Photocuring of a Thiol-ene System Based on an Unsaturated Polyester

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ABSTRACT: To produce a photocurable thiol-ene system, unsaturated polyester was prepared from the condensation reaction of ethylene glycol, diethylene glycol, and fumaric acid. Diallyl groups were introduced into the ends of the unsaturated polyester by a sequential condensation reaction. The coating formulation studied contained an equimolar ratio of thiol and vinyl groups of the prepared unsaturated polyester, including 1 wt % Irgacure 184. The curing behaviors of the unsaturated polyester with multifunctional thiols were investigated using real-time FTIR spectroscopy. The rates of disappearance of thiol and vinyl groups of the unsaturated polyester were similar, demonstrating that there was little free-radical homopolymerization of the internal fumaric group or the end-capped vinyl ether group during the photocuring process and that the thiol-ene reaction is the dominant process. The kinetics of the model compounds demonstrated that the reaction of the terminal allyl double bond with the thiyl radical is faster than that of the internal fumaric double bond in the UV curing of the unsaturated polyester. The storage stability of the thiol-ene system based on unsaturated polyester was effectively increased by the addition of N-PAL. The Raman spectra revealed that the presence of a multifunctional thiol (penta 3-MP4) in the coating formulation increased the degree of surface curing due to the chain-transfer ability of the thiyl radical. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 342–350, 2005

Key words: crosslinking; FT-IR; polyester; thiol-ene; photocuring

INTRODUCTION

The addition of thiols to olefin in the presence of a peroxide catalyst or under UV-light exposure has been extensively studied since the discovery of photoinduced polymerization by Posner in 1905.[1] The photoinduced polymerization of thiol-ene systems has been reviewed by Jacobine[2] The thiol-ene reaction proceeds by the addition of thiols to double bonds via a free-radical mechanism and the orientation obeying an anti-Markovnikov rule (Scheme 1).[3]

The main advantage of thiol-ene reactions is that they do not suffer from oxygen inhibition; rapid curing and good adhesion to many different substrates are other attractive properties.[4,5] Furthermore, it has been found that UV irradiation of thiol-ene systems in the absence of an added photoinitiator yields colorless films with excellent resistance to UV-light exposure within reasonable cure times. An important advantage of this thiol-ene crosslinking reaction over aziridine-, isocyanate-, or heavy-metal-catalyzed unsaturated curing systems is its relatively low toxicity, which makes it especially suitable for high-performance, environmentally friendly, and nonhazardous coatings.

The use of unsaturated polyester resins in various applications is well known. For example, commercial unsaturated polyesters containing a heavy-metal dryer such as cobalt, lead, or zinc naphthenate have been used for low-temperature curing of wood coatings.[6-8] However, the toxicity of heavy metals has lead to substantial restrictions on the use of such coating formulations, and this has lead to our interest in searching for nontoxic crosslinking systems for use with unsaturated polyesters. The possibility of applying a thiol-ene system to the unsaturated polyester crosslinking reaction lead us to embark on a comprehensive study of the UV-induced addition of multifunctional thiols to the unsaturated polyester polymer.

In this study we prepared an unsaturated polyester based on fumaric acid and trimethylolpropane diallyl ether and investigated the UV-curing behaviors of the prepared polyester with multifunctional thiols for use as a nontoxic crosslinking system. The storage stability in the presence of radical scavenger was also investigated, for application as a thiol-ene system involving photocuring of an unsaturated polyester. The surface-curing behavior in thiol-ene–cured films, which can

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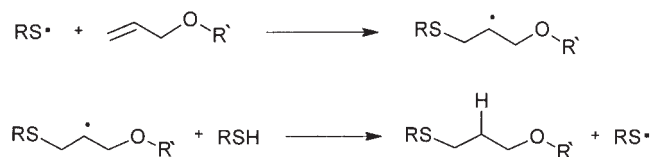
Scheme 1 Anti-Markovnikov orientation of a thiol-ene reaction.

suffer from oxygen inhibition, were investigated using Raman spectroscopy.

EXPERIMENTAL

Materials

Scheme 2 shows the chemical formulas of the compounds used in the thiol-ene systems. Penta 3-MP4 [pentaerythritol tetrakis(3-mercaptopropionate)] was used as supplied from Bruno Bock (Germany). The photoinitiator, 1-hydroxycyclohexylphenyl ketone (Irgacure 184, Ciba Specialty Chemicals), was used as received. Radical scavengers were purchased from Wako Chemical and Aldrich Chemical: aluminum tris(*N*-nitroso-*N*-phenylhydroxylamine) (*N*-PAL), and 4-methoxyphenol and pyrogallol, respectively. Allyl butyl ether, fumaric acid, trimethylolpropane diallyl ether, diethylene glycol, and ethylene glycol were purchased from Aldrich Chemical.

Synthesis of unsaturated polyester

Unsaturated polyester was synthesized using different molar ratios of fumaric acid (as unsaturated acid), ethylene glycol, and diethylene glycol in a 3-L flask equipped with a thermometer, mechanical stirrer, and reflux condenser with column for removing water. Fumaric acid (785.5 g, 5.45 mol), ethylene glycol (262.4 g, 4.22 mol), and diethylene glycol (262.4 g, 2.46 mol) were mixed together and heated to 150°C. The reac-

tion temperature was gradually increased to 200°C over 4 h, while removing water, and maintained until the acid value reached 75–80 mg/KOH. The reaction mixture was cooled to 130°C, and trimethylolpropane diallyl ether (424.2 g, 1.97 mol) and 4-methoxyphenol (0.2 g) were added. The reaction temperature was increased from 130 to 170°C over 4 h and maintained until the acid value of the resulting unsaturated polyester reached 25–28 mg/KOH. The ^{1}H nuclear magnetic resonance (NMR) of the resulting polyester diluted in CDCl$_3$ was determined using a Varian Gemini 2000 at a resonance frequency of 300 MHz: δ 6.85 ppm (fumaric –C*H*=C*H*–), δ 5.90 ppm (allyl=C*H*–), and δ 5.21 ppm (allyl=C*H*$_2$), as shown in Figure 1.

Synthesis of bis(2-butoxyethyl)fumarate

Fumaric acid (146.2 g, 2.52 mol), 2-butoxyethanol (661.8 g, 5.60 mol), *p*-toluenesulfonic acid (3.0 g), 4-methoxy phenol (1.50 g), and toluene (80.0 g) were mixed together under nitrogen and heated (150 $\sim$ 210°C) with stirring in an apparatus equipped with a Dean–Stark trap until no more reaction product was formed. After neutralization with calcium hydroxide, the toluene and excess of 2-butoxyethanol were removed by vacuum distillation, and the residue was filtered. The resulting product was characterized by ^{1}H-NMR: δ 6.88 ppm (2H, –C*H*=), δ 4.35 ppm (4H, –OC*H*$_2$CH$_2$O–), δ 3.67 ppm (4H, –OCH$_2$C*H*$_2$O–), δ 3.48 ppm (4H, –OC*H*$_2$CH$_2$CH$_2$CH$_3$), δ 1.58 ppm (4H, –CH$_2$C*H*$_2$CH$_2$CH$_3$), δ 1.41 ppm (4H, –OCH$_2$CH$_2$C*H*$_2$CH$_3$), and δ 0.92 ppm (6H, –OCH$_2$CH$_2$CH$_2$C*H*$_3$).

Investigation of crosslinking reaction kinetics

Real-time FTIR spectra were obtained using a ReactIR 1000 spectrometer (ASI Applied System) equipped with a diamond-composite insertion probe. The samples were exposed for 30 s to the UV radiation from a
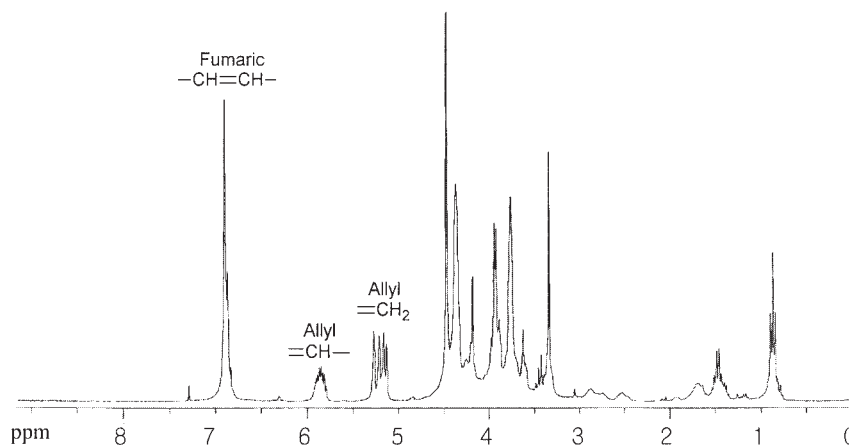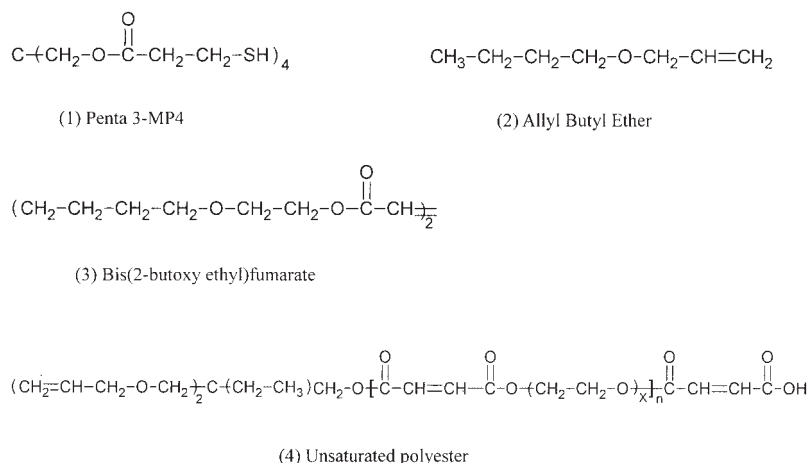

Figure 1 ^{1}H-NMR spectrum of the prepared unsaturated polyester (4) end capped with a diallyl group.

(1) Penta 3-MP4

(2) Allyl Butyl Ether

(3) Bis(2-butoxy ethyl)fumarate

(4) Unsaturated polyester

Scheme 2 Schematic representations of the compounds used in the thiol-ene system.

metal-halide lamp (EFOS UV System) via a fiberoptic light guide. The UV-light intensity at the sample was 465 mW/cm^2 over a wavelength range of 320–420 nm.

Raman spectroscopy

Raman spectra were obtained using a Jobin-Yvon T64000 device at room temperature. The 514.5-nm line of an argon laser was used for excitation, and the laser power at the sample was 200 mW. The resolution of the spectra was $\pm$ 0.72 cm^{-1}.

RESULTS AND DISCUSSION

Synthesis of unsaturated polyester

Unsaturated polyester was prepared by sequential reactions according to the protocol shown in Scheme 3. An unsaturated polyester based on fumaric acid was first produced with carboxylic groups at the ends of the polymer. Ethylene glycol and diethylene glycol

were used as a diol in the polycondensation reaction. Allyl groups were subsequently introduced to the chain ends of the unsaturated polyester by a reaction with trimethylolpropane diallyl ether. The molecular weights of the unsaturated polyester containing the allyl groups were $M_n = 1,130$ and $M_w = 3,960$, as found by gel permeation chromatography with a poly(styrene) standard (M_n is the number-average molar mass, M_w is the weight-average molar mass). The vinyl-group content of the prepared unsaturated polyester was calculated to be 5.42 mEq/g of polymer.

### Photocuring behaviors of unsaturated polyester

It is known that thiol-ene reactions proceed stoichiometrically between the thiol and vinyl groups. We therefore preliminarily prepared the coating formulation at an equimolar ratio of the thiol and vinyl groups, including 1 wt % Irgacure 184. The prepared unsaturated polyester has allyl and fumaric groups

x = 1 or 2
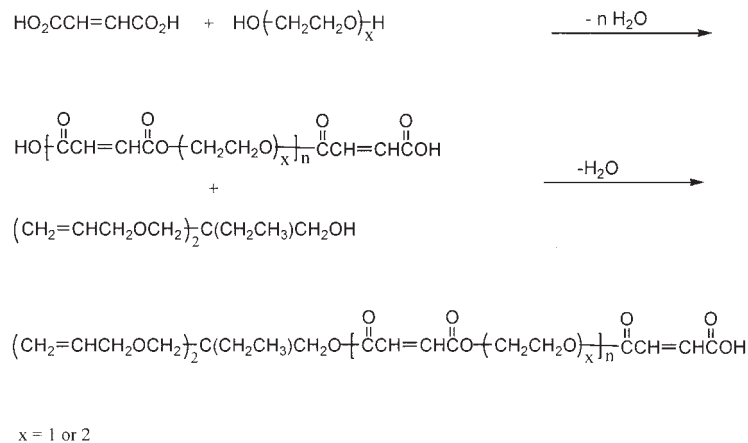
Scheme 3 The preparation of unsaturated polyester (4) partially end capped with a diallyl group.
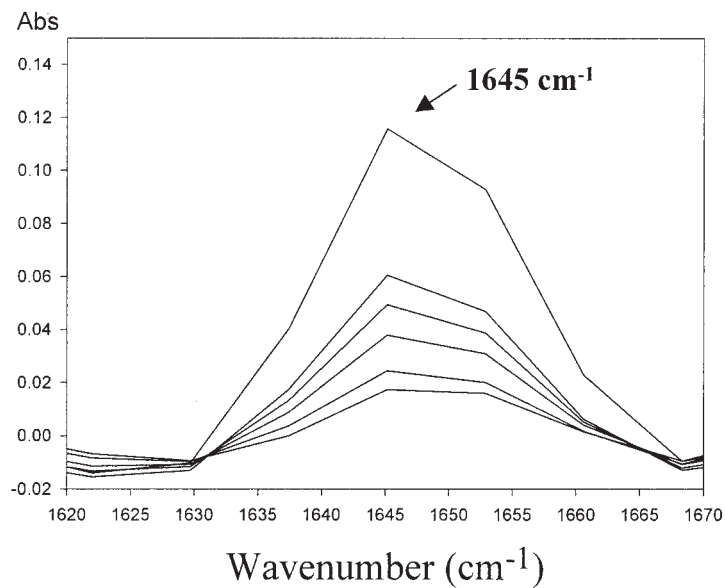
(a)
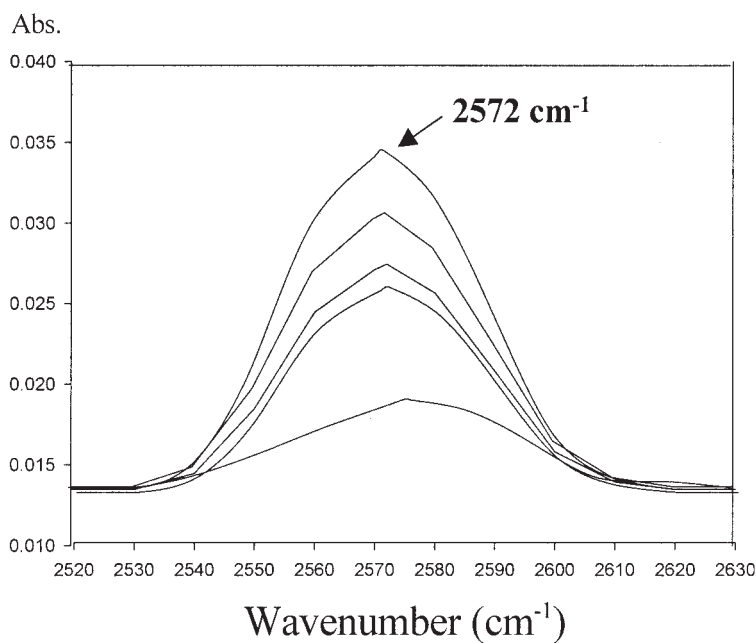
(b)

Figure 2 Decrease in the stretching vibration bands of the (a) allyl and fumaric double bond at 1,645 cm^{-1} and (b) thiol functioning group at 2,572 cm^{-1} during UV coating.

that can be independently reacted with the multifunctional thiols to produce a curing reaction upon UV irradiation. The reaction conversions and rates of double-bond formation with thiol compounds were studied using real-time FTIR. Figure 2 shows the decreases in the stretching vibration band of the double bonds and the thiol S–H bond during the UV curing. During the UV curing of the unsaturated polyester, it was observed that the S–H stretching band at 2,572 cm^{-1} and the double-bond stretching band at 1,645 cm^{-1}
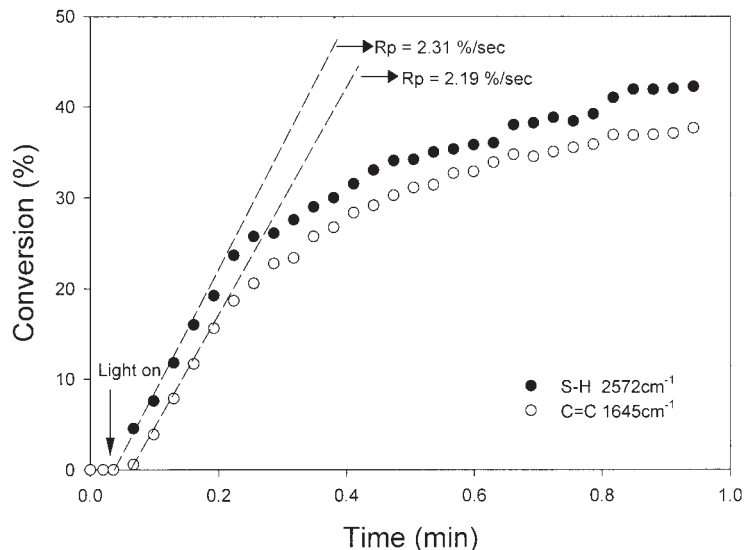
Figure 3 The conversion curves of photopolymerization for the mixture of the unsaturated polyester and penta 3-MP4 in the presence of 1.0 wt % Igacure 184.

were decreased simultaneously. These results imply that UV curing proceeded through the addition of thiol to the double bonds of the fumaric and allyl groups in the unsaturated polyester.

Figure 3 shows the conversion curves of photopolymerization for the coating formulation based on penta 3-MP4 and the prepared unsaturated polyester in the presence of 1 wt % Irgacure 184. The C=C stretching vibrations of the unsaturated polyester at 1,645 cm^{-1} and the S–H stretching vibrations of the thiol functional groups at 2,572 cm^{-1} were used to calculate conversions. The conversion (α) was calculated at various intervals using the following equation:

$$\alpha(\%) = \frac{[I]_o - [I]_t}{[I]_o} \times 100$$

where $[I]_o$ and $[I]_t$ are the absorbance before and after UV exposure, respectively. As in this equation, relative intensity is normally used because the absolute intensity varies from sample to sample. However, since it is difficult to find the reference peak from the infrared spectra of the crosslinking system, the degree of photopolymerization was based on the absolute intensities. The kinetics of photopolymerization were also analyzed using the method described by Decker and Moussa[9] and the steady-state equation given below:

$$R_p(\%/s) = \frac{\alpha_{t_2} - \alpha_{t_1}}{t_2 - t_1}$$

where R_p is the rate of polymerization (in percent per second), and are the conversions in the straight-line region of the sigmoid curve, and t_2 and t_1 are the times (in seconds) that correspond to the conversions α_{t_2} and α_{t_1}.

As shown in Figure 3, the rates of disappearance of the thiol and vinyl groups of unsaturated polyester were indistinguishable (within the experimental error). These results demonstrate that there was little free-radical homopolymerization of the internal fumaric group or the end-capped allyl ether group during the photocuring process and that the thiol-ene reaction is the major process. The reactivity of alkenes toward thiyl (RS·) radicals has been reported to decrease in the order of vinyl ether > allyl ether > n-alkene > acrylates.[2] In these studies, the higher reactivity of ally ether to thiyl radical and the steric hindrance of internal fumaric group may lead to eliminate the possibility of free-radical homopolymerization during the photocuring process. In contrast, Lecamp et al.[10] recently reported that methacrylate homopolymerization was the major reaction rather than the thiol-ene reaction in studies into the kinetics of photocuring of a thiol–methacrylate system.

Model reactions of multifunctional thiols with fumaric and allyl compounds

The prepared unsaturated polyester has allyl and fumaric groups as different double bonds curable by UV irradiation, but these could not be differentiated in the real-time FTIR spectra because their absorption bands overlap. We therefore studied model reactions of fumaric and allyl compounds, as shown in Scheme 4. In this study, the fumaric component of the model compounds was prepared by a condensation reaction of
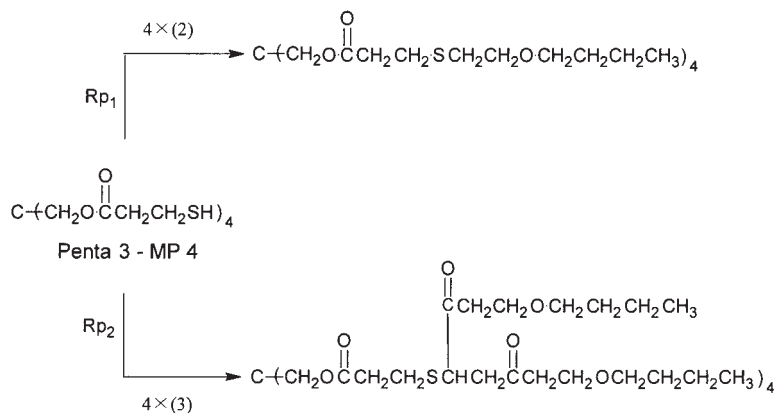
Scheme 4 Model reactions of allyl butyl ether (2) and bis(2-butoxyethyl)fumarate (3) with penta 3-MP4.

fumaric acid and 2-butoxyethanol. Figure 4 shows the UV-curing behaviors in the reaction rates and the conversions of the allyl butyl ether and the prepared fumaric compound from real-time FTIR spectroscopy.

The conversion (α) of allyl butyl ether (60.87%) was lower than that of the fumaric compound (67.76%), but the reaction rate (R_p) of the butyl allyl ether (7.18%/s) was faster than that of the fumaric compound (5.07%/s). As expected from results of the above photocuring behaviors of unsaturated polyester, the rate of disappearance of the thiol was close to those of butyl ally ether within the experimental error. Similarly the rates of disappearance of thiol and fumaric compound occur at the same rate. This may reflect that the thiyl radical approach to the terminal allyl compound is easier than that to the internal fumaric compound, and thiyl radical addition to an electron-rich alkene (vinyl ether) compared to an electron-deficient alkene (fumaric double bond). From the results of the above model reaction, one can deduce that the reaction of the terminal allyl double bond with thiyl radical is faster than that of the internal fumaric double bond in the UV curing of the unsaturated polyester.

Storage stability of the thiol-ene system in the presence of photoinitiator

It is known that all thiol-ene reactions exhibit spontaneous dark reactions, yielding polymers (oligomers) in the absence of initiator.[11,12] This severe instability of the thiol-ene system has prohibited its practical application. Some approaches to overcome the stability problems of the thiol-ene system have used a radical scavenger. In our experiments, we added pyrogallol, 4-methoxy phenol, or N-PAL as a storage stabilizer to the mixture of unsaturated polyester and penta 3-MP4. The stability during storage can be determined
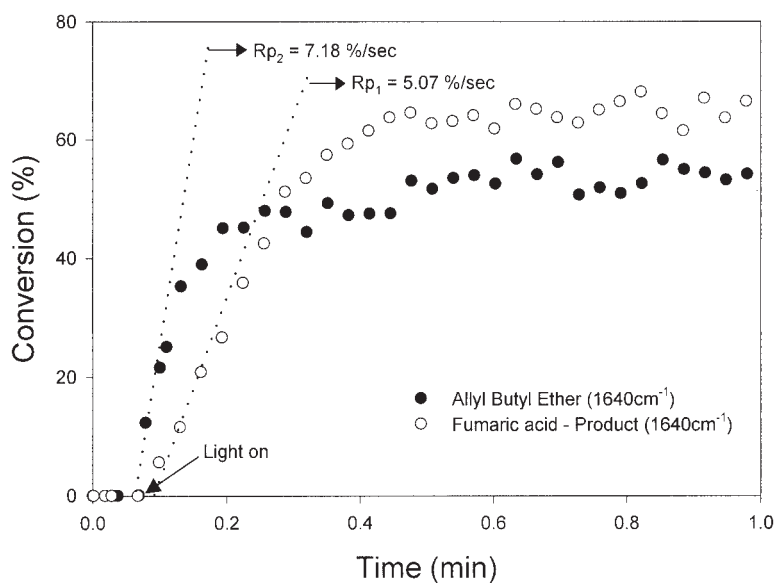

Figure 4 The conversion curves of photopolymerization for allyl butyl ether (2) and bis(2-butoxyethyl)fumarate (3).
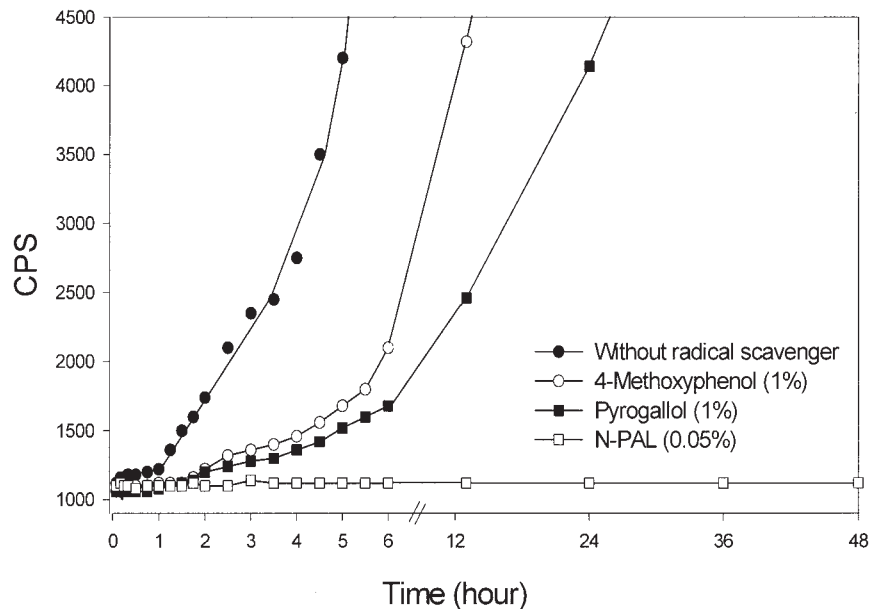
Figure 5 Viscosity profiles of the mixture of the unsaturated polyester (4) and penta 3-MP4 (1) with or without one of three radical scavengers: 4-methoxy phenol, pyrogallol, or *N*-PAL.

by measuring any changes in the viscosity of the thiol-ene system from just after preparation of the mixture. Figure 5 shows the viscosity profile of the mixture of the unsaturated polyester and penta 3-MP4 in the presence of a radical scavenger. Pyrogallol and 4-methoxy phenol at the relatively high concentration of 1 wt % did not result in any viscosity increase within 3 h of storage, but this high concentration of radical scavenger severely retarded photopolymerization.

In contrast, *N*-PAL was an effective radical scavenger for stabilization of the mixture of the unsaturated polyester and penta 3-MP4.[13] The product was an aluminum salt containing the polyatomic *N*-PAL and it exhibited excellent storage stability at a low concentration of 0.05 wt % without interrupting photopolymerization. Recently, Christmas et al.[14] reported the storage stability and the curing efficiency of the photocurable thiol-acrylate system in the presence of radical scavenger. They showed that the negative effect of the radical scavenger on curing efficiency was significantly decreased with increasing the molar ratios of thiol or photo initiator to the stabilizer.[14] In our study, the coating formulation at an equimolar ratio of the thiol and vinyl groups, including 1 wt % Irgacure 184 and 0.05 wt % *N*-PAL, is correspondent to the high molar ratio of thiol or photo initiator to radical scavenger. The curing rate of the stabilized formulation showed the comparable reactivity to that of unstabilized formulation.

Degree of surface curing in the thiol-ene system

Figure 6 shows the 1,400–1,800 cm^{-1} region of the Raman spectra collected at the film–air interface of the

UV-cured films. We assumed that the 1,450 cm^{-1} band due to the asymmetric bending of methyl in the unsaturated polyester is independent from the crosslinking reaction and used this band as the internal reference peak. Unlike infrared spectra, Raman spectra clearly show the C=C stretching vibrations of the allyl and fumaric functional groups, at 1,645 and 1,660 cm^{-1}, respectively. It is clearly seen from the figure that the degree of surface curing decreases as the concentration of penta 3-MP4 increases in the formulation, indicating that the multifunctional thiols effectively prohibit oxygen inhibition through the forming of the thiyl radical. The formed thiyl radical at the surface may reinitiate the radical polymerization, resulting in the high degree of surface curing by UV irradiation.

To clarify the oxygen-inhibition effect of UV curing with penta 3-MP4, we prepared UV-cured films in both air and nitrogen. Figure 7 shows that the Raman intensity ratio, as a function of the penta 3-MP4 concentration at the film–air interface, varied significantly depending on whether air or nitrogen was present. In contrast, the UV-cured films containing penta 3-MP4 exhibited a negligible difference in the Raman intensity ratio whether in air or in nitrogen. This result clearly demonstrates that the UV-cured films with penta 3-MP4 are less inhibited by oxygen than films without penta 3-MP4.

CONCLUSION

The results of our preliminary study demonstrate that photocuring of thiol-ene systems based on an unsat-
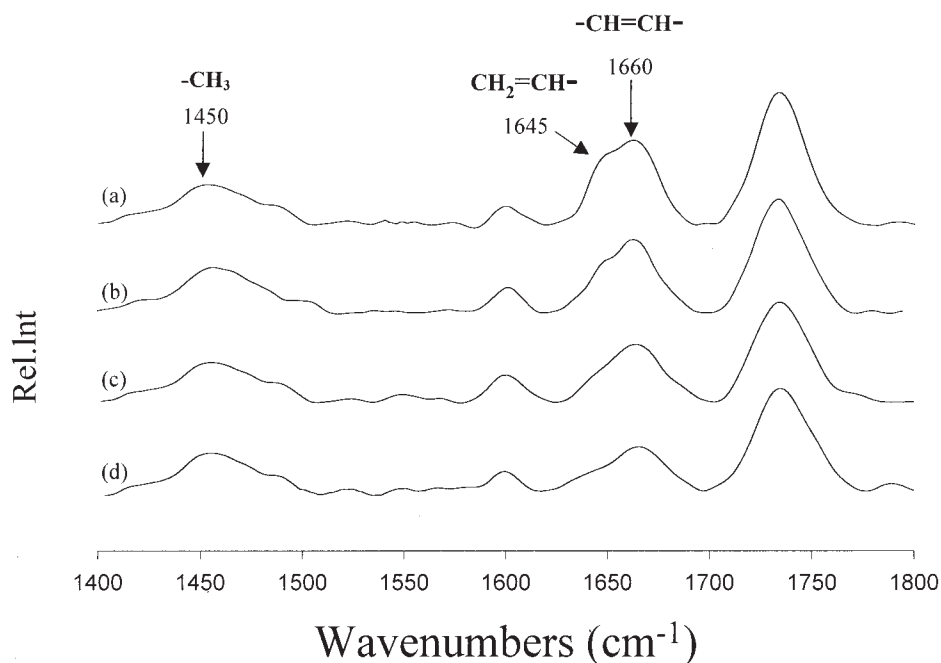
Figure 6 Raman spectra in the 1,400–1,800 cm^{-1} range recorded at the film—air interface of UV-cured films: (a) without penta 3-MP4, (b) with 10 wt % penta 3-MP4, with 20 wt % penta 3-MP4, and (d) with 30 wt % penta 3-MP4.

urated polyester can offer unique opportunities as a substitute to heavy-metal dryers such as cobalt, lead, and zinc naphthenate. The curing behaviors of the unsaturated polyester with multifunctional thiols were investigated using real-time FTIR spectroscopy. Similar rates of disappearance of the thiol and vinyl groups of the unsaturated polyester demonstrate that

there was little free-radical homopolymerization of the internal fumaric group or the end-capped vinyl ether group during the photocuring process and that the thiol-ene reaction is the major process. From the kinetics of the model compounds, it was deduced that the reaction of the terminal allyl double bond with thiyl radical is faster than that of the internal fumaric dou-
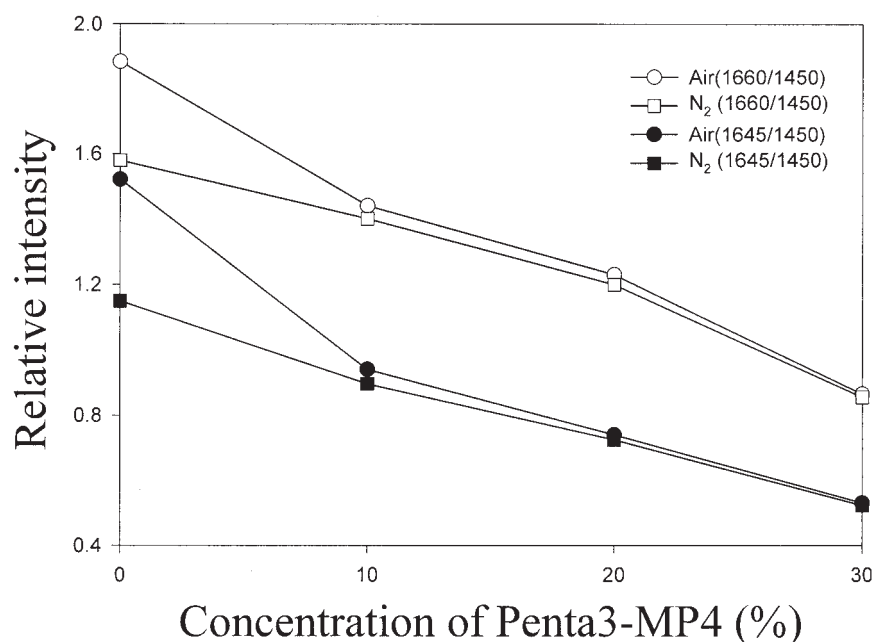

Figure 7 Plot of Raman intensity ratio versus concentration of penta 3-MP4 at the film—air interface in the presence of nitrogen or air: allyl group (●, ■), fumaric group (○, □).

ble bond in the UV curing of the unsaturated polyes-
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3-MP4 in the coating formulation increases the degree
of surface curing due to the chain-transfer ability of
the thiyl radical.

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