Synthesis and Curing Behaviors of Cross-Linkable Polynaphthols from Renewable Resources: Preparation of Artificial Urushi

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ABSTRACT: This paper describes the synthesis and curing of cross-linkable polynaphthols from renewable resources. Naphthol monomers bearing an unsaturated group from renewable triglyceride oils were designed and oxidatively polymerized to produce new cross-linkable precursor polymers. The monomers were prepared by acylation of hydroxynaphthoic acids with unsaturated alcohols, obtained by reduction of natural oils. The oxidative polymerization was carried out by Fe-salen catalyst to give soluble polynaphthols. NMR analysis showed that the naphthol moiety was chemoselectively reacted during the polymerization, yielding the polymers possessing the unsaturated group in the side chain. The resulting polymers were readily cured by thermal treatment or cobalt naphthenate catalyst to give the cross-linked film ("artificial urushi") with high hardness and gloss surface.

Introduction

Replacement of petroleum-derivated raw materials with plant-based ones is strongly desired from environmental viewpoints. Therefore, preparation of polymeric materials from renewable resources has been of great significance economically and ecologically. Natural oils of plant and animal origins are employed in the largest portion of the current consumption of renewable raw materials in chemical industry. They provide various potential applications, which are often difficult to realize by petrochemical sources.¹

Urushi is a typical Japanese traditional lacquer, which is prepared from sap of the tree *Rhus vernicifera*.² The main components of urushi are urushiols, catechol derivatives bearing a C15 unsaturated hydrocarbon chain at the 3- or 4-position.³ Film-forming of the urushiol proceeds under air at room temperature without organic solvents; hence, urushi seems very desirable for coating materials from the environmental standpoint. We have developed "artificial urushi" by an enzymatic curing of new urushiol analogues, in which a C18 unsaturated group derived from plant oils is connected with the catechol group through an ester linkage.⁴ Furthermore, cross-linkable polyphenols were developed by an oxidative polymerization of another urushiol analogues, i.e., the phenols possessing the plant oil-based unsaturated fatty acid moiety.⁵ Cardanol, a phenol derivative from cashew nut shell liquid, was also oxidatively polymerized, yielding a soluble polyphenol having an unsaturated alkyl group.⁶ These polyphenols were readily cured to produce a transparent cross-linked film (also artificial urushi) showing an excellent dynamic viscoelasticity. We have also developed new crosslinkable polyesters from plant oils. Aliphatic polyesters having the unsaturated fatty acid or its epoxidized group in the side chain were synthesized by using lipase catalyst, which were cured by thermal treatment to give biodegradable cured polymers.⁷

It was reported that polynaphthols were synthesized by oxidative polymerization of naphthol derivatives using transition-metal complexes⁸ or enzymes⁹ as catalyst. The present study deals with synthesis and curing of cross-linkable polynaphthols having an unsaturated alkyl group in the side chain (Scheme 1). For preparation of the precursor polymers, new urushiol analogue monomers of naphthol derivatives having the unsaturated alkyl group derived from linseed oil and fish oil were designed and synthesized. Chain stiffening of the polynaphthol is expected to improve film properties of the cured polymer.

Plant and animal oils have excellent properties which can be utilized for production of valuable polymeric materials such as epoxy resins, alkyds, and polyurethanes in addition to their other applications in agriculture and food industries.¹⁰ Linseed oil is one of the most popular drying oils used for a wide variety of applications in the field of coatings and paints. Since linseed oil has a triglyceride structure with a high percentage of linoleic acid and linolenic acid, it dries faster than other seed oils, providing better coating properties.¹¹ Large amounts of polyunsaturated fatty acid groups are also contained in fish oils, which currently attract much interest in the nutrition area because of their desired properties for human health.¹² Thus, fish oil derivatives have been increasingly applied for pharmaceutical products, food additives, and health supplements. Among them, the concentrates of eicosapentanoic and docosahexanoic acids are main components for the applications. Fish oil-based thermosetting polymers were also reported.¹³ Here, polyunsaturated alcohols prepared by reduction of linseed and fish oils were used for introduction of the unsaturated group into the naphthol derivatives. The main components of unsaturated fatty acids in linseed oil are linolenic acid (56%), oleic acid (20%), and linoleic acid (15%). Palmitic acid (27%), docosahexanoic acid (20%), oleic acid (15%), and eicosapentaenic acid (13%) are mainly contained as fatty acid components in a fish oil.

Experimental Section

Reduction of Linseed Oil.¹⁴ Lithium aluminum hydride (6.8 g, 180 mmol) was dispersed in 450 mL of tetrahydrofuran (THF) under nitrogen. Linseed oil (17.5 g, 20 mmol) was added with stirring. The reaction mixture was then stirred continuously at room temperature. After 7 h, 40 mL of water was slowly added. The mixture was further stirred for 15 min and filtered. The solvent was removed under reduced pressure to



High-performance Coatings ("Artificial Urushi")



ROH : Alcohol derived from linseed oil (a) or fish oil (b)

give the corresponding alcohol (14.1 g, yield 89%). ¹H NMR (CDCl₃) δ : 0.9 (t, CH₃), 1.4 (br, $-CCH_2C-$), 1.6 (m, $-CH_2CH_2OH$), 1.7 (s, $-CH_2OH$), 2.0 (m, $-CH=CHCH_2C-$), 2.8 (m, $-CH=CHCH_2CH=CH-$), 3.6 (t, $-CH_2OH$), 5.4 (m, -CH=CH-).

Similarly, the alcohol derived from a fish oil was synthesized and the structure was confirmed by 1 H NMR.

Synthesis of 1a. Monomer **1a** was synthesized according to Scheme 2. A mixture of 6-hydroxy-1-naphthoic acid (52.8 g, 280 mmol) and acetic anhydride (100 mL) was heated at 60 °C with gentle stirring under nitrogen. After 5 h, a large amount of water was added to the mixture. The formed solid was separated by filtration and dried in vacuo to give 55.7 g of 6-acetoxy-1-naphthoic acid (**3**). Then, **3** (55.7 g) was heated

 Table 1. Oxidative Polymerization of Naphthol

 Monomers (1 and 2)^a

			polymer		
entry	monomer	catalyst ^b (%)	yield ^c (%)	$M_{ m n}{}^d$ (×10 ⁻³)	$M_{\rm w}/M_{\rm n}^{d}$
1	1a	0.3	85	3.5	1.5
2	1a	0.5	85	4.2	1.6
3	1a	0.7	85	4.6	1.9
4	1a	1.0	84	4.5	1.5
5	1b	0.5	81	3.0	1.3
6	2a	0.5	83	4.0	1.4
7	2b	0.5	87	3.3	1.5

^{*a*} Polymerization of the monomer (3.0 mmol) using Fe-salen as catalyst in THF (10 mL) at room temperature for 2 h under air. ^{*b*} Mol % for monomer. ^{*c*} Methanol-insoluble part. ^{*d*} Determined by SEC using THF eluent.

with thionyl chloride (100 mL) at 40 °C with gentle stirring under nitrogen. After 2 h, unreacted thionyl chloride was removed under reduced pressure to give 60.5 g of 6-acetoxy-1-naphthoic chloride (4). Under nitrogen, 4 (60.5 g) was dissolved in dichloromethane (300 mL). A dichloromethane solution of unsaturated alcohol derived from linseed oil (62.6 g) and 4-(dimethylamino)pyridine (DMAP) (34.7 g) was added dropwise to the solution of 4, and the mixture was stirred at room temperature overnight. The reaction mixture was washed successively with 1 N HCl solution, saturated NaHCO3 solution, and saturated NaCl solution. The mixture was dried over Na₂SO₄, and the solvent was removed under reduced pressure to give 93.8 g of 5a. Under nitrogen, 5a (93.8 g) was dissolved in THF/methanol (1/1) (400 mL). To the solution, 200 mL of 0.1 N NaOH solution was added, and the mixture was stirred at room temperature. After 7 h, the pH of the solution was adjusted to 4-5 with 1 N HCl, and the product was extracted with ethyl acetate. The organic layer was washed successively with water and saturated NaCl solution and dried over Na2-SO₄. The solvent was removed under reduced pressure and purified by silica gel column using hexane/ethyl acetate (3/1) as eluent to give 58.9 g of **1a** (yield 84%). ¹H NMR (CDCl₃) δ : 0.9 (t, CH₃), 1.4 (br, $-CCH_2C$), 1.8 (m, $-C(=O)OCH_2CH_2C$ -), 2.0 (m, -CH=CHCH2C-), 2.8 (m, -CH=CHCH2CH=CH-), 4.4 (t, $-C(=O)OCH_2-$), 5.4 (m, -CH=CH-), 7.2, 7.4, 7.8, 8.0, 8.8 (m, Ar).

Similarly, **1b**, **2a**, and **2b** were synthesized and their structures were confirmed by ¹H NMR.

Oxidative Polymerization of 1a. A typical run of the polymerization was as follows (entry 2 in Table 1). Under air, **1a** (1.3 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% aqueous solution, 68 μ L, 0.6 mmol) was added to the mixture every 15 min at 5 times at room temperature. 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 1.1 g of poly(**1a**) (yield 85%). ¹H NMR (CDCl₃) δ : 0.9 (t, CH₃), 1.3 (br, $-CCH_2C-)$, 1.8 (br, $-C(=O)OCH_2CH_2C-)$, 2.1 (br, $-CH=CHCH_2C-)$, 2.8 (br, $-CH=CHCH_2CH=CH-)$, 4.4 (m, $-C(=O)OCH_2-)$, 5.3 (m, -CH=CHC-), 6.8–9.2 (br, Ar).

Similarly, **1b**, **2a**, and **2b** were polymerized, and structures of the resulting polymers were confirmed by ¹H NMR.

Measurements. SEC analysis was carried out using a Tosoh SC8010 or SC8020 apparatus with a refractive index (RI) detector under the following conditions: TSKgel G3000H_{HR} column and THF eluent at a flow rate of 1.0 mL/min. The calibration curves for SEC analysis were obtained using polystyrene standards. NMR spectra were recorded on a Bruker DPX400 spectrometer. Film hardness was evaluated by a Fischerscope H100VS microhardness tester with test force of 200 mN (Helmut Fisher). Gloss value of films was measured at 60° by a Horiba IG-330 gloss checker. Dynamic mechanical analysis was carried out by using an Orientec Reoviron DDV-II-EP with frequency of 3.5 Hz at a heating rate of 2 °C/min. FT-IR spectra were recorded on a Horiba FT720 spectrometer.

Results and Discussion

Synthesis of Urushiol Analogue Monomers. In this study, 2-naphthol derivatives having an unsaturated alkyl group through an ester linkage (1 and 2) were designed. Monomer 1 was synthesized according to Scheme 2. The hydroxyl group of 6-hydroxy-1-naphthoic acid was acetylated by acetic anhydride to 3. The carboxylic acid group of 3 was converted to the acid chloride by thionyl chloride, followed by esterification with an unsaturated alcohol derived from linseed oil or fish oil to give 5. The deprotection by the alkaline hydrolysis of the acetyl group of 5 produced 1 in good yield (84% for 1a). Monomer 2 was synthesized according to similar processes from 6-hydroxy-2-naphthoic acid.

Oxidative Polymerization of Urushiol Analogues. Recently, an oxidative coupling of phenol derivatives by enzymes and enzyme-related catalysts has been widely investigated, ^{15,16} which is anticipated as an alternative method for the production of conventional phenolic resins involving the use of toxic formaldehyde. The resulting polyphenols often have a structure of a mixture of phenylene and oxyphenylene units, which are formed by C–C and C–O couplings, respectively, showing high thermal stability. In the case of phenolic monomers having an unsaturated group, the enzyme catalysis induced the chemoselective polymerization, yielding photochemically or thermally curable polyphenols.¹⁷

For the oxidative polymerization of the naphthol monomers, iron–N,N-ethylenebis(salicylideneamine) (Fe-salen) was used as catalyst. Fe-salen is regarded as a model catalyst of peroxidases. We previously showed a high catalytic activity of Fe-salen for the oxidative polymerization of phenols.¹⁸ Fe-salen catalyzed an oxidative polymerization of *p*-*tert*-butylphenol and bisphenol A, yielding soluble polyphenols. 2,6-Dimethyl- and 2,6-difluorophenols were polymerized by Fe-salen catalyst to give poly(1,4-phenylene oxide) derivatives. The latter polymer showed crystallinity with melting point higher than 250 °C.

The polymerization of monomers **1** and **2** catalyzed by the Fe-salen catalyst was performed using hydrogen peroxide as oxidizing agent in THF at room temperature under air. After the polymerization, the reaction mixture was poured into a large amount of methanol to give an oily precipitate, which was collected by centrifugation. During the reprecipitation procedure, the oligomers soluble in the nonsolvent might be lost. The molecular weight was estimated by size exclusion chromatographic (SEC) analysis using THF eluent. Polymerization results are summarized in Table 1.

In all cases examined, the polymerization of the naphthol derivatives produced oily polymers with molecular weight of several thousand in high yields. The resulting polymers were soluble in THF, CHCl₃, and N,N-dimethylformamide (DMF) but insoluble in water and methanol. The catalyst amount and side-chain structure of the monomer scarcely affected the polymerization behaviors.

The polymer structure was analyzed by ¹H NMR and titration of the residual naphthol group. In the ¹H NMR spectrum of the polymer, the peaks' pattern was similar to that of the corresponding monomer, although all the peaks became broader (Figure 1). A characteristic peak at δ 5.4 due to the unsaturated group in the side chain remained unchanged. These data suggest that the unsaturated moiety was not reacted during the polymerization. The residual OH group in the polymer was



Figure 1. ¹H NMR spectra of (A) **1a** and (B) poly(**1a**) (entry 2 in Table 1). A typical monomer structure was shown at the top of the figure.

titrated, which showed that the phenylene unit values of poly(**1a**) (entry 2) and poly(**2a**) (entry 6) were 48% and 50%, respectively. These data strongly suggest that the present polynaphthols (prepolymers) were of mixture of phenylene and oxyphenylene unit structures.

Curing of Polynaphthols to Artificial Urushi. The curing of the prepolymer to artificial urushi was examined by two methods: the thermal treatment (150 °C, 2 h, no catalyst) and the oxidation catalyzed by cobalt naphthenate at 25 °C (a conventional drier, 0.18 wt % for the prepolymer) in air. The sample film was prepared on a glass slide by using applicator for 50 μ m thickness and stood at 25 °C under the humidity of 70%. During the curing, the unsaturated groups in the side chain were reacted with each other, yielding an insoluble film. The curing behavior was monitored by a dynamic microhardness tester and FT-IR spectrometer.

In the thermal treatment, all samples were quickly cured without any catalysts to give brown gloss films. The hardness of the films from polynaphthols except poly(**2b**) was over 100 N/mm² after 2 h (Figure 2). The hardness reached larger than 150 N/mm² after 1 day, which is hard enough for practical uses. Afterward, the hardness was almost constant. In the previous work on curing of polyphenols having an unsaturated fatty acid group, the hardness of the film after 7 days was ca. 100 N/mm^{2.5} These data strongly suggest that the polynaphthol structure provides harder materials.

The curing of polynaphthols by the cobalt naphthenate catalyst proceeded at 25 °C to produce yellow crosslinked films. The curing gradually proceeded, whose behaviors were different from those by the thermal treatment. These data suggest the higher reactivity of the unsaturated group at 150 °C without any additives than at 25 °C with the catalyst. The curing rate of poly-(**1b**) and poly(**2b**) was larger than that of poly(**1a**) and poly(**2a**). This difference may be due to the highly reactive unsaturated group derived from eicosapentanoic acid and docosahexanoic acid of the fish oil in poly(**1b**) and poly(**2b**). The curing of poly(**2a**) proceeded faster than that of poly(**1a**), which may be owing to the structural difference of the polymer main chain between



Figure 2. Time course of universal hardness in hardening of polynaphthols by (A) thermal treatment and (B) cobalt naphthenate catalyst: (\blacklozenge) poly(**1a**), (\blacklozenge) poly(**1b**), (\blacktriangle) poly(**2a**), and (\blacksquare) poly(**2b**).

 Table 2. Properties of Cured Films from Cross-Linkable

 Polynaphthols

entry	polymer	curing ^a	HU ^b (N/mm ²)	gloss value ^c
1	poly(1a)	Т	195	114
2	poly(1a)	С	210	112
3	poly(1b)	Т	187	105
4	poly(1b)	С	94	107
5	poly(2a)	Т	163	112
6	poly(2a)	С	117	114
7	poly(2b)	Т	91	107
8	poly(2b)	С	106	108

^{*a*} Curing method: T = thermal treatment (150 °C, 2 h); C = addition of catalyst (0.18 wt % of cobalt naphthenate for prepolymer). ^{*b*} Universal hardness, data after 1 week. ^{*c*} Measured at 60 °C, data after 1 week.

poly(**1a**) and poly(**2a**). In the curing by the cobalt naphthenate, the hardness of the cured film from poly-(**1a**) was the highest after 7 days (Table 2). This may be owing to the rigid structure of poly(**1**) and C18 alkyl group of linsed oil in the side chain of the polymer. In most cases, the hardness value of the cured polymer obtained by the thermal treatment was larger than that by the cobalt-catalyzed curing. A similar behavior was observed in the curing of phenolic polymers containing unsaturated groups in the side chain.^{5,6}

The gloss value of films by both curing methods were ca. 100 at 60 °C, indicating the formation of the brilliant films with high gloss surface from poly(1) and poly(2), which is comparable to those of natural urushi.

The temperature dependence of dynamic mechanical properties of the film from poly(1a) with thermal treatment is shown in Figure 3. The initial storage modulus (*E*) was 1.2×10^{10} Pa at room temperature and fell down slowly as the polymer passed through the glass transition temperature (T_g) at 115 °C. This transition might be caused by the main-chain motion of polynaphthol. The storage modulus was of 1 order of magnitude larger than that of natural urushi,¹⁹ indicating the formation of a tough cured film. A smooth trace



Figure 3. Dynamic viscoelasticity of the cross-linked film from poly(**1a**) with thermal treatment.



Figure 4. FT-IR spectra of (A) poly(**1a**) and (B) the cured film from poly(**1a**) by cobalt naphthenate catalyst.

of dissipation factor (tan δ) clearly suggests the homogeneous structure of the film. In high-temperature region, E was constant, suggesting that almost all of unsaturated groups in the side chain were reacted and the film possessed a high thermal stability.

Figure 4 shows FT-IR spectra before and after the curing of the film from poly(**1a**). The prepolymer had a characteristic peak at 3010 cm⁻¹ ascribed to C-H stretching of the inner olefin moiety. After the curing, this peak completely disappeared.⁴ The cross-linking reaction of the unsaturated moiety in the side chain was also observed by change of characteristic C-H bending peaks at 994, 976, and 730 cm⁻¹, which are ascribed to the conjugated cis-trans double bond, nonconjugated trans double bond, and nonconjugated cis double bond, respectively.⁴ The gradual decrease of the peak at 730 cm⁻¹ was observed, whereas the peak intensity at 976 cm⁻¹ gradually increased. The peak at 994 cm⁻¹ became larger at the early stage of the curing and afterward smaller. Furthermore, a peak at 1075 cm^{-1} newly appeared, which is due to C-O-C stretching of the resulting cross-linked moiety. A broad peak ascribed to O-H stretching became larger, which is due to the formation of the hydroxy-terminated polymer. Similar spectral changes were observed in the curing of other prepolymers. These suggest that the cross-linking mechanism is similar to that of oil autoxidation.²⁰

Conclusion

Novel cross-linkable polynaphthols were synthesized by the oxidative polymerization of the naphthol monomers having an unsaturated group derived from natural oils. During the polymerization using Fe-salen catalyst, only the naphthol moiety was exclusively reacted to give soluble polynaphthols in high yields. The resulting polymers were cured by thermal treatment or cobalt naphthenate catalyst to give the brilliant film ("artificial urushi") with high hardness and gloss surface.

Recently, polymeric materials from renewable naturalbased substrates have worldwide received much attention in social and environmental viewpoints, since their use contributes to global sustainability without depletion of scare resources.²¹ The present study provides a new route of high-performance coatings from renewable abundant triglycerides. Further studies on synthesis of useful polymeric materials from natural oils are under way in our laboratory.

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