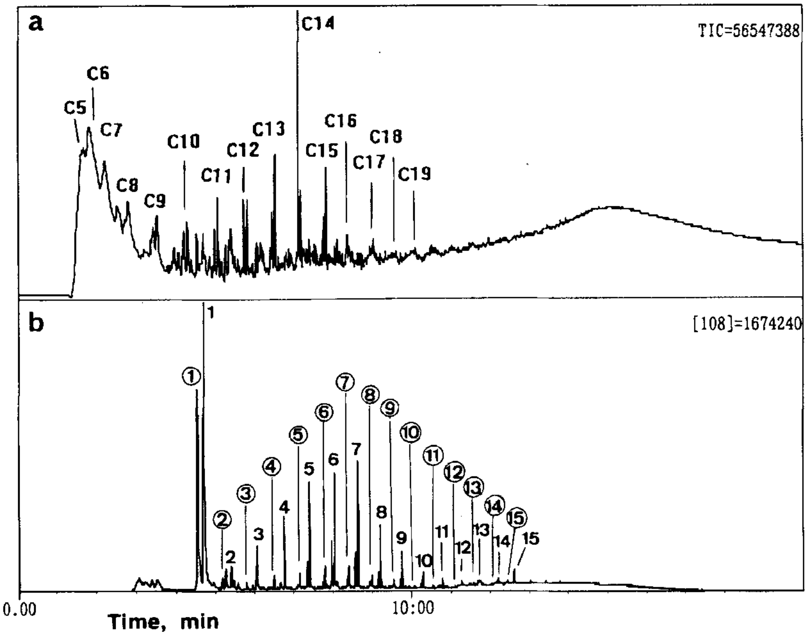
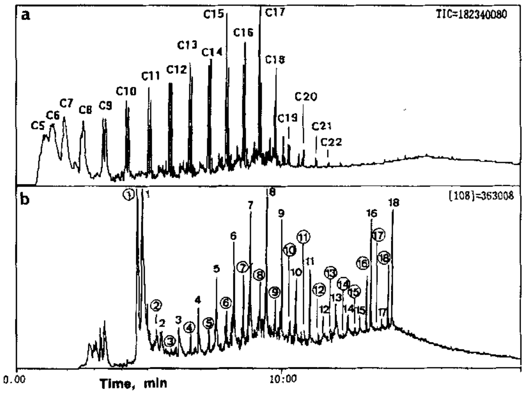


FIGURE 5 TIC and mass chromatogram of natural lacquer film obtained by pyrolysis at 500°C after pyrolysis at 400°C. a) TIC: C5: pentane; C6: 1-hexene; C7: heptane; C8; 1-octene, octane; C9: 1-nonene, nonane; C10: 1-decene, decane; C11: 1-undecene, undecane; C12: 1-dodecene, dodecane; C13; 1-tridecene, tridecane; C14: 1-tetradecene, tetradecane C15: 1-pentadecene, pentadecane; C16: 1-hexadecene, hexadecane; C17: 1-heptadecane; heptadecane; C18: 1-octadecene, octadecane; C19: 1-nonadecene, nonadecane; b) Mass chromatogram (m/z 108): ① 3-methylphenol; ② 3-ethylphenol; ③ 3-propylphenol; ④ 3-butylphenol; ⑤ 3-pentylphenol; ⑥ 3-hexylphenol; ⑦ 3-heptylphenol; ⑧ 3-octylphenol; ⑨ 3-nonylphenol; ⑩ 3-decylphenol; ⑪3-undecylphenol; ⑫ 3-dodecylphenol;⑬ 3-tridecylphenol; ⑭ 3-tetradecylphenol; ⑮3-pentadecylphenol; 1: 2-methylphenol; 2: 2-ethylphenol; 3: 2-propylphenol; 4: 2-butylphenol; 5: 2-pentylphenol; 6: 2-hexylphenol; 7: 2-heptylphenol; 8: 2-octylphenol; 9: 2-nonylphenol; 10: 2-decylphenol; 11: 2-undecylphenol; 12: 2-dodecylphenol; 13: 2-tridecylphenol; 14: 2-tetradecylphenol; 15: 2-pentadecylphenol

octadecenylphenols, octadecylphenols eicosenylphenols and eicosylphenols were formed from the terminal groups like the natural lacquer film. Based on these results, the polymerization of synthesized urushiol proceeds through the laccase-catalyzed nucleus-side chain C-O coupling and the polymer mainly terminated with alkyl- and monoenylcatechol as is the natural lacquer film.

Alkenes and alkanes were detected in the respective lacquer films as shown in each TIC. The relative peak intensity of the 1-tetradecene and

Synthesized lacquer film A



Synthesized lacquer film B

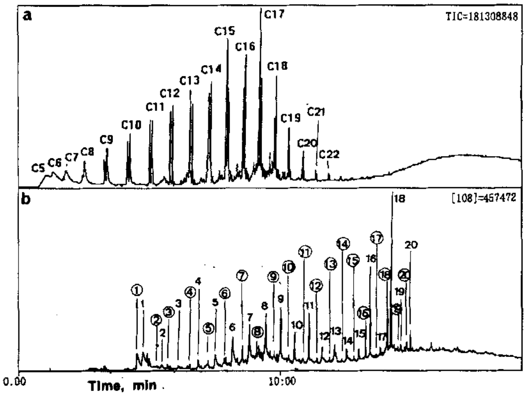


FIGURE 6 TIC and mass chromatograms of the synthesized lacquer films A and B obtained by pyrolysis at 500°C after pyrolysis at 400°C. a) TIC: C5: pentane; C6: 1-hexene; C7: heptane; C8: 1-octene, octane; C9: 1-nonene, nonane; C10: 1-decene, decane; C11: 1-undecene, undecane; C12: 1-dodecene, dodecane; C13: 1-tridecene, tridecane; C14: 1-tetradecene, tetradecane; C15: 1-pentadecene, pentadecane; C16: 1-hexadecene, hexadecane; C17: 1-heptadecene, heptadecane; C18: 1-octadecene, octadecane; C19: 1-nonadecene, nonadecane; C20: 1-eicosene, eicosane; C21: 1-heneicosene, heneicosane; C22: 1-docosene, docosane b) Mass chromatogram (m/z 108): ① 3-methylphenol; ② 3-ethylphenol; ③ 3-propylphenol; ④ 3-butylphenol; ⑤ 3-pentylphenol;⑥ 3-hexylphenol; ⑦ 3-heptylphenol; ⑧ 3-octylphenol; ⑨ 3-nonylphenol; ⑩ 3-decylphenol; ⑪ 3-undecylphenol; ⑫ 3-dodecylphenol; ⑬ 3-tridecylphenol; ⑭ 3-tetradecylphenol; ⑮ 3-pentadecylphenol; ⑯ 3-hexadecylphenol; ⑰ 3-heptadecylphenol; ⑱ 3-octadecylphenol; ⑲ 3-nonadecylphenol; ⑳ 3-eicosylphenol; 1: 2-methylphenol; 2: 2-ethylphenol; 3: 2-propylphenol; 4: 2-butylphenol; 5: 2-pentylphenol; 6: 2-hexylphenol; 7: 2-heptylphenol; 8: 2-octylphenol; 9: 2-nonylphenol; 10: 2-decylphenol; 11: 2-undecylphenol; 12: 2-dodecylphenol; 13: 2-tridecylphenol; 14; 2-tetradecylphenol; 15: 2-pentadecylphenol; 16: 2-hexadecylphenol; 17: 2-heptadecylphenol; 18: 2-octadecylphenol; 19: 2-nonadecylphenol; 20: 2-eicosylphenol

tetradecane (C14 hydrocarbons) is the highest in the natural lacquer film, while in the synthesized lacquer film, that of 1-heptadecene and heptadecane(C17 hydrocarbons) is the highest. The highest yield of these compounds cannot be attributed to the trienyl and dienyl side chains of natural and synthesized urushiol, because the α- and β-positions relative to the double bonds of the olefin are reported to be the most susceptible to thermal cleavage.[11] Shorter hydrocarbons could be formed from the trienyl and dienyl chains through scissions at thermally liable α- and β-positions relative to the double bonds, rather than from the C14 and C17 hydrocarbons. However, the degradation pathway generally proposed for macromolecular-bound aromatic moieties is cleavage of the carbon-carbon bond between the α- and β-carbon atoms ("β- scission") of the side chain through which the aromatic nucleus is linked.[18–20] Therefore, the highest yield of the C14 hydrocarbons and C17 hydrocarbons can be attributed to the preferential cleavage of the terminal pentadecyl-, octadecyl-, pentadecenyl- and octadecenyl- side chains at the β-position relative to the aromatic ring.

In the natural lacquer film, some alkenes and alkanes have carbon chains longer than the side chains of urushiol. Lacquer is reported to be autoxidized in air in addition to the laccase-catalyzed oxidative coupling.[12] Additionally, side chain oxidized dimers of urushiol were observed by the oxidation of the side chains in urushiol from the laccase-catalyzed polymerization of natural lacquer.[10] The usual autoxidation mechanisms for polymerization of unsaturated fatty acids may be applicable, because the interaction of molecular oxygen with metal complexes may produce reactive oxygen species such as superoxide and peroxide as precursors in this mechanism.[13–15] However, not much structural information is yet available on the secondary oxidation products with high molecular weights, which appear to be important in unsaturated fatty acids such as linoleate and linolenate.[16] Autoxidation of the unsaturated side chain of urushiol leads to the formation of hydroperoxides. These hydroperoxides participate in the cross-linking reaction of urushiol as well as the autoxidative polymerization of unsaturated fatty acids.[17] Accordingly, dimeric products generated by the autoxidative side chain-side chain C-C coupling of natural urushiol were cleaved by pyrolysis and that the long-chain alkanes and alkenes were produced as a result of that cleavage.

It is observed that some alkenes and alkanes also have carbon chains longer than the side chains of synthesized urushiol in the synthesized lacquer film. These must be pyrolysis products of the autoxidative side chain-side chain C-C coupling polymer of synthesized urushiol, because the synthesized urushiol has the unsaturated side chains, as does natural urushiol. These side chains lead to the cross-linking reaction of synthesized urushiol.

As shown above, the polymerization of synthesized urushiol proceeds through the autoxidative side chain-side chain C-C coupling in addition to the laccase-catalyzed nucleus-side chain coupling as is true of natural urushiol.

CONCLUSIONS

Two kinds of synthesized lacquer films, in which the monomers were synthesized from linseed oil and tung oil by alkylation and intramolecular cyclization, were investigated and compared with natural lacquer film using two-stage pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Monoenyl and saturated synthesized urushiol was detected by the pyrolysis at 400°C, and alkenylphenols, alkylphenols, alkenes and alkanes, which have longer carbon chains than the side chains of synthesized uru-shiol, were detected by pyrolysis at 500°C after pyrolysis at 400°C of the respective lacquer films.

Based on these results, it was shown that the synthesized lacquer films are terminated with the monoenyl and saturated urushiol, and the polymerization of synthesized urushiol proceeds through the laccase-catalyzed nucleus-side chain C-O coupling and the autoxidative side chain-side chain C-C coupling the same as natural lacquer film. Since the structure and polymerization mechanisms of the synthesized lacquer films are very similar to those of the natural lacquer film, these lacquer films must be tough and brilliant enough to be used as preservative surface coating materials like the natural lacquer film.

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