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Polymer 43 (2002) 3475–3481

polymer

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Synthesis and curing behaviors of a crosslinkable polymer from cashew nut shell liquid

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Dedicated to Professor Imanishi on the occasion of his retirement

Received 4 December 2001; received in revised form 4 January 2002; accepted 8 January 2002

Abstract

In the present study, we have oxidatively polymerized cashew nut shell liquid (CNSL), whose main component is cardanol, a phenol derivative having a meta substituent of a C15 unsaturated hydrocarbon chain with one to three double bonds as the major, and examined the curing behaviors of the resulting polymer. Fe–salen efficiently catalyzed the polymerization in bulk at room temperature to give a soluble crosslinkable polymer in a good yield. Various metal complexes also catalyzed the polymerization at 80 °C, although their catalytic activity was lower than that of Fe–salen. The curing by cobalt naphthenate catalyst or thermal treatment took place to give the crosslinked film (artificial urushi) with high hardness and gloss surface. In the curing of polyCNSL by the thermal treatment, the crosslinking behaviors and properties of the resulting film were similar to those of a commercially available CNSL–formaldehyde resin.

Keywords: Cashew nut shell liquid; Oxidative polymerization; Curing

1. Introduction

Phenol–formaldehyde resins using prepolymers such as novolaks and resols are widely used in industrial fields, since these resins show excellent toughness and temperature-resistant properties [1]. However, toxic nature of formaldehyde has problems in their manufacture and use. Therefore, an alternative process for preparation of phenol polymers without using formaldehyde has been strongly desired.

A new class of polyphenols have been synthesized by an oxidative polymerization of phenol derivatives using oxidoreductase as catalyst [2–9]. Some advantages for enzymatic synthesis of the polyphenols are as follows: (i) an oxidative polymerization of phenols proceeds under mild reaction conditions without 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 enzymatic polymerization of phenol in an aqueous methanol produced a soluble polymer with the controlled structure [10–12]. Furthermore, the enzyme catalysis has enabled production of various functional and high-performance phenolic polymers [2–9]. For example, the peroxidase catalysis induced the chemoselective polymerization to give thermally and photochemically crosslinkable polyphenols [13,14].

We have enzymatically synthesized artificial urushi, new crosslinked polymeric films on the basis of design of new urushiol analogs (phenols having an unsaturated group in the side chain) [15–18]. The laccase-catalyzed curing of the urushiol analogs proceeded under mild reaction conditions to produce the crosslinked film ('artificial urushi') with high hardness and gloss surface. This new concept has expanded the scope of the enzyme catalysis to the development of environmentally benign production of the functional coating materials; the curing of the urushiol analogs from renewable resources took place via laccase catalysis under mild reaction conditions without the use of organic solvents. Recently, vinyl polymers having a phenolic

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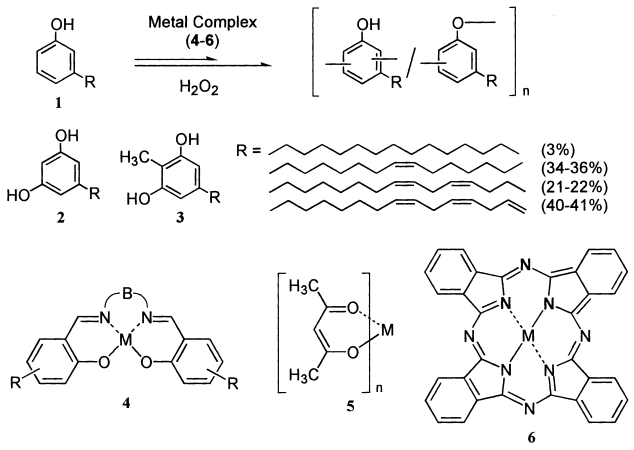
0032-3861/02/$ - see front matter
PII: S0032-3861(02)00062-9



Scheme 1.

moiety in the side chain were reported to be cured by laccase, yielding crosslinked films [19].

We reported that iron–*N*,*N*′-ethylenebis(salicylideneamine) (Fe–salen), a model of peroxidase, showed high catalytic activity for oxidative polymerization of various phenols in organic solvents [20–22]. The first synthesis of crystalline fluorinated PPO was achieved by the Fe–salen-catalyzed polymerization of 2,6-difluorophenol [22].

Cashew nut shell liquid (CNSL) constitutes nearly one third of the total nut weight; thus, much amount of CNSL is formed as by-product from mechanical processes for the edible use of the cashew kernel. Thermally treated CNSL, whose main component is cardanol, a phenol derivative having a *meta*-substituent of a C15 unsaturated hydrocarbon chain mainly with 1–3 double bonds, has various potential industrial utilizations such as resins, friction lining materials, and surface coatings [23]; however, only a small part of CNSL is used in industrial field. Recently, we reported that catalysis of soybean peroxidase induced the oxidative polymerization of thermally treated CNSL in an aqueous acetone to produce the oily soluble polymer with M_n of several thousands [24]. Furthermore, the yield of the soluble polymer improved by using Fe–salen as catalyst in an organic solvent. The resulting polymer was subjected to curing by cobalt naphthenate catalyst or thermal treatment, yielding the crosslinked film (artificial urushi) with high gloss surface [25]. The present paper describes the oxidative polymerization of CNSL using metal complexes as catalyst in bulk and curing behaviors of the resulting crosslinkable polyCNSL.

2. Results and discussion

2.1. Polymerization of CNSL

Commercially available CNSL is a mixture of cardanol (**1**), cardol (**2**), and 2-methylcardol (**3**), whose contents are 83–84, 8–11, and 2%, respectively (Scheme 1). Previously, we reported that the polymerization of CNSL efficiently proceeded by using Fe–salen as catalyst in 1,4-dioxane or tetrahydrofuran (THF) [25]. In this study, the polymerization was carried out in bulk for practical applications. Polymerization results using Fe–salen catalyst are summarized in Table 1. The yield and molecular weight of the resulting polymer were estimated by size exclusion chromatography (SEC).

In the range of the catalyst amount from 0.5 to 1.5%, a soluble polyCNSL was obtained and the yield increased as a function of the catalyst amount. The molecular weight of the polymer obtained by using 0.5% Fe–salen catalyst was lower than that by 1.0 or 1.5% catalyst (entries 1, 3, and 8). The reaction proceeded relatively fast; the yield and molecular weight of the polymer obtained for 0.5 h were close to those for 2 h (entries 2 and 3). The concentration of hydrogen peroxide concentration scarcely affected the present polymerization (entries 3 and 4).

During the bulk polymerization of CNSL, the temperature reached up to 140 °C owing to the exothermic reaction. For suppression of the temperature increase, the polymerization

Table 1
Oxidative polymerization of CNSL catalyzed by Fe–salen (polymerization of CNSL (6.0 g) using Fe–salen catalyst in bulk under air)

Entry	Polymerization				Polymer		
	Catalyst[a] (%)	Time (h)	H_2O_2 (%)	Additive[b]	Yield[c] (%)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]
1	0.5	2.0	30	–	38	1.4	1.6
2	1.0	0.5	30	–	70	2.8	2.8
3	1.0	2.0	30	–	70	3.0	3.0
4	1.0	2.0	60	–	70	2.7	3.6
5	1.0	2.0	30	Water (1.0)	67	2.3	3.7
6	1.0	2.0	30	Water (2.0)	71	2.7	4.2
7	1.0	2.0	30	Pyridine (0.4)	49	1.7	1.6
8	1.5	2.0	30	–	80	2.9	4.5
9	2.0	2.0	30	–	Partly gelation		

[a] mol% for monomer.
[b] In parenthesis, volume of additive (ml).
[c] Determined by SEC.

Table 2
Oxidative polymerization of CNSL catalyzed by metal complexes (**4**) with salen or its related ligands (polymerization of CNSL (6.0 g) using metal complex (0.20 mmol) as catalyst in bulk under air)

Entry	Catalyst (**4**)			Temperature (°C)	Time (h)	Yield[a] (%)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[a]
	M	B	R					
1	Fe	$(CH_2)_2$	H	rt	2	70	3.0	3.0
2	Fe	$(CH_2)_2$	5-OCH_3	rt	2	43	1.5	1.6
3	Fe	$(CH_2)_2$	3,4-(t-Bu)$_2$	rt	2	48	1.5	1.5
4	Fe	$(CH_2)_3$	H	rt	2	64	2.3	2.4
5	Fe	$(CH_2)_4$	H	rt	24	31	1.2	1.3
6	Fe	$(CH_2)_5$	H	rt	24	34	1.2	1.3
7	Fe	$(CH_2)_6$	H	rt	24	33	1.2	1.3
8	Co	$(CH_2)_2$	H	80	24	46	2.0	2.7
9	Cu	$(CH_2)_2$	H	80	24	32	1.4	1.6
10	Mn	$(CH_2)_2$	H	80	24	38	1.3	1.5
11	Ni	$(CH_2)_2$	H	80	24	Partly gelation		
12	Zn	$(CH_2)_2$	H	80	24	43	1.6	2.2
13	V=O	$(CH_2)_2$	H	80	24	33	1.4	1.6

[a] Determined by SEC.

was carried out in the presence of a small amount of water; however, the polymerization results were almost the same as those without water (entries 5 and 6). In the solution polymerization of phenols catalyzed by Fe–salen, the addition of pyridine improved the yield [20,21]. On the other hand, in case of the polymerization of CNSL in bulk, the yield decreased by the addition of pyridine (entry 7).

Next, various metal catalysts (**4**–**6**) having a salen ligand or its derivatives have been screened for the polymerization of CNSL (Table 2). Iron complex of 5-methoxy or 3,4-bis(t-butyl) salen ligand catalyzed the polymerization of CNSL at room temperature; however, the yield and molecular weight were lower than those by Fe–salen catalyst (entries 1–3). The methylene chain length of the ligand bridge affected the polymerization results. The catalyst with the ligand of 1,3-propylene bridge produced the polymer in a slightly lower yield than Fe–salen (entry 4). On the other hand, the enormous decrease of the catalytic activity was seen in using the catalyst with the methylene chain length larger than 4; even after 24 h, the yield and molecular weight were much lower than those by Fe–salen (entries 5–7).

As for the salen complexes of other metals, the polymerization scarcely occurred at room temperature. At higher temperature (80 °C), the soluble polymer was formed except the polymerization by the Ni–salen catalyst; however, their catalytic activity was lower than that of Fe–salen. In using Ni–salen as catalyst, the gelation took place at 80 °C for 2 h (entry 11).

Other metal complexes with acetylacetone and phthalocyanine ligands (**5** and **6**, respectively) have been examined for the production of polyCNSL (Table 3). In all cases, the polymerization proceeded at 80 °C. Iron(III) acetylacetone and phthalocyanine complexes did not catalyze the polymerization at room temperature (entries 3 and 8), suggesting that the salen ligand was suitable as catalyst for the oxidative polymerization of phenols. All the metal complexes examined in this study also catalyzed the solution polymerization of CNSL at 80 °C and the polymerization results were close to those in bulk (data not shown).

The polymer structure was confirmed by NMR and IR

Table 3
Oxidative polymerization of CNSL catalyzed by metal complexes with acetylacetone or phthalocyanine ligands (polymerization of CNSL (6.0 g) using metal complex (0.20 mmol) as catalyst at 80 °C for 24 h in bulk under air)

Entry	Catalyst	Yield[a] (%)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[a]
1	Cobalt(II) acetylacetone	60	2.5	2.9
2	Copper(II) acetylacetone	41	1.4	1.6
3	Iron(III) acetylacetone	33	1.4	1.5
4	Manganese(III) acetylacetone	39	1.4	1.7
5	Vanadyl(II) acetylacetone	34	1.4	1.6
6	Manganese(III) phthalocyanine	35	1.6	1.8
7	Copper(II) phthalocyanine[b]	50	1.9	2.5
8	Iron(II) phthalocyanine	48	1.6	1.7

[a] Determined by SEC.
[b] Copper(II) 2,3,9,10,11,16,17,23,24-octakis(octyloxy)-29*H*,31*H*-phthalocyanine.

Table 4
Curing of CNSL polymer

Sample	Polymer			Curing						
	Cardanol[a] (%)	M_n[b] ($\times 10^{-3}$)	M_w/M_n[b]	Drying time[c] (h)	Universal hardness[d]		Scratch hardness[e]		Gloss[f]	
					Drier[g] (N/mm^2)	Thermal[h] (N/mm^2)	Drier[g]	Thermal[h]	Drier[g]	Thermal[h]
1[i]	< 3	5.9	1.5	0.67	99 (7)	80 (21)	HB (7)	2H (21)	106	111
2	23	3.1	4.4	58	62 (19)	105 (19)	HB (15)	2H (7)	117	111
3	27	2.7	3.4	112	42 (19)	107 (19)	HB (15)	2H (7)	120	112
4	33	2.4	2.5	174	28 (19)	108 (19)	H (15)	2H (7)	111	110
5	41	2.1	2.1	296	15 (19)	107 (19)	H (15)	2H (7)	102	105
6[j]	17	2.8	1.8	4.0	94 (19)	114 (19)	2H (15)	2H (7)	115	107
7[k]	–	–	–	0.50	147 (19)	175 (19)	2H (15)	H (7)	99	104

[a] Content of unreacted cardanol in polymer.
[b] Determined by SEC.
[c] Data of the curing by cobalt naphthenate, determined by drying recorder.
[d] Determined by microhardness tester.
[e] Pencil scratch hardness (JIS K-5400).
[f] Specular gloss of 60°. Data of drying period of 15 days.
[g] Cured by cobalt naphthenate catalyst (3 wt% for the polymer). In parenthesis, drying period (days).
[h] Cured by thermal treatment (sample 1: 150 °C for 30 min; samples 2–7: 180 °C for 30 min). In parenthesis, drying period (days).
[i] Reprecipitated from methanol.
[j] Commercially available CNSL–formaldehyde resin.
[k] Sugurome-urushi from China.

analysis [24,25]. From ^{1}H NMR analysis of the polymer, it was found that the unsaturated moiety was not reacted during the polymerization. In a GC trace of the reaction mixture, peaks due to **1** became smaller and peaks of **2** and **3** almost disappeared, suggesting that **2** and **3** showed higher oxidative reactivity than **1**. Little effects of the number of the unsaturated group in the side chain on the oxidative reactivity were found.

2.2. Curing of CNSL polymer

For curing test, the preparative production of polyCNSL was performed (Table 4). Samples 1 and 2 were synthesized in 1,4-dioxane and samples 3–5 were prepared in bulk. As for sample 1, the residual monomer was removed by reprecipitation using methanol as non-solvent. For practical coating applications, other samples were used without further purification; 23–41% unreacted monomer was contained in the product. Curing of commercially available CNSL coating prepolymer (CNSL–formaldehyde resin) and natural sugurome urushi [26] (samples 6 and 7, respectively) were also examined for reference. The CNSL–formaldehyde resin contained 17% unreacted monomers and organic solvents as diluent. The curing was examined by two methods: catalysis of cobalt naphthenate (3 wt% for CNSL polymer) and thermal treatment (150 °C (sample 1) or 180 °C (samples 2–7) for 30 min) [25]. The film hardness was monitored by using a dynamic microhardness tester and pencil scratch hardness.

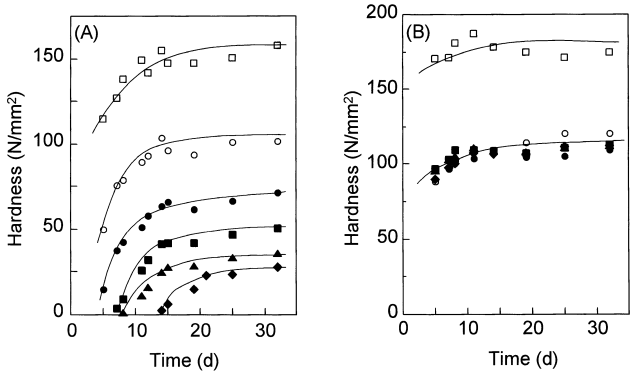


Fig. 1. Time–universal hardness curves in the curing by (A) cobalt naphthenate catalyst and (B) thermal treatment: (●) sample 2; (■) sample 3; (▲) sample 4; (◆) sample 5; (○) sample 6; (□) sample 7. As for samples 6 and 7 in (A), no catalyst was added.

As for the reprecipitated polyCNSL (sample 1), the curing took place relatively fast; the drying time was 40 min. As for the universal hardness, the value of the film prepared by using cobalt naphthenate was larger than that by thermal treatment, whereas the opposite tendency was observed for the pencil scratch hardness. These data were close to those of the commercially available CNSL paint, indicating that the present cured film showed high hardness enough for practical use.

Fig. 1(A) shows time-universal hardness curves in the curing of samples 2–5 by cobalt naphthenate. The hardness value decreased as a function of the amount of the residual monomer and lower than that obtained from the reprecipitated polyCNSL (sample 1), the CNSL–formaldehyde resin, or natural urushi. The drying time increased as the residual monomer amount increased (Table 1). In all cases, the hardness value was almost constant after three weeks. These data suggest that the

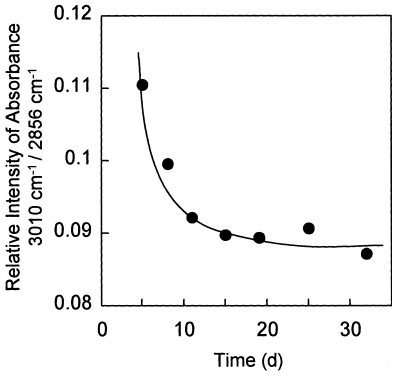


Fig. 2. Curing monitoring of polyCNSL (sample 2) by cobalt naphthenate catalyst using FT-IR spectroscopy.

curing of polyCNSL by cobalt naphthenate proceeded relatively slowly.

The curing behavior was monitored by FT-IR. In the curing of polyCNSL (sample 2) by cobalt naphthenate, the intensity of a peak at 3010 cm^{-1} ascribed to C–H vibration of the unsaturated group in the side chain on the basis of a peak at 2856 cm^{-1} due to C–H vibration of the terminal methyl group decreased for three weeks, and afterwards, almost the constant (Fig. 2); such a behavior might be correlated with that of the hardness (Fig. 1(A)).

On the other hand, in case of the thermal curing, the hardness value became almost constant after one week to give the crosslinked film with the high hardness (Fig. 1(B)). Furthermore, the hardness hardly depended on the amount of the residual monomer, and was comparable with that from the CNSL–formaldehyde resin. As for the pencil scratch hardness, the data by thermal treatment were slightly superior to those by using cobalt naphthenate catalyst. The scratch hardness of the thermally treated samples reached to 4H after three weeks (data not shown). No significant difference of the pencil scratch hardness was observed between the curing film of the CNSL polymer, CNSL–formaldehyde resin, and natural urushi.

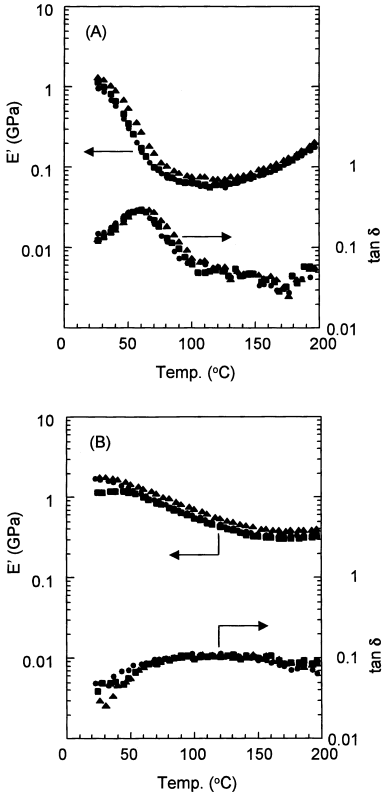


Fig. 3. Dynamic viscoelasticity of the films from sample 2 with different drying periods cured by (A) cobalt naphthenate catalyst and (B) thermal treatment: (●) 14 days; (■) 30 days; (▲) 60 days.

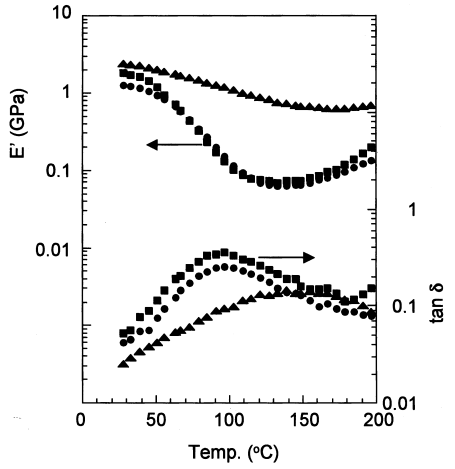


Fig. 4. Dynamic viscoelasticity of the cured films from (●) polyCNSL of sample 1 (reprecipitated) using cobalt naphthenate catalyst; (■) CNSL–formaldehyde resin, and (▲) natural urushi.

Storage modulus (E') and dissipation factor (tan δ) of the cured film from polyCNSL (sample 2) as a function of temperature, are shown in Fig. 3. The glass transition temperature (T_g) of the crosslinked film cured by cobalt naphthenate was observed at ca. 60 °C (Fig. 3(A)). From the increase of E' in the region of high temperature, it is suggested that the unreacted unsaturated carbon–carbon double bonds remained in the measured sample. The smooth trace of tan δ means the homogeneous structure of the present cured film. Significant difference of the dynamic viscoelasticity was not observed in the samples of different drying periods. On the other hand, in case of the cured film obtained by thermal treatment, no clear T_g was observed (Fig. 3(B)). E' traces were almost flat at high temperature, suggesting the complete crosslinking of the unsaturated group in the side chain of polyCNSL.

Fig. 4 shows dynamic viscoelasticity behaviors of the crosslinked films from the reprecipitated polyCNSL (sample 1), CNSL–formaldehyde resin, and natural urushi, which were cured at room temperature. T_g of the film of sample 1 was ca. 90 °C, higher than that of polyCNSL containing unreacted CNSL monomers (Fig. 3). E' and tan δ traces of the films from polyCNSL were similar to

those from the CNSL–formaldehyde resin. The dynamic viscoelasticity behaviors of thermally treated film of polyCNSL (Fig. 3) were similar to those of the natural urushi, indicating that polyCNSL afforded the cured film with excellent viscoelastic properties.

The surface gloss value of the films from polyCNSL was more than 100, which was comparable with that of the CNSL–formaldehyde resin or natural urushi coating (Table 4). Resistance test of the resulting films toward distilled water, acid (47% sulfuric acid) and basic (1N NaOH) solutions was carried out (Table 5). The samples after drying 33 days were used for the evaluation. The film on the glass slide was immersed in the solution at room temperature. After 24 h (distilled water or NaOH) or 96 h (sulfuric acid), the film was washed with water and kept for 2 h for the observation of the film appearance.

Some of the films were peeled from the glass slide in the distilled water; however, the appearance of the peeled film was not changed. In the test of the film cured by cobalt naphthenate toward the acid solution, only the film from sample 2 was peeled from the glass slide. All the samples prepared by the thermal treatment were subjected to peeling in the acid solution. No change of the appearance of the peeled film by the acidic treatment was found. Similar behaviors were observed in the film from the CNSL–formaldehyde resin and natural urushi.

On the other hand, in case of the film crosslinked by cobalt naphthenate, all the films were discolored and wrinkled in the alkaline solution. The film obtained by the thermal treatment was peeled from the glass in the alkaline solution, whose appearance was not changed. These data suggest that the film cured by the thermal treatment was stable under both acidic and basic conditions, and the film stability cured by the cobalt naphthenate catalyst was lower toward the alkaline solution.

3. Experimental part

3.1. Materials

CNSL of technical grade was provided by Tohoku Kako Co. and used as received. Some metal complexes were prepared according to the modification of the literature [27]. Natural urushi was purchased from Tajima Urushi Store. Other catalysts and reagents were commercially available and used without further purifications.

3.2. Oxidative polymerization

The following is a typical procedure for the polymerization (entry 3 in Table 1). Under air, CNSL (6.0 g, 20 mmol) and Fe–salen (64 mg, 0.20 mmol) were placed in a dried glass flask. Hydrogen peroxide (30% aq. solution, 2.3 ml, 20 mmol) was added under gentle stirring in air. After 2 h, a small portion of the reaction mixture was sampled for determination of the conversion of cardanol and of molecular weight of the polymer by SEC.

3.3. Measurements

SEC analysis was carried out using a Tosoh SC8020 apparatus with a refractive index detector under the following conditions: four TSKgel G4000H_{XL}, G3000H_{XL}, G2500H_{XL}, and G2000H_{XL} columns and THF eluent with a flow rate of 1 ml/min at 40 °C. The calibration curves for SEC analysis were obtained using polystyrene standards. NMR spectra were recorded on a Jeol JNM-LA 600 spectrometer. IR measurement was carried out with a Perkin Elmer Paragon 1000. GC analysis was performed with a Hewlett-Packard HP 6890 gas chromatograph equipped with FID detector using a J&W DB-17 column. Film hardness was evaluated by a Fischerscope H100VS microhardness tester

Table 5
Resistance test of cured film (sample after 33 days drying was immersed in the test solution for 24 h (distilled water or alkaline solution) or 96 h (acidic solution))

Sample[a]	Curing[b]	Distilled water	Acidic solution[c]	Alkaline solution[d]
2	A	No change	Peeling	Discoloration, wrinkling
2	B	Peeling	Peeling	Peeling
3	A	No change	No change	Discoloration, wrinkling
3	B	Peeling	Peeling	Peeling
4	A	No change	No change	Discoloration, wrinkling
4	B	No change	Peeling	Peeling
5	A	No change	No change	Discoloration, wrinkling
5	B	No change	Peeling	Peeling
6	A	Peeling	Peeling	Discoloration, wrinkling
6	B	Peeling	Peeling	Peeling
7	A	Peeling	Peeling	Discoloration
7	B	No change	Peeling	Discoloration

[a] See Table 4.
[b] A: curing by cobalt naphthenate catalyst; B: curing by thermal treatment.
[c] 47% sulfuric acid.
[d] 1N NaOH solution.

(Helmut Fischer). Drying time was measured by RCI type drying time recorder (Taiyu Kizai) using 1.5 mil film applicator at 20 °C in 70% humidity. Gloss value of films was measured at 60° by a Minolta CM-3610d gloss meter. Dynamic viscoelasticity was measured using a Toyo Baldwin Rheovibron DDV-II-EA with frequency of 3.5 Hz at a heating rate of 1 °C/min.

Acknowledgements

This work was partly supported by NEDO for the project on Technology for Novel High-Functional Materials in Industrial Science and Technology Frontier Program, AIST.

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