

NOTES

## A New Crosslinking Method of Vinyl Polymers Having a Phenol Moiety via Oxidative Coupling

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Synthesis of polyaromatics using oxidoreductases and their model complexes as catalyst has been extensively developed for the last decade.<sup>1–7</sup> Peroxidases induced an oxidative polymerization of various phenol derivatives, yielding a new class of polyphenols showing high thermal stability.<sup>8–11</sup> This enzymatic process is expected to be an alternative way for preparation of phenol polymers without using toxic formaldehyde, which is a monomer for production of conventional phenolic resins (phenol-formaldehyde resins). Recently, we have found that Fe(III)-salen complex efficiently catalyzed an oxidative polymerization of phenols.<sup>12–15</sup> We regarded Fe-salen as model complex of peroxidase having a heme as catalytic active site. The first synthesis of crystalline fluorine-containing poly(1,4-phenylene oxide) was achieved by the Fe-salen catalyzed polymerization of 2,6-difluorophenol.<sup>15</sup>

Very recently, enzymatic polymerizations have been expanded to laccase-catalyzed curing. “Artificial urushi” was prepared by laccase-catalyzed curing of new urushiol analogues.<sup>16, 17</sup> The curing of the catechol derivative having a linolenoyl group proceeded in the presence of acetone powder, yielding the crosslinked film with high hardness and gloss surface, which are comparable with those of natural urushi coating. A crosslinked polymeric film was also obtained by laccase-catalyzed curing of an oily hydrophilic vinyl polymer having a phenolic group in the side chain,<sup>18</sup> however, the use of the laccase catalyst is limited in liquids which can be mixed with the laccase aqueous solution. The present study deals with crosslinking of phenol-containing vinyl polymers by Fe-salen cat-

alyst, which provides a new method of gel formation from vinyl polymers through the oxidative coupling. This method will exhibit considerable advantages compared to the conventional ones; mild reaction conditions, formation of minimum byproduct (only water), quick gel formation, and easily control of gel properties by changing amount of hydrogen peroxide. Relevant to this study, gel formation of poly(4-vinyl phenol) (**1**) using potassium persulfate as oxidizing agent in an alkaline solution was claimed, in which much amount of potassium persulfate was required for the gel formation.<sup>19</sup>

### RESULTS AND DISCUSSION

In this study, poly(4-vinylphenol) (**1**) ( $M_n = 4.5 \times 10^3$ ,  $M_w/M_n = 1.7$ ) and poly[2-(4-hydroxyphenyl)ethyl methacrylate] (**2**)<sup>18</sup> ( $M_n = 1.2 \times 10^4$ ,  $M_w/M_n = 2.3$ ) were used as starting substrate. The Fe-salen-catalyzed curing reaction was carried out using hydrogen peroxide as oxidizing agent in tetrahydrofuran (THF) at 30°C. Curing results are summarized in Table I. After the addition of hydrogen peroxide, brown powdery gels were immediately formed (within 10 s) from both polymers in the case of entries 5, 6, and 9.

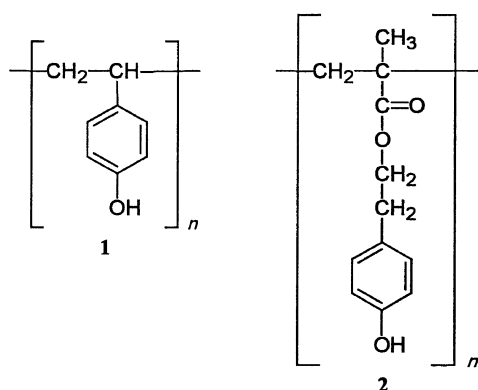
The gel formation was not observed without the catalyst (entries 1 and 7), indicating that the present curing takes place *via* catalysis of Fe-salen. The absence of hydrogen peroxide did not afford the gel (entries 3 and 8). The effects of reaction parameters on the gel production have been examined in the curing of **1**. In using a smaller amount of Fe-salen (entry 2), the crosslinking did not occur. The gel was obtained in high yields when

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**Table I.** Crosslinking of Vinyl Polymers by Fe-Salen Catalyst<sup>a</sup>

Entry	Polymer	Amount <sup>b</sup>		Yield %
		Fe-Salen %	H <sub>2</sub> O <sub>2</sub> %	
1	<b>1</b>	0	100	0
2	<b>1</b>	0.20	100	0
3	<b>1</b>	1.0	0	0
4	<b>1</b>	1.0	25	10
5	<b>1</b>	1.0	50	89
6	<b>1</b>	1.0	100	95
7	<b>2</b>	0	100	0
8	<b>2</b>	1.0	0	0
9	<b>2</b>	1.0	100	88

<sup>a</sup>Crosslinking was carried out in THF at 30°C for 1 h. <sup>b</sup>Molar ratio for monomer unit of polymer.

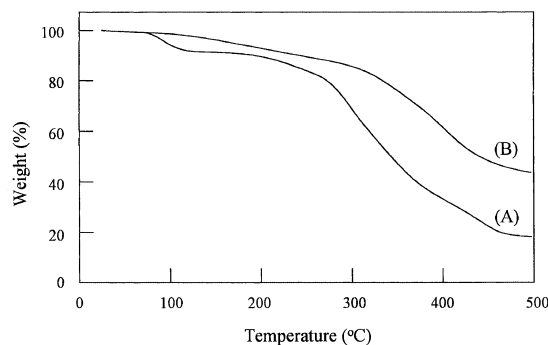


the hydrogen peroxide amount was 50 or 100% for the monomer unit of **1**, whereas no gel formation was seen in using 25% of hydrogen peroxide (entries 4–6).

Structure of the gel from **2** was confirmed by FT-IR spectroscopy. Peaks at 3400 cm<sup>-1</sup> due to the vibration of O–H linkage of phenolic group and at 825 cm<sup>-1</sup> due to the vibration of C–H linkage of 1,4-disubstituted benzene became slightly smaller and peaks at 1270, 1230, and 1150 cm<sup>-1</sup> ascribed to the vibrations of the C–O–C and/or C–OH linkages became broader. In case of the polymerization of phenolic monomers by the Fe-salen catalyst to produce the polyphenols consisting of a mixture of phenylene and oxyphenylene units, the similar IR spectra were obtained.<sup>12</sup> These data suggest that the crosslinking occurred at the phenol moiety without any side-reactions. Similar spectral changes were observed also in the curing of **1**.

Thermal properties of the resulting gels were evaluated by using differential scanning calorimetry (DSC) and thermogravimetry (TG). Polymers **1** and **2** possess glass transition temperature (*T*<sub>g</sub>) of 177 and 100°C, respectively, on the other hand, clear *T*<sub>g</sub> was not observed in the gel samples from **1** and **2** (entries 6 and 9, respectively).

Figure 1 shows TG traces before and after the curing of **2**. The thermal decomposition of the gel proceeded

**Figure 1.** TG traces of (A) polymer **2** and (B) its crosslinked gel, measured under argon.

more slowly than that from **2**. The residual ratio of the gel at 500°C (44%) was larger than that of **2** (18%). These data indicate that the oxidative crosslinking of **2** improved the thermal stability. Thermal treatment of the gel from **1** at 500°C also yielded the carbonized product in a higher yield (54%) than that of **1** (12%).

## CONCLUSIONS

Oxidative crosslinking of vinyl polymers having a phenolic group proceeded by using Fe-salen and hydrogen peroxide as catalyst and oxidizing agent, respectively, yielding the gel showing higher thermal stability. The present study provides a new method of functional gels *via* an environmentally benign processes. The phenol-containing gels possess large potential in their applications such as metal-chelating and antioxidant agents. Furthermore, the present method can be applicable to curing of a variety of phenol moiety-containing polymers, leading to the production of functional gels. Further studies on synthesis of new functional gels by oxidative crosslinking and applications of the crosslinked gels are under way in our laboratory.

## EXPERIMENTAL

**1** was purchased from Aldrich. **2** was synthesized according to the literature.<sup>18</sup> Other reagents and solvents were commercially available and were used as received.

A typical run was as follows (entry 9). A mixture of **2** (50 mg, 0.24 mmol of monomer unit) and Fe-salen (0.80 mg, 2.4 μmol) was dissolved in 5 mL of THF and kept at 30°C. To the mixture, 30% hydrogen peroxide (28 μL, 0.24 mmol) was added and the mixture was gently stirred for 1 h. The precipitated materials were collected by filtration and washed with THF, followed by drying in vacuo to give 44 mg of the gel (yield 88%).

DSC measurement was made at a 10°C min<sup>-1</sup> heating rate under argon using a Mac Science DSC-3200S differential scanning calorimeter calibrated with an

indium reference standard. TG analysis was performed using a Mac Science TG-DTA-2000S apparatus for thermogravimetry/differential thermal analysis at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in an argon flow rate of  $200\text{ mL min}^{-1}$ . IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrometer.

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