

Preparation and Characterization of a New Lacquer Based on Blending Urushiol with Thitsiol

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ABSTRACT: A new lacquer that blends *R. vernicifera* (Chinese lacquer, urushiol) with *Melanorrhæa usitata* (Thai lacquer, thitsiol) was prepared. The main properties, viscosities, drying times, drying mechanism, and the nature of the lacquer films as a coating material, were examined. In addition, the mechanism of transfer radical reaction that occurred between urushiol and thitsiol is discussed based on the results of two-dimensional nuclear magnetic resonance (NMR) and field desorption mass spectrometry (FD-MS) measurements. A blended lacquer

with 70% *R. vernicifera* and 30% *M. usitata* showed almost the same drying time as 100% *R. vernicifera* as examined in an automatic drying time recorder but had higher surface smoothness and gloss. Furthermore, the molecular weight distribution, UV resistance, and glass transition temperature (T_g) also were investigated in detail. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2734–2742, 2011

Key words: blended; urushiol; thitsiol; drying time; gloss

INTRODUCTION

Lacquer sap tapped from lacquer trees grown in various Asian countries have been investigated in our previous works.¹ The lacquer sap from *Melanorrhæa usitata*, which has thitsiol as the main component, has a slower drying time and requires more severe drying conditions than sap from *R. vernicifera*, which has urushiol as the main component, and produces a smoother and glossier film surface. However, the lacquer sap from *M. usitata* is about 2000–3000 yen kg⁻¹ in the Japanese market, which is cheaper than that from *R. vernicifera* (10,000–12,000 yen kg⁻¹ in the Japanese market). Therefore, how to effectively use this inexpensive lacquer sap in the coating industry becomes a very important subject for research.

Previously, we developed a series of fast-drying lacquers using kurome,² hybridized,^{3–5} and blended methods.⁶ Using these techniques to improve the slow drying time of thitsiol, in this study, we tried blending urushiol with thitsiol to make a new blended lacquer. By comparing the viscosities, drying properties, and film characteristics and analyzing the results from two-dimensional nuclear magnetic

resonance (NMR) and field desorption mass spectrometry (FD-MS), the reaction mechanism between urushiol and thitsiol was elucidated. In the future, we wish to explore the use of thitsiol in the coating industry based on the results of this research.

EXPERIMENTAL

Materials

The raw *R. vernicifera* lacquer was the sap of a Chinese lacquer tree in Chengkou, in the province of Hubei, China, and *M. usitata* was the sap of a Thai lacquer tree. Both produced in the year 2008, and were purchased from Tohtyū, Osaka, Japan. The raw lacquer saps were used directly in this study.

Methods

The two raw lacquer saps were mixed in various ratios, as showed in Table I, in plastic sample cups and stirred at room temperature at least for 10 min. After putting aside for more than 30 min, the mixed samples were used in viscosity and drying time measurements, and the proportions of monomers, oligomers, and polymers were determined.

The viscosities were determined at room temperature using a Brookfield Engineering Laboratories, programmable DV-II+ viscometer, and a CPE-51 spindle. The rotation speed was 5–20 rpm, and the measurement volume was 0.5 mL.

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TABLE I
Ratios of Blended Chinese and Thai Lacquers

Blended lacquer name	Chinese lacquer (wt %)	Thai lacquer (wt %)
BL-1	100	0
BL-2	100	10
BL-3	100	30
BL-4	100	50
BL-5	100	100
BL-6	0	100

The proportions of monomers, oligomers, and polymers in the blended lacquer were determined at 40°C by aqueous-phase gel permeation chromatography [GPC; TSKgel columns α -3000, α -4000, and α -M, ϕ 7.8 mm \times 300 mm \times 3, Tosoh] using dimethylformamide (DMF) with 0.01 mol of LiBr as an eluent on a high-performance liquid chromatography system using a refractive-index detector with polystyrene standards having molecular weights of 1.90×10^5 , 4.39×10^4 , 5.40×10^3 , and 5.00×10^2 . The elution rate and pressure of the DMF eluent were 0.8 mL min⁻¹ and 48 kgf cm⁻², respectively.

A rigid-body pendulum physical property-testing (RPT) instrument (A&D, Japan) was used to determine the viscoelasticity of lacquer films. The RPT oven was programmed to rise from 25 to 250°C at a rate of 2°C min⁻¹.

The drying properties of the blended lacquers were measured with an automatic drying time recorder (Tai Yu Equipment, Osaka, Japan). The thickness of the tested lacquer films was 76 μ m. The lacquer drying process could be divided into three stages: dust-free dry (DF), touch-free dry (TF), and hardened dry (HD).⁷ The time until the mark of the needle appears on the glass board is equivalent to DF, the time until the mark of the needle appears on the lacquer film surface is equivalent to TF, and the time until the mark of the needle on the lacquer film surface disappears completely is equivalent to HD.

UV irradiation from one side of the square glass plate film was measured using a Handy UV800 system (ORC, Tokyo, Japan), equipped with a high-pressure mercury lamp HHL-800/C-FL (80 W cm⁻¹, emission light length 100 mm). The distance from the source of UV irradiation in the experiment was 82.5 mm.

IR spectra were determined using a JASCO Fourier transform infrared 460+ spectrometer (Tokyo, Japan). Because it was possible for the moisture in the lacquer exudates to melt a KBr or NaCl crystal, a polyvinylidene chloride film (Saran Wrap, Asahi Kasei, Tokyo, Japan) were used to support the IR samples. The lacquer saps were spread thinly on the polyvinylidene chloride film with a spatula, and the same kind of polyvinylidene chloride film was used

as a blank. Spectra of samples were acquired at 2 cm⁻¹ resolution ranging from 500 to 4000 cm⁻¹.

The enzyme-catalyzed reaction products of the blended lacquers were separated with acetone (50 mL) at 3.5 h, and the TF stage and HD stage were determined after drying in a chamber with 80% relative humidity at 30°C. The acetone solution was filtered off to obtain the acetone-insoluble fraction, namely acetone powder, which includes the enzyme laccase and polysaccharides. The acetone-soluble fraction was evaporated under vacuum to obtain the residue. This residue was analyzed by an HPLC LC-908 system (Japan Analytical, Tokyo, Japan) equipped with an HPLC column (Tosoh, TSK-gel G1000H6, 7.6 mm (i.d.) \times 300 mm \times 2; exclusion limit $M_r = 1000$) and an RI and UV (254 nm) detector. The sample (5 mg) was dissolved in 2 mL of CHCl₃. The resulting solution was injected using a 5 mL syringe into the column through a pretreatment PTFE cartridge containing an H-13-5 filter disc into the column, and then the column was eluted with CHCl₃ at a rate of 2.0 mL min⁻¹ polystyrenes with molecular weights of 200, 400, 600, and 1000 were used as standards.

The blended lacquers were dried in 80% RH at 30°C, and then used as NMR samples in the three stages of DF, TF, and HD. All NMR spectra including two-dimensional NMR such as double quantum filtered correlated spectroscopy (COSY), heteronuclear multiple quantum coherence, and heteronuclear multiple bond coherence (HMBC) were recorded at 500 MHz on a JEOL JNM-ECA500 spectrometer by using the phase-sensitive mode and a field-gradient probe. DMSO-*d*₆ was used as a solvent for tetramethylsilane (TMS) as the internal standard. JEOL standard software was applied to the two-dimensional spectra.

FD-MS measurement was carried out using a JEOL JMS-700 QQ-type spectrometer system at the acceleration voltage of 6 kv with a mass range from $m/z = 45$ –1000 with Me₂CO as the analysis solvent.

RESULTS AND DISCUSSION

Ratios of monomers, oligomers, and polymers

The proportions of monomers, oligomers, and polymers in the blended lacquers were determined at 40°C by GPC measurement, and the calculated data were summarized in Table II. The results showed that as the ratio of thitsiol increased in the blended lacquers, monomers decreased and oligomers and polymers increased. The increase in the percentages of oligomers and polymers corresponded to the increased ratio of thitsiol, suggesting that a reaction between urushiol and thitsiol had occurred.

TABLE II
Molecular Weight Distribution and Viscosities of Blended Lacquers

Blended lacquer name	Monomer	Oligomer	Polymer	Viscosities (mPa s ⁻¹)
BL-1	85.3	14.7	0	1251
BL-2	83.3	16.5	0.2	1635
BL-3	76.2	22.7	1.1	2238
BL-4	69.2	28.2	2.6	3678
BL-5	64.4	32.5	3.1	4857
BL-6	52.6	40.3	7.1	7047

Viscosities

The viscosities of blended lacquers were measured using a Brookfield programmable DV-II+ viscometer, and the results also are summarized in Table II. Because thitsiol contains more oligomers and polymers than urushiol, the viscosities of the blended lacquers increased with the addition of thitsiol, in good agreement with the increase in the proportions of oligomers and polymers in the blended lacquers due to the thitsiol. All viscosities of the blended lacquers are suitable for coating (1000–7000 mPa s⁻¹).

Drying properties

The drying times of the blended lacquers were measured by using an automatic drying time recorder under 80% relative humidity at 30°C. The results are summarized in Table III. It can be observed that the drying times after adding 50 wt % (BL4) and 100 wt % (BL5) of thitsiol to the urushiol have the same DF after 2 h, HD after 5 h, and HB hardness after 5 days. The blended lacquers added Thai lacquer 10 W% to Chinese lacquer (BL2) and 30 wt % (BL3) thitsiol had DF after 1 h and 2H hardness after 5 days, the same as *R. vernicifera* lacquer (BL1). The reason will be discussed in the following section. There was no change in the drying time of the *M. usitata* lacquer (BL6) even when the laccase separated from *R. vernicifera* lacquer was added, implying that the polymerization of thitsiol is activated by the active intermediates of urushiol. This conjecture was confirmed by the results

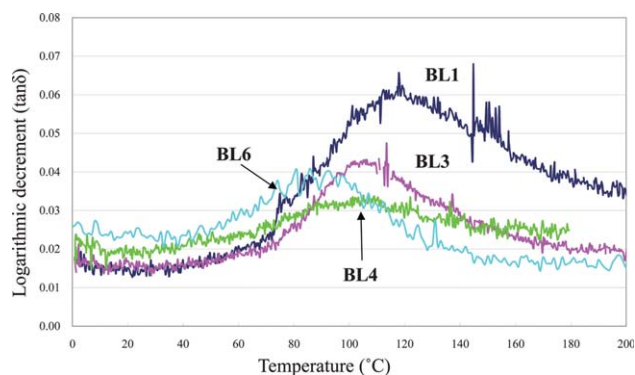


Figure 1 T_g of blended lacquer films with RPT measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

from two-dimensional NMR and FD-MS measurements described in the following section.

Glass transition temperature

The surface morphology, molecular motion, and glass transition behavior of polymer films are quite important because many properties such as chemical and abrasion resistance and wettability are determined predominantly by the structure within a few nanometers of the surface.^{8,9} To reveal the surface properties of the blended lacquer films, the glass transition temperature (T_g) was analyzed by RPT measurement. All blended lacquer samples were dried under 80% relative humidity at 30°C for 7 days. The results in Figure 1 show that the T_g decreased with the increase of the percentage of thitsiol. Compared with the T_g of 119°C for the *R. vernicifera* lacquer film, the T_g of the blended lacquer films were lower, that is, 108°C for 30 wt %, 104°C for 50 wt %, but higher than the 79°C of the *M. usitata* lacquer film. All T_g of the blended lacquer films were higher than that of the Thai lacquer film, suggesting that the cross-linkage polymerization in blended lacquers is faster than that in Thai lacquer. All properties of the lacquer films, such as color, gloss, and T_g , changed depending on the drying time and drying conditions because the side chains of urushiol and/or thitsiol undergo continuous auto-oxidation during the drying process.

TABLE III
Drying Properties of Blended Lacquers Under 80% Relative Humidity at 30°C

Names	Drying properties									
	1 h	2 h	3 h	4 h	5 h	1 day	2 day	3 day	4 day	5 day
BL-1	DF	TF	HD	HD	6B	F	F	H	2H	2H
BL-2	DF	TF	HD	HD	6B	F	F	H	2H	2H
BL-3	DF	DF	TF	HD	6B	F	F	F	2H	2H
BL-4	ND	DF	TF	TF	HD	B	B	B	B	HB
BL-5	ND	DF	TF	TF	HD	2B	B	B	B	HB
BL-6	ND	ND	ND	ND	ND	TF	HB	6B	6B	6B

Abbreviations: DF, dust-free dry; TF, touch-free dry; and HD, hardened dry.

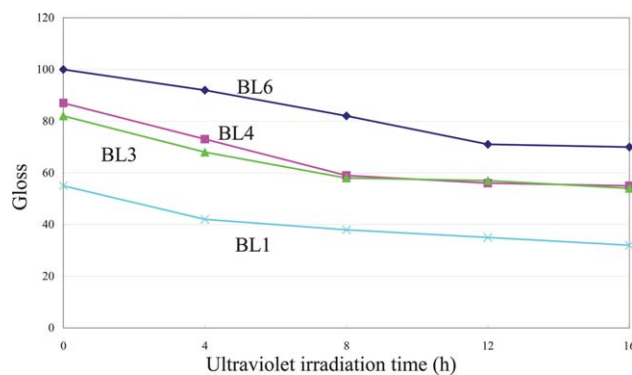


Figure 2 Gloss maintenance of blended lacquer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

UV resistance

BL3 and BL4 samples were subjected to the ultraviolet light resistance test, and the results were compared with those of BL1 and BL6. All samples were applied to glass sheets ($40 \times 20 \times 1 \text{ mm}^3$) at $76 \mu\text{m}$ thickness and dried in 80% relative humidity at 30°C for over 1 month. The decrease in the gloss of the blended lacquer films is shown in Figure 2. The glosses of the blended lacquer films were lower than those of the pure Thai lacquer film (BL6), but higher than those of the pure China lacquer film (BL1). The gloss maintenance was calculated from Figure 2 as 70% for BL1, 63% for BL3, 66% for BL4, and 53% for BL6, respectively. Because a reaction between urushiol and thitsiol occurred to form polymer networks, it can be concluded that maintenance of the gloss of blended lacquer film may be contribution of the thitsiol component.

IR measurement

To examine the behavior of the enzymatic dehydrogenative polymerization of blended lacquers during the drying process, a time course of IR spectra was carried out. All lacquer samples were dried in 80% RH at 30°C for 0, 1, 3, 6, 24, and 72 h. Figure 3 shows the IR spectra of BL5 blended lacquers that were dried over the time course. The peaks at 3400 and 1400 cm^{-1} due to the absorption of the hydroxyl groups decreased, suggesting that laccase-catalyzed polymerization had occurred. However, the absorption peaks at 1470 and 1080 cm^{-1} of quinone-olefin and/or dibenzofuran did not appear, and the absorptions at 3013 , 1280 , 732 , and 698 cm^{-1} were decreased, indicating that monomeric urushiols decreased as the laccase-catalyzed polymerization advanced.

NMR measurement

The structures of oligomers produced by the laccase-catalyzed dehydrogenative polymerization of blended lac-

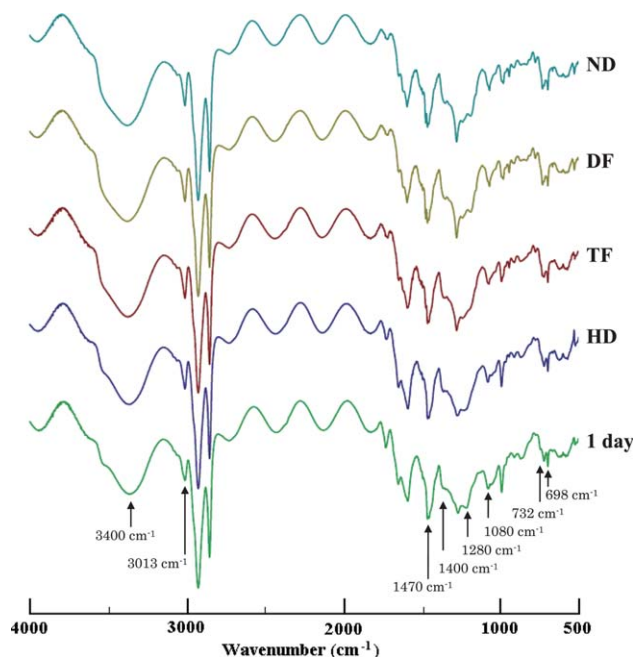


Figure 3 IR spectra of BL-5 blended lacquer dried at ND, DF, TF, HD, and 1 day. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quers were analyzed over the time course by proton-NMR and two-dimensional NMR measurements. The samples were dried in 80% RH at 30°C , and then immersed into acetone for 30 min, the dissolution was taken as NMR samples in the three stages of DF, TF, and HD. Figure 4 shows the ^1H NMR spectra of BL5 blended lacquers in three stages (DF, TF, and HD) due to the enzymatic dehydrogenative polymerization, ND stands for nondry (wet blended lacquer); and "1 day" stands for lacquers dried for 1 day. In the ^1H NMR spectra, signals in the δ_{H} -range of 5–6 showed that as olefin protons of the urushiol side chain decrease rapidly due to the occurrence of laccase-catalyzed dehydrogenative polymerization occurred between urushiol and thitsiol. It can be observed

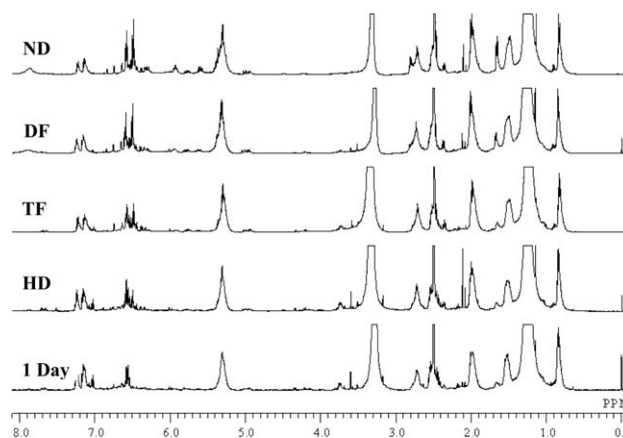


Figure 4 ^1H NMR spectra of the BL-5 blended lacquers.

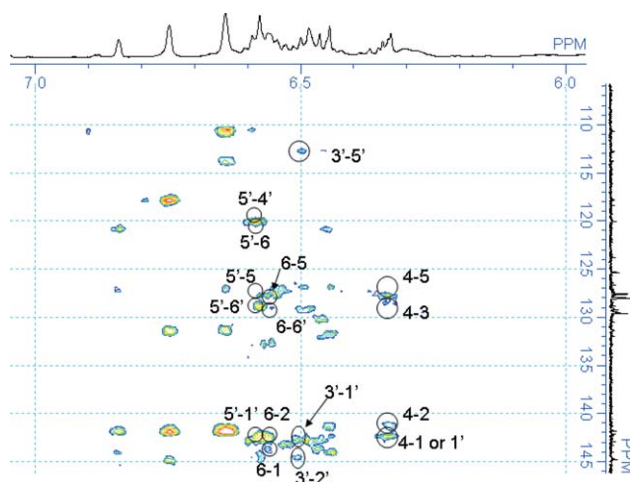


Figure 5 HMBC spectrum of the BL-5 blended lacquers (DMSO- d_6 as solvent, 25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the enzymatic dehydrogenative polymerization of urushiol is higher than that of thitsiol. The difference in number of C—C double bonds is about 4.6H in the side chains of urushiol and about 3.2H in those of thitsiol. Figure 4 also shows that the signals for protons at δ_H -range of 6.37–6.67, corresponding to biphenyl units increased in the integrated area ratio due to the coupling of urushiol and thitsiol, suggesting that radical coupling products of nucleus–nucleus (Ph–Ph) and nucleus–side chain (Ph–C) were generated.¹⁰ Consequently, hydroxyl groups had decreased with the progress of the laccase-catalyzed dehydrogenative polymerization.

To characterize the chemical reaction occurred between urushiol and thitsiol, two-dimensional NMR measurement was carried out. Figure 5 is one of the HMBC spectra of blended lacquer dried to the stage of DF; all correlation signals were assigned, and the data was summarized in Table IV. From Table IV, it can be concluded that an urushiol–thitsiol dimer was generated. After assigning all two-dimensional NMR spectra, we estimated that the urushiol radicals were first generated in the early stages of polymerization due to enzyme-catalyzed reaction, and then semiquinone radicals were generated as the radicals shifted. Some semiquinone radicals coupled to form biphenyl and/or dibenzofuran types of urushiol dimers. On the other hand, some urushiol semiquinone radicals as initiators attack thitsiol to form thitsiol radicals, so that three kinds of dimers, urushiol–urushiol, urushiol–thitsiol, and thitsiol–thitsiol, were generated and detected in NMR measurements. Based on these results, the reaction mechanism will be discussed in following section.

FD-MS measurement

The FD-MS spectrum obtained from the ether extract of the laccase-catalyzed dehydrogenative polymeriza-

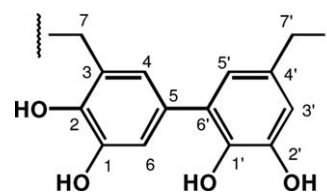
tion of urushiol (BL1) exhibited a mixture of dimethyl ethers of monomers and dimers. The peaks with the $m/z = 342$ (C_{15} -triene type), 344 (C_{15} -diene type), 346 (C_{15} -monoene type), and 348 (C_{15} saturated type) were *O*-dimethyl ethers of unreacted monomers (figure not shown). However, the prominent peaks in the m/z -range of 684–692 correspond to the *O*-tetramethylated ethers of dimeric products [Fig. 6(A)] that were produced by the laccase-catalyzed dehydrogenative polymerization.

Similarly, the FD-MS spectrum of thitsiol (BL6) also exhibited a mixture of *O*-dimethyl ethers of monomers and dimers. The peaks at the $m/z = 370$ (C_{17} -triene type), 372 (C_{17} -diene type), 374 (C_{17} -monoene type), 376 (C_{17} -saturated type), and 382 [$C_6H_5-(CH_2)_{12}C_6H_3-(OH)_2$ type] correspond to thitsiol and 12-phenyldodecylcatechol *O*-dimethyl ethers of unreacted monomers (figure not shown). The prominent peaks in the m/z range of 724–752 correspond to the *O*-di- and *O*-tetramethylated ethers to thitsiol dimeric products [Fig. 6(B)]. These dimeric ion peaks clearly indicate that the dimeric products were produced by coupling of thitsiol radicals due to the laccase-catalyzed dehydrogenative polymerization.

Furthermore, the FD-MS spectrum of BL5 exhibits a mixture of monomers and dimers of thitsiol and urushiol *O*-dimethyl ethers. The peaks at the $m/z = 342$ (C_{15} -triene type), 344 (C_{15} -diene type), 346 (C_{15} -monoene type), 348 (C_{15} saturated type), corresponding to urushiol *O*-dimethyl ethers and $m/z = 370$ (C_{17} -triene type), 372 (C_{17} -diene type), 374 (C_{17} -monoene type), 376 (C_{17} -saturated type), and 382 [$C_6H_5-(CH_2)_{12}C_6H_3-(OH)_2$ type], were *O*-dimethylated ethers of thitsiols and 12-phenyldodecylcatechol

TABLE IV
Assignments of Correlations in HMBC of Blended Lacquer

Peaks (ppm)	Coupling	Peaks (ppm)	Coupling
6.34–29.74	4-7	6.56–141.39	6-2
6.34–127.87	4-5	6.56–142.504	6-1
6.34–128.56	4-3	6.58–120.08	5'-4'
6.43–141.39	4-2	6.58–120.24	5'-6
6.43–142.50	4-1 or 4-1'	6.58–129.18	5'-6'
6.50–112.73	3'-5'	6.58–142.50	5'-1'
6.50–142.62	3'-1'	6.58–127.87	5'-5
6.50–144.58	3'-2'	2.36–118.67	3'-7'
6.56–127.87	6-5	2.53–121.07	4-7
6.56–129.18	6-6'		



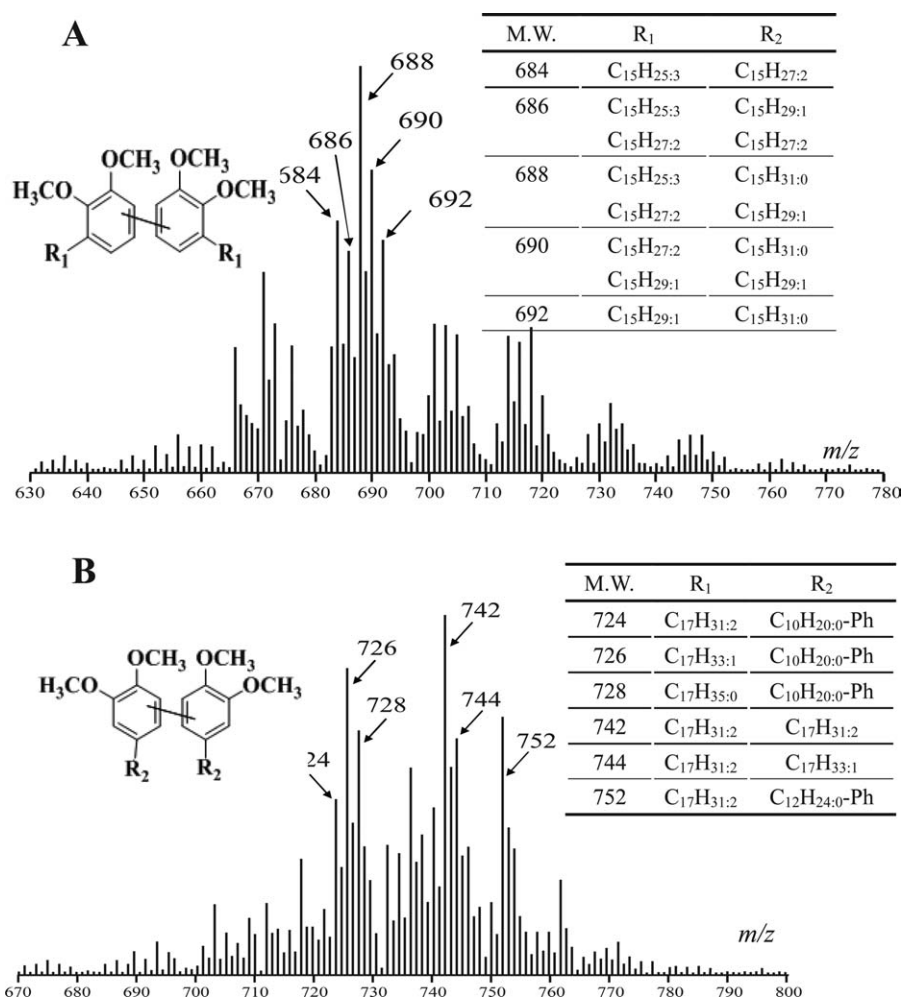


Figure 6 FD-MS results of dimeric reaction of (A) urushiol and (B) thitsiol.

(figure not shown). The peaks at the m/z -range of 684–692 correspond to *O*-dimethyl ethers of urushiol dimers, whereas the peaks in the m/z -range of 724–752 correspond to *O*-dimethyl ethers of thitsiol dimers. In addition, the spectrum exhibits several new molecular ions peaks in the m/z -range of 712–718, which correspond to the *O*-dimethylated ethers of dimers produced by cross-coupling among urushiols, thitsiols, and 10-phenyldodecanylcatechols including 12-phenyldodecylcatechol (Fig. 7). These new dimeric molecular ions clearly indicate the occurrence of cross-coupling among radical species produced from laccase-catalyzed urushiol, thitsiol, and 10-phenyldodecanylcatechols types by enzymatic single-electron dehydrogenation to produce the corresponding compounds.

Reaction mechanism

Radical formation of urushiol with the enzyme laccase occurred rapidly under 30°C in an 80% relative humidity environment, because urushiol is easily dried to form a film by enzymatic polymerization, but radical

formation of thitsiol by the laccase was very slow in the same conditions. However, the blended lacquer with 30 wt % of thitsiol dried almost as fast as urushiol in the same drying conditions. The reaction mechanism in the blended lacquers can be described as follows: the laccase-catalyzed dehydrogenative formation of phenoxyl radicals from urushiol is first catalyzed by enzymatic oxidation, then thitsiol radicals are produced from thitsiols with phenoxyl radicals of urushiol by a radical transfer reaction,¹¹ and then a coupling reaction between these two radical species occurs to form dimers. In the propagation step, the dimeric products would further undergo both radical transfer reactions and dehydrogenative oxidation by laccase under presence of dioxygen in the atmosphere. The resulting radical species including monomer radical species would then couple among themselves to give the higher molecular weight polymer, as shown in Scheme 1.

Scheme 1 suggests that phenoxyl radicals of urushiols are formed by laccase-catalyzed oxidation in the presence of dioxygen in the atmosphere; then, thitsiol radicals are formed by the radical transfer of the radical species of urushiols in the presence of laccase.

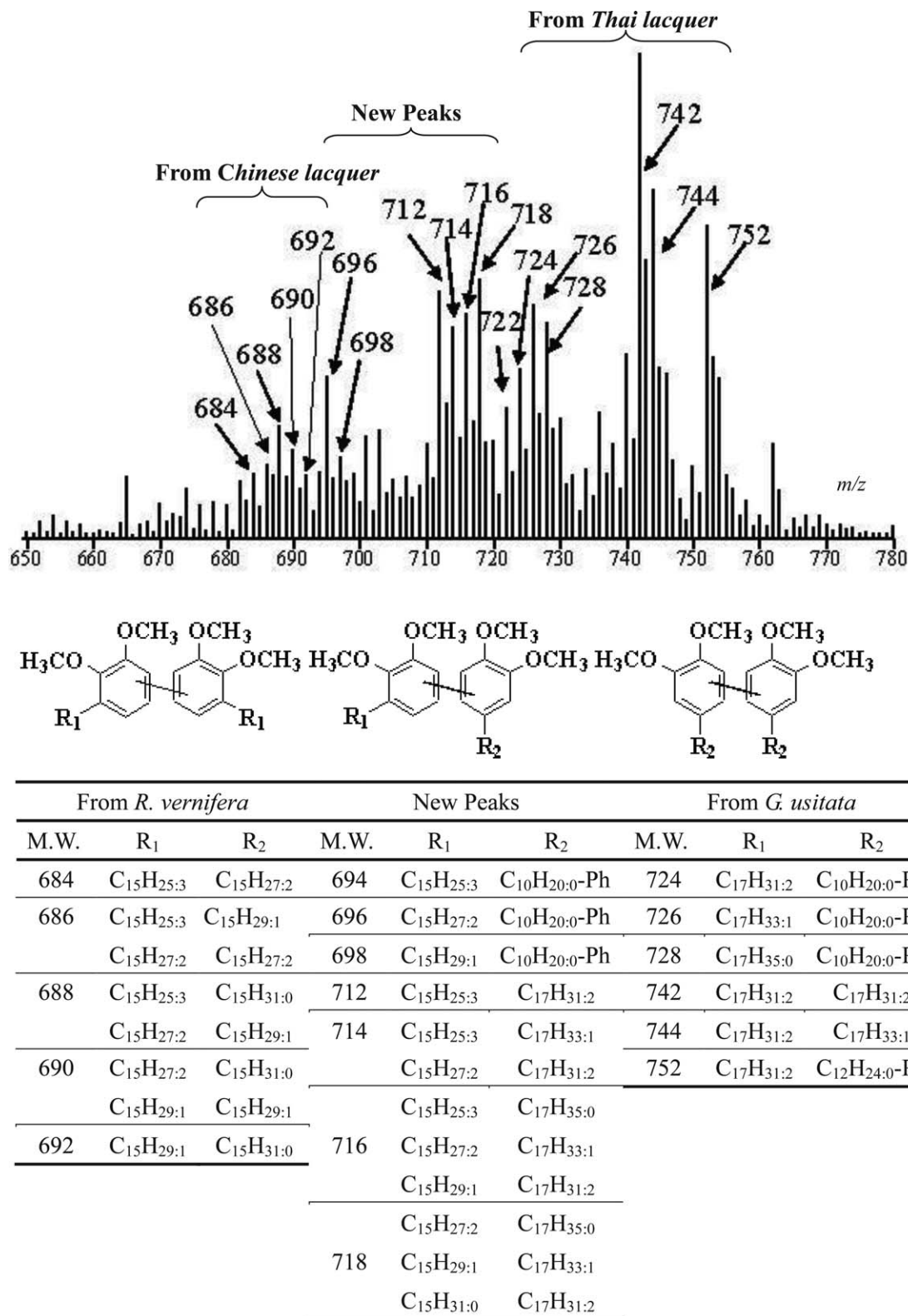


Figure 7 FD-MS results of dimeric reaction of blended lacquers.

Subsequently, the radical coupling takes place among these radical species, leading to the formation of urushiol-thitsiol mixed polymers. These results clearly show

that urushiol and thitsiol can be copolymerized via radical transfer reaction by the enzymatic oxidative coupling.

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