

# Photocure Properties of High-Heat-Resistant Photoreactive Polymers with Cinnamate Groups

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**ABSTRACT:** New high-heat-resistant photoreactive polymers with cinnamate groups were synthesized by the reaction of cinnamic acid (CA) and epoxy resins. Their photocure properties were investigated with Fourier transform infrared spectroscopy, UV-visible spectroscopy, and thermogravimetric analysis (TGA). Their photocure reaction rates and the extent of reaction conversion increased with the intensity of UV irradiation. To investigate their photocure reaction kinetics, their reaction conversion rates were plotted against reaction conversion so that their photocure reactions could be analyzed in terms of an  $n$ th-order kinetics reaction equation. The YX4000H-CA photoreactive polymer with a biphenyl moiety, which was expected to have strong molecular interactions, showed a lower reaction conversion rate and reaction constant, and the highest

reaction conversion rate and reaction constant was observed in XP2030-CA with an optimum cure reaction space and a reduction of molecular interactions compared with the other photoreactive polymers. Thermal stability was studied by observation of the changes in the transmittance of the photocured polymer films upon heating and by measurement of the weight loss with temperature with TGA. These photoreactive polymers showed good thermal properties, with almost no transmittance change in the visible range even after they were heated at 250°C for 1 h, and they exhibited little weight loss up to about 250°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3615–3624, 2008

**Key words:** curing of polymers; kinetics(polym.); photopolymerization; thermal properties

## INTRODUCTION

As the rapid progress of the information society has brought about a boost in the dramatic growth of liquid crystal displays, the improvement of color filters (CF) has progressed quickly.<sup>1,2</sup> CFs are a key component for the production of color images; they require low power consumption, high color purity and transmittance, high contrast, low reflection, and high stability against heat, light, and chemicals. In particular, the most significant challenges have been in the area of improving the thermal resistance, transparency, and cost effectiveness of CF resists for color patterning.<sup>3–5</sup> In previous studies,<sup>6–8</sup> new methacrylate-type prepolymers that included a cyclohexane moiety and biphenyl group were synthesized and characterized to improve the heat resistance and transparency of the binder resin systems for CF resists.

In this study, new cinnamate-type photoreactive polymers with a cyclopentadiene moiety and various aromatic groups, that included biphenyl and naphthalene moieties, were synthesized by the reaction with epoxy resins and cinnamic acid (CA). We

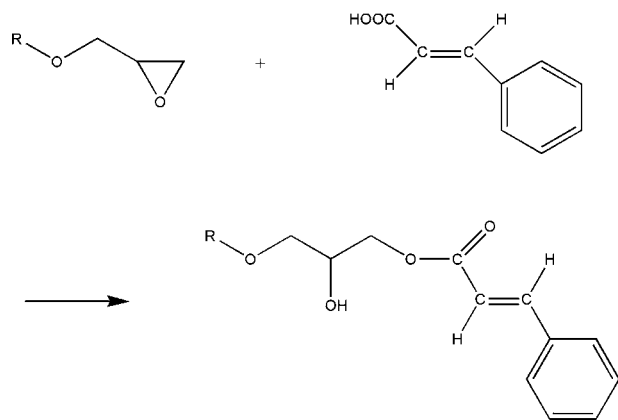
expected that the rigid aromatic groups from the epoxy resin and double bonds from CA would give rise to thermal stability and photocrosslinking, respectively, without photoinitiators for cost effectiveness.<sup>9,10</sup> The photocure kinetics of the polymers were investigated with Fourier transform infrared (FTIR) spectroscopy, and their thermal stability was measured with thermogravimetric analysis (TGA) and by monitoring of the change in the transmittance of the polymer film upon heating. The photocure reactions of these polymers with light intensity were interpreted by means of an  $n$ th-order mechanism, and the curing kinetics in the overall conversion region were analyzed with this kinetic model.

## EXPERIMENTAL

### Synthesis of a photoreactive polymer with cinnamate groups

The synthesis of a photoreactive polymer with cinnamate groups was performed by the reaction with CA and an epoxy resin containing different aromatic groups, which is described in Scheme 1. The epoxy resins used in this experiment were YX-4000H (Japan Epoxy Resin Co., Tokyo, Japan) and NC-3000, XP-2030, XD-1000-2L, and NC-7300L obtained from Nippon Kayaku Co. (Tokyo, Japan). Detailed chemi-

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**Scheme 1** Synthetic reaction of the photoreactive polymer with cinnamate groups.

cal structure descriptions of the epoxy resins used in this study are summarized in Table I. As shown in Table I, YX-4000H and NC-3000 were epoxy resins

with biphenyl moieties, and XP-2030, XD-1000-2L, and NC-7300L were epoxy resins with different aromatic groups, such as benzene, cyclopentadiene, and naphthalene moieties, respectively. CA was received from Aldrich Chemical Co. (Milwaukee, WI). The reaction was carried out with tetramethyl ammonium chloride as a catalyst in methyl ethyl ketone at 70°C for 80 h. Detailed experimental and characterization methods were presented in previous reports.<sup>6,10</sup> We confirmed the chemical structure of the photoreactive polymers with <sup>1</sup>H-NMR and FTIR spectroscopy. As shown in Figure 1, the doublet proton NMR peaks of 6.52 and 6.47 ppm corresponding to the protons of the cinnamate double bond were measured, and the typical FTIR peaks of 1715 cm<sup>-1</sup> (carbonyl group of cinnamate) and 1635 cm<sup>-1</sup> (cinnamate double bond) were observed.<sup>11</sup> The doublet proton NMR peaks near 6.5 ppm and the FTIR peaks of 1635 cm<sup>-1</sup> were observed in other photoreactive polymers with cinnamate groups.

**TABLE I**  
Description of the Epoxy Resins Used in This Study

Grade name	Structure	Remarks
YX-4000H		EEW = 193
NC-3000		EEW = 276
XP-2030		EEW = 234
XD-1000-2L		EEW = 243
NC-7300L		EEW = 214

EEW = epoxy equivalent weight (g/equiv).

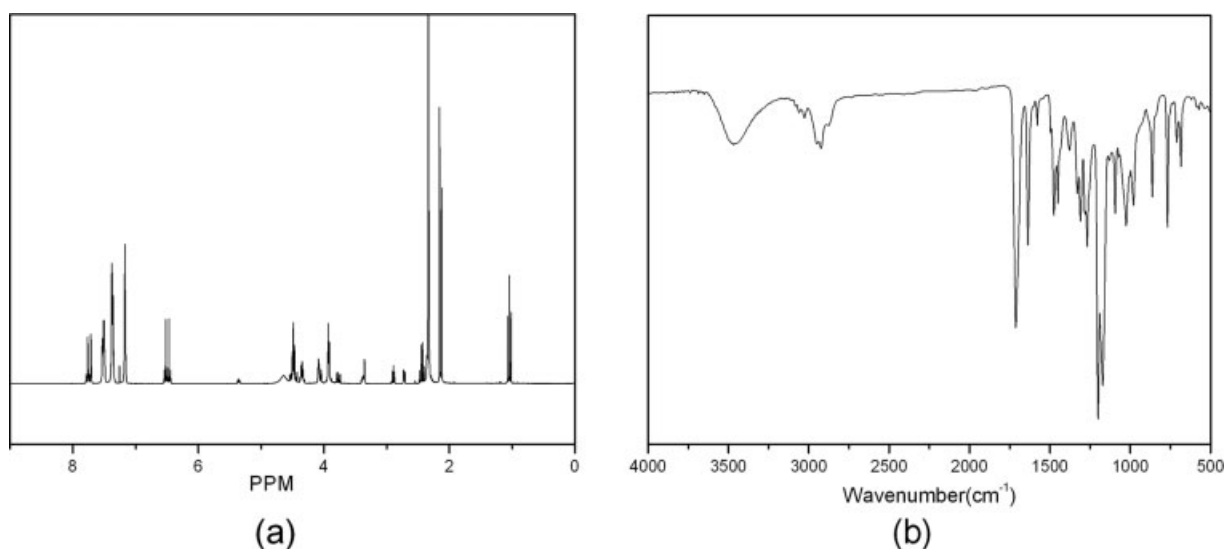


Figure 1 (a)  $^1\text{H-NMR}$  and (b) FTIR spectra of YX4000H-CA.

### Photocure reaction of photoreactive polymers with cinnamate groups

These photoreactive polymers were dissolved in solvents such as monochlorobenzene, tetrahydrofuran, methyl ethyl ketone, and toluene. Each solution was filtered through a 0.2- $\mu\text{m}$  membrane filter and spin-coated on a quartz substrate. These polymer films were then dried at 70°C for 30 min, which led to excellent quality film with a thickness of about 1  $\mu\text{m}$ . The photocure of the photoreactive polymer films was carried out by exposure to 254- or 365-nm UV light radiated from a high-pressure mercury lamp at various intensities. The irradiation systems and measurement methods are described in a previous report.<sup>12</sup> The photocure behavior and thermal stability were studied with FTIR spectroscopy, UV-visible spectroscopy, and TGA. The photocure conversions of these photoreactive polymers were determined by the normalization of the peak area of the cinnamate double bond at 1635  $\text{cm}^{-1}$  with respect to the peak area of the carbonyl group at 1715  $\text{cm}^{-1}$  as a reference with the following equation:

$$\alpha_t = 1 - \frac{(A_f/A_r)_t}{(A_f/A_r)_s} \quad (1)$$

where  $\alpha_t$  is the photocure reaction conversion at each UV irradiation time;  $A_f$  is the absorption peak area of the cinnamate double bond at 1635  $\text{cm}^{-1}$ ;  $A_r$  is the absorption peak area of the reference group, which did not change during UV irradiation (1715  $\text{cm}^{-1}$ , which represents the absorption peak of the carbonyl group in the cinnamate group); and the subscripts  $t$  and  $s$  are the UV irradiation time after  $t$  minutes and the reference irradiation time (where  $s = 0$  min), respectively. A typical FTIR spectrum of

this photoreactive polymer according to the UV irradiation time is shown in Figure 2. Thermal stability was investigated with TGA and UV-visible spectroscopy by observation of the change in the transmittance of the photocured polymer film upon heating at 250°C for 1 h.

## RESULTS AND DISCUSSION

We assumed that YX4000H-CA and so on were the reaction products of the parent epoxy resins with CA, and these are summarized in Table II. These products performed photocure reactions by intermolecular or intramolecular photocycloaddition reactions. The changes in the degree of photocure conversion with the change of UV intensity in the YX4000H-CA and NC3000-CA photoreactive polymers are shown in Figure 3, and those in XP2030-

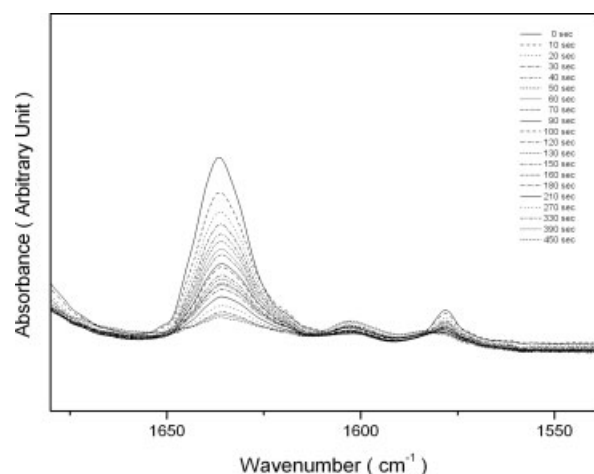


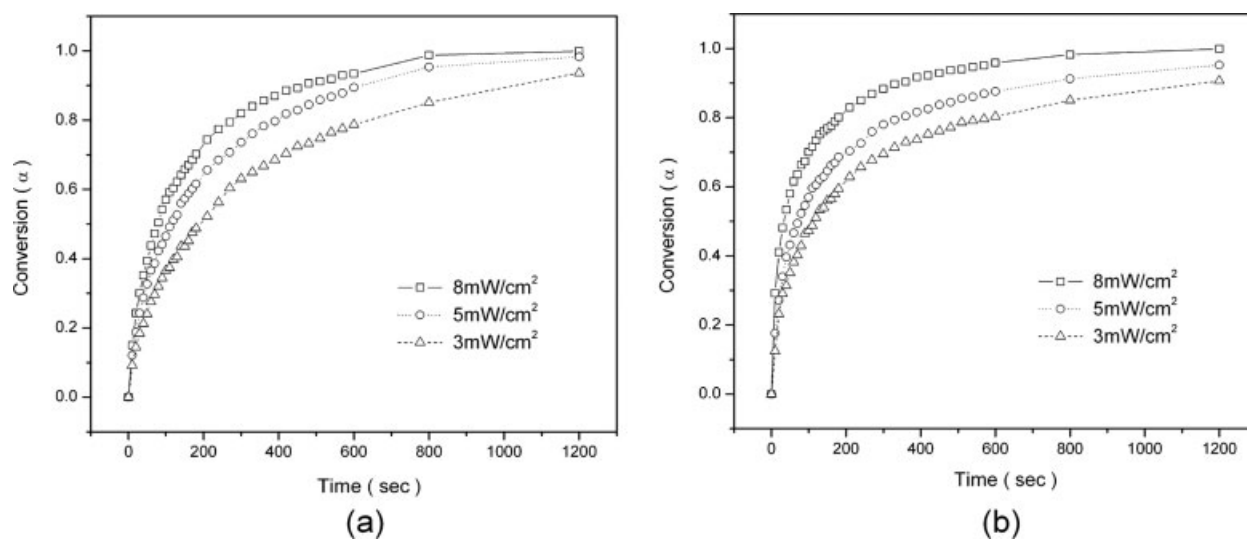
Figure 2 Change in the absorbance of the photoreactive polymer at 1635  $\text{cm}^{-1}$  with the UV irradiation time.

**TABLE II**  
Description of the Epoxy Resin-CA Products

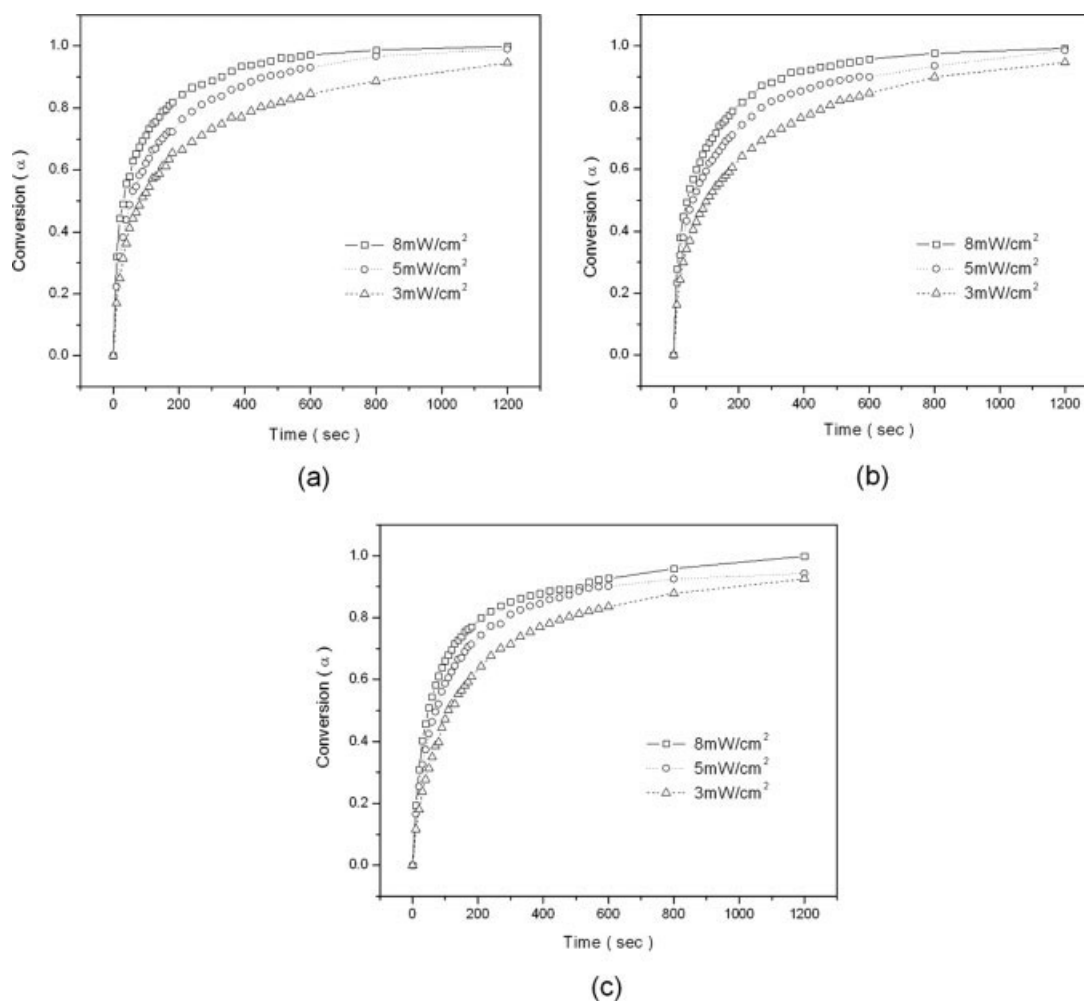
Grade name	Structure
YX4000H-CA	
NC3000-CA	
XP2030-CA	
XD1000-2L-CA	
NC7300L-CA	

CA, XD1000-2L-CA, and NC7300L-CA are shown in Figure 4. As shown in Figure 3 and 4, the extent of the photocure reaction conversion increased with UV intensity in these photoreactive polymers. Although a distinct feature of photoinitiated polymerization is that the initiation rate can be varied in

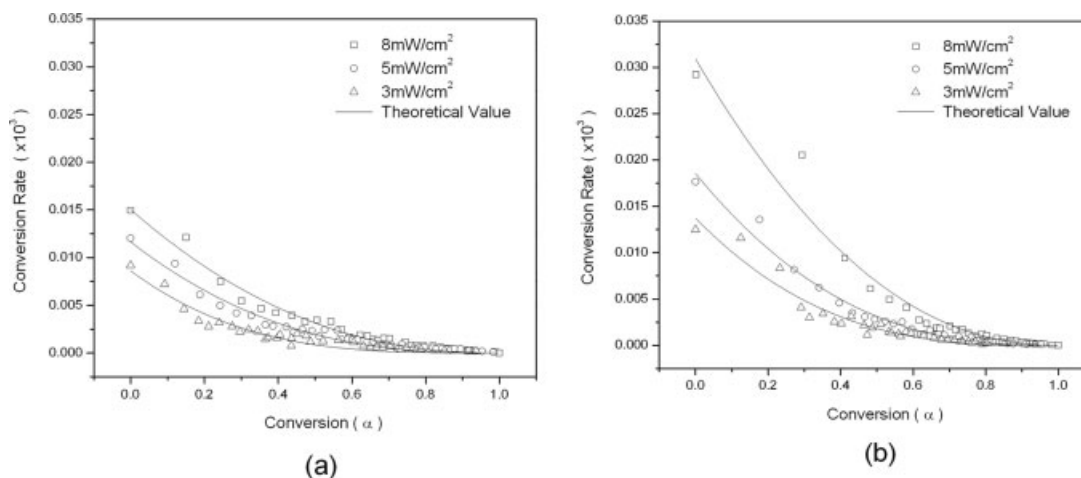
a large range by a change in the light intensity because of polymerization quantum yield,<sup>13</sup> the rate constant in cinnamate photoreactions such as with these photoreactive polymers without photoinitiators is linearly dependent on the intensity of incident light.<sup>14</sup>



**Figure 3** Change in the photocure reaction conversion of the photoreactive polymers with cinnamate groups according to the UV irradiation time at different UV intensities: (a) YX400H-CA and (b) NC3000-CA.



**Figure 4** Change in the photocure reaction conversion of the photoreactive polymers with cinnamate groups according to the UV irradiation time at different UV intensities: (a) XP2030-CA, (b) XD1000-2L-CA, and (c) NC7300L-CA.



**Figure 5** Comparisons between the experimental and theoretical photocure conversion rates as a function of the conversion of the photoreactive polymers with cinnamate groups in terms of the  $n$ th-order equation: (a) YX4000H-CA and (b) NC3000-CA.

The reaction conversion rates of these photopolymers are presented in Figures 5 and 6 to illustrate the photocure reaction kinetics. The reaction conversion rates of the photoreactive polymers that included biphenyl moieties, such as YX4000H-CA and NC3000-CA, are shown in Figure 5, and those with different aromatic groups, such as XP2030-CA, XD1000-2L-CA, and NC7300L-CA, are plotted against reaction conversion in Figure 6. As shown in Figures 5 and 6, the experimental data of these reaction rates show the behavior of an  $n$ th-order kinetics reaction as described in the following equation:<sup>15,16</sup>

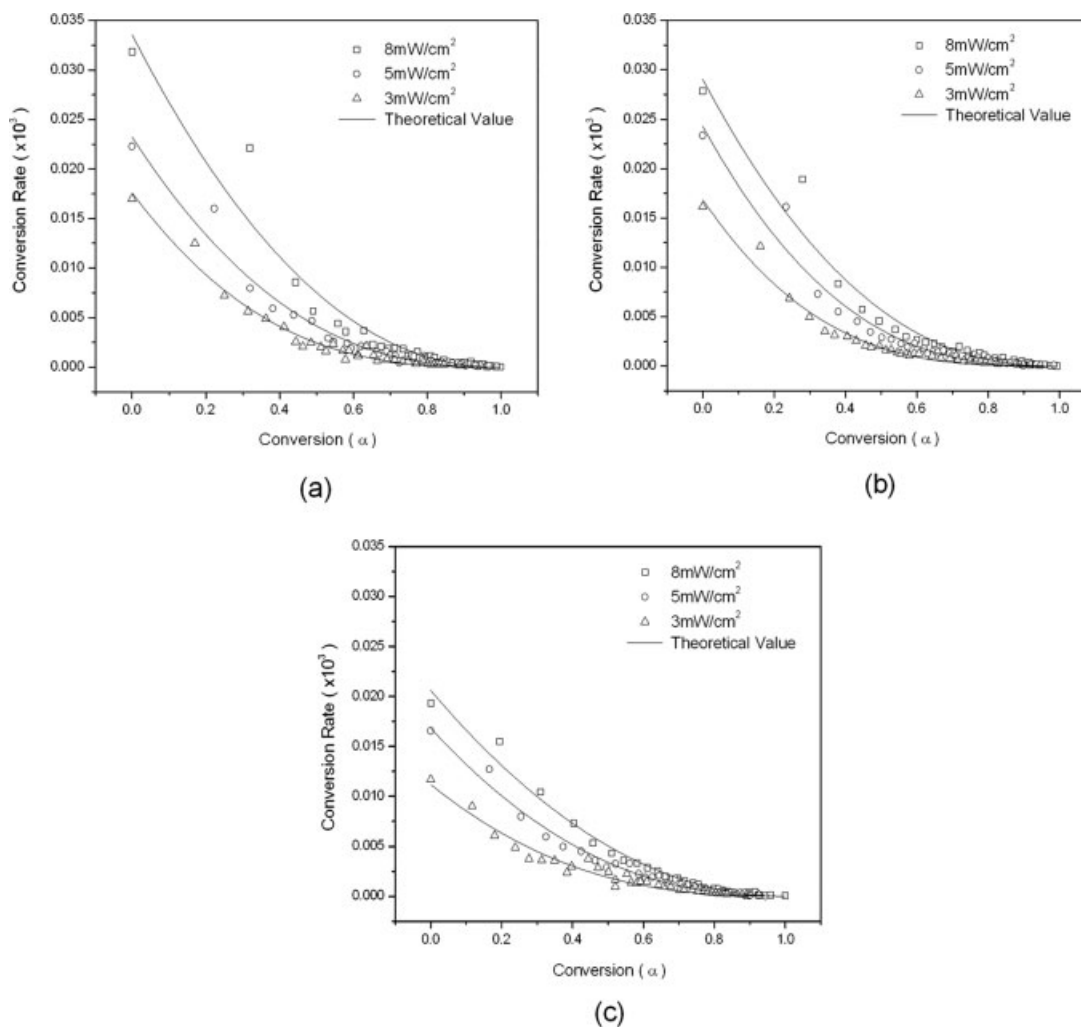
$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (2)$$

where  $\alpha$  is the extent of reaction conversion,  $t$  is time,  $k$  is the rate constant, and  $n$  is the reaction order. All kinetic constants of each photoreactive polymer calculated with this equation are summarized in Table III. Figure 5 and 6 show the comparisons between the experimental values of the reaction conversion rate and the values calculated by eq. (2), in which good agreements between them were found over the whole range for all of these photopolymers.

For the photoreactive polymers that included biphenyl moieties, such as YX4000H-CA and NC3000-CA, the conversion rate and rate constant of YX4000H-CA with only biphenyl groups were lower than those of NC3000-CA, which included other aromatic groups as well as biphenyl groups, as shown in Figure 5 and Table III. For the photodimerization of cinnamate groups, a particular spatial conformation is required so that cyclobutane rings can be formed. Photoreactive polymers have a certain degree of mobility to perform the photoreaction in

the solid state, and photopolymers with rigid chain are less reactive.<sup>17,18</sup> Similar results were observed in the thermal curing reaction of YX-4000H epoxy resin systems with different phenolic hardeners, in which the conversion rate of YX-4000H epoxy resin systems increased with bulky phenolic hardeners.<sup>19</sup> This implies that there are decreases in the molecular interactions between biphenyl groups in accordance with the increase in distance between the biphenyl epoxy resin units. It can be postulated that the higher conversion rate of NC3000-CA compared to that of the YX4000H-CA photopolymer was due to the increase in segment mobility according to the introduction of the benzene ring to weaken the molecular interactions between biphenyl groups.

The reaction conversion rates of the photoreactive polymers without biphenyl moieties were plotted against the reaction conversion in Figure 6. The conversion reaction rates of XP2030-CA, which includes only a benzene ring, and XD1000-2L-CA, with a cyclopentadiene moiety, were higher than that of NC7300L-CA, which includes a naphthalene moiety. Thermal curing reaction studies of XP2030 and XD1000 epoxy resin systems showed that the conversion rate of these epoxy resin systems were higher than that of YX4000H epoxy resin systems.<sup>20</sup> The introduction of these bulky groups contributed to the formation of an optimum cure reaction space and a reduction in the molecular interactions between biphenyl moieties. It can be considered that the higher conversion rates of XP2030-CA and XD1000-2L-CA compared to that of the NC7300L-CA photopolymer was due to the optimum cure reaction space and decreases in molecular interactions between the benzene groups of XP2030-CA and the cyclopentadiene moieties of XD1000-2L-CA



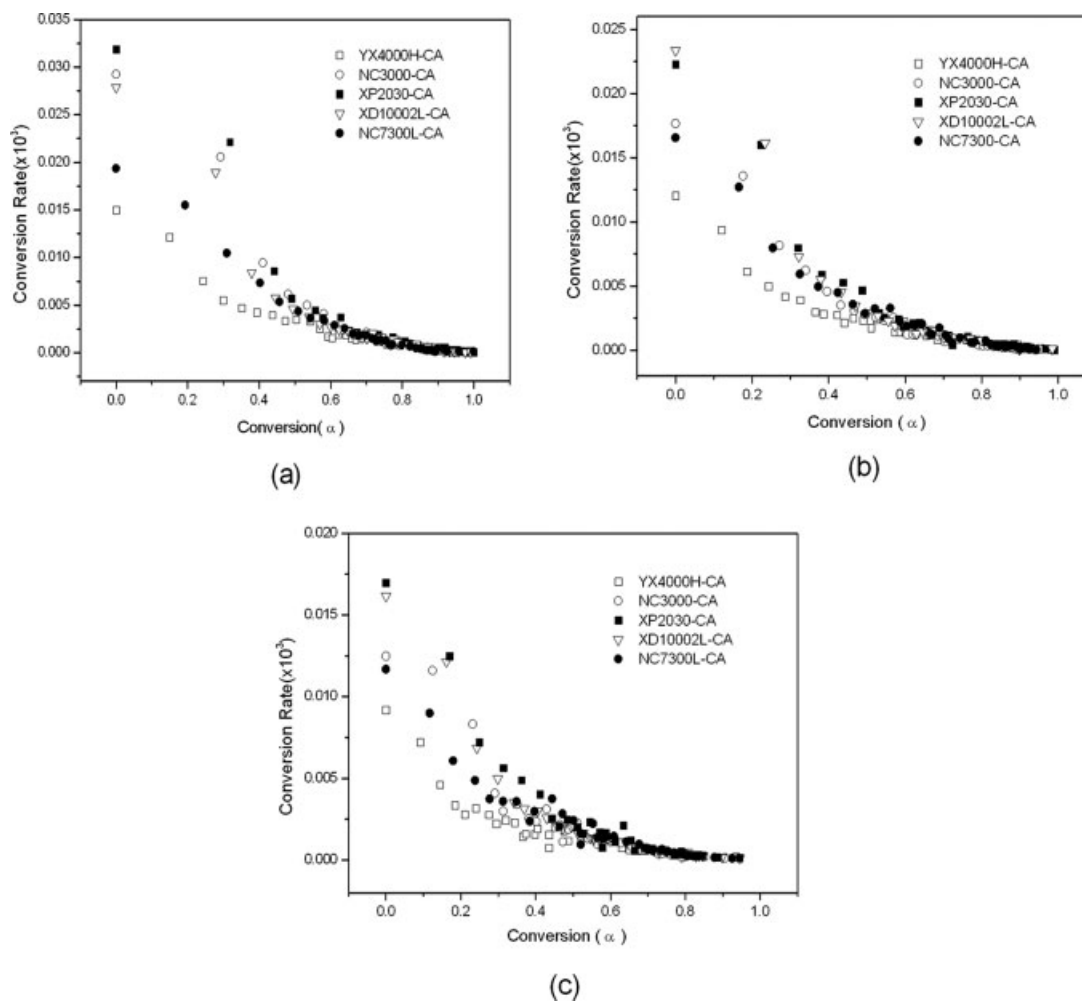
**Figure 6** Comparisons between the experimental and theoretical photocure conversion rates as a function of the conversion of the photoreactive polymers with cinnamate groups in terms of the  $n$ th-order equation: (a) XP2030-CA, (b) XD1000-2L-CA, and (c) NC7300L-CA.

compared with molecular interactions between the naphthalene groups of NC7300L-CA.

The changes in the conversion rate of these photoreactive polymers with light intensity are presented in Figure 7. The conversion rates of YX4000H-CA, with biphenyl groups, and NC7300L-CA, with naphthalene moieties, had lower values than those of the other photoreactive polymers. Particularly, the lowest values of the conversion rate was found in the YX4000H-CA photopolymer, regardless of the light intensity change. We suppose that molecular interactions between the biphenyl moieties were stronger than between the other aromatic groups. The photoreactive polymers with optimum reaction spaces and increases in segmental mobility, including XP2030-CA, XD1000-2L-CA, and NC3000-CA, had higher reaction conversion rates; however, the reaction conversion rates of these photopolymers were depend-

**TABLE III**  
Kinetic Parameters of the Photoreactive Polymers with Cinnamate Groups

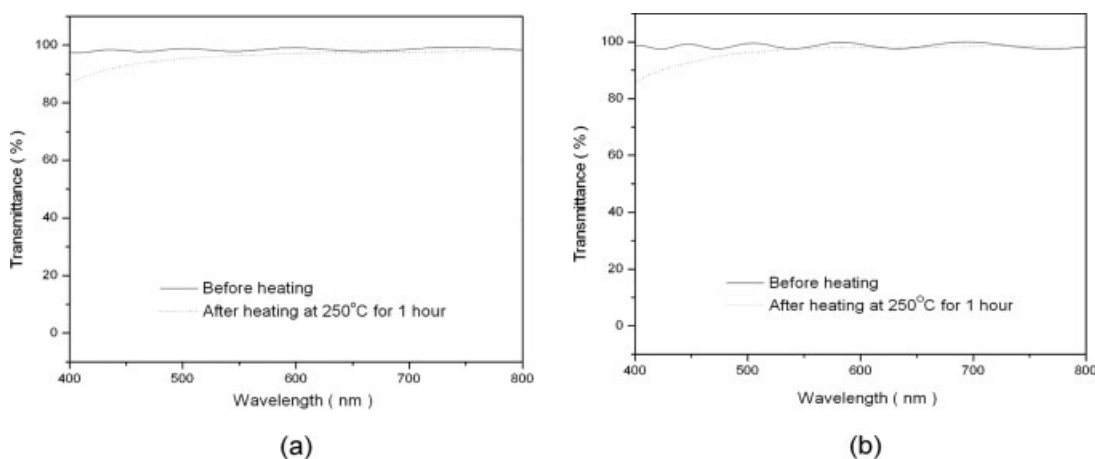
Photoreactive polymer	Intensity (mW/cm <sup>2</sup> )	$k$	$n$
YX4000H-CA	8	$1.50 \times 10^{-2}$	2.26
	5	$1.16 \times 10^{-2}$	2.57
	3	$0.86 \times 10^{-2}$	3.32
NC3000-CA	8	$3.09 \times 10^{-2}$	2.17
	5	$1.85 \times 10^{-2}$	2.58
	3	$1.37 \times 10^{-2}$	2.92
XP2030-CA	8	$3.35 \times 10^{-2}$	2.16
	5	$2.32 \times 10^{-2}$	2.48
	3	$1.76 \times 10^{-2}$	2.85
XD1000-2L-CA	8	$2.91 \times 10^{-2}$	2.35
	5	$2.43 \times 10^{-2}$	2.72
	3	$1.68 \times 10^{-2}$	3.16
NC7300-CA	8	$2.06 \times 10^{-2}$	2.03
	5	$1.68 \times 10^{-2}$	2.31
	3	$1.12 \times 10^{-2}$	2.56



**Figure 7** Photocure conversion rate as a function of the conversion of the photoreactive polymers with cinnamate groups according to the change in UV intensity: (a) 8, (b) 5, and (c) 3 mW/cm<sup>2</sup>.

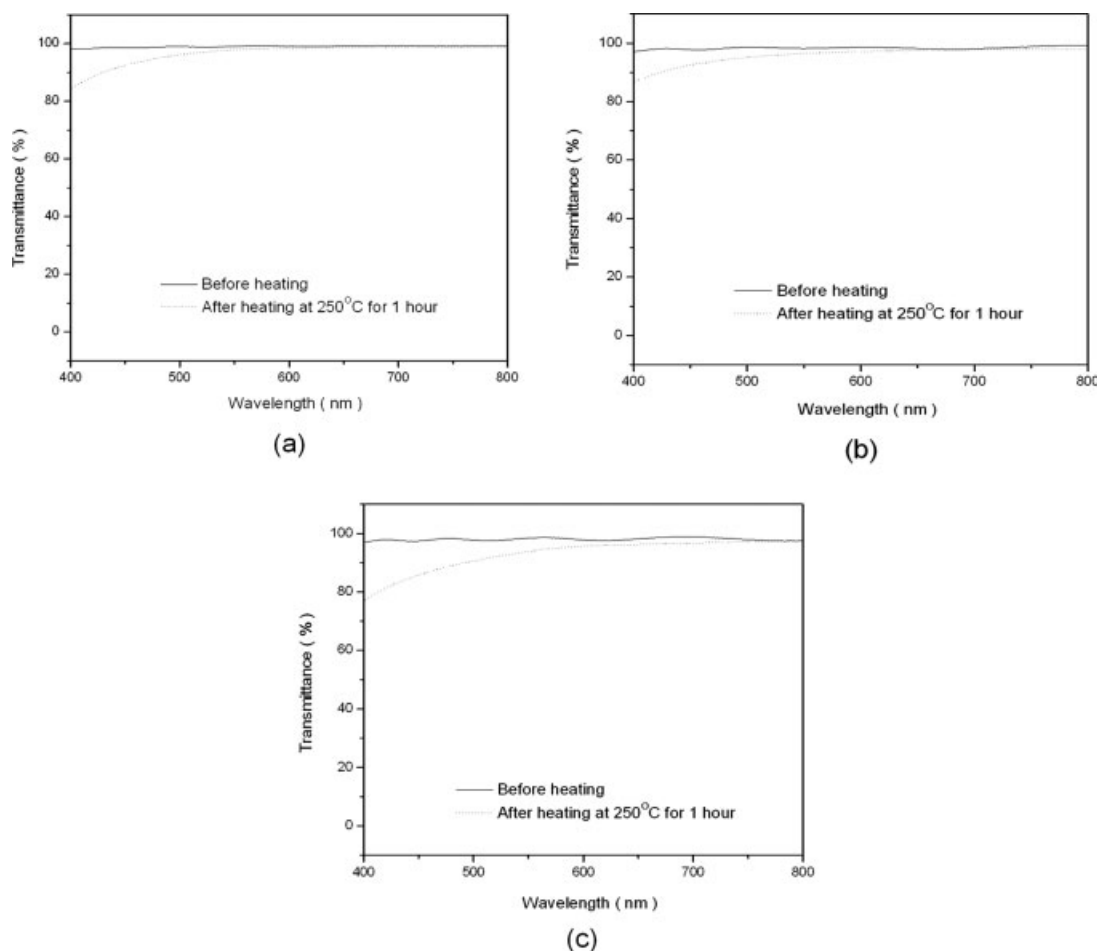
ent on light intensity. The reaction rate constants of these photoreactive polymers increased with light intensity, and their reaction orders decreased with light intensity, as shown in Table III. For these pho-

toreactive polymers, the reaction order converged to 2.0 according to increasing light intensity, which showed that the photodimerization reactions proceeded more easily with increasing light intensity.



**Figure 8** Change in the transmittance of the photocured films before heating and after heating at 250°C for 1 h: (a) YX4000H-CA and (b) NC3000-CA.



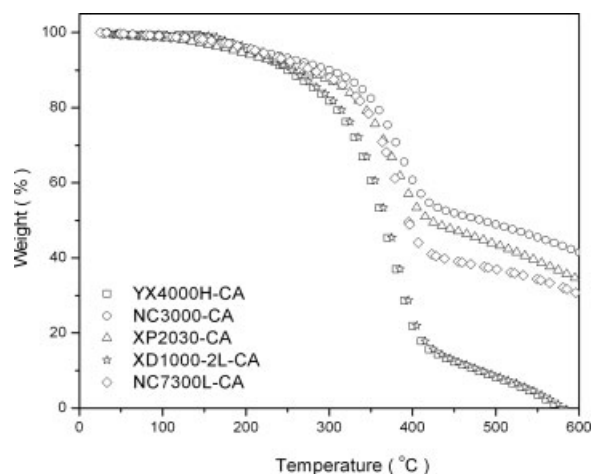


**Figure 9** Change in the transmittance of the photocured films before heating and after heating at 250°C for 1 h: (a) XP2030-CA, (b) XD1000-2L-CA, and (c) NC7300L-CA.

To investigate optical properties with heating of these photoreactive polymers, the transmittance changes upon heating of the photocured films that included biphenyl moieties, including YX4000H-CA and NC3000-CA, are shown in Figure 8, and those of the polymers with different aromatic groups, including XP2030-CA, XD1000-2L-CA, and NC7300L-CA, are presented in Figure 9. As shown in Figures 8 and 9, the photocured films showed almost no change in transmittance in the visible region even after they were heated at 250°C for 1 h compared with the unheated photocured film. The NC7300L-CA photoreactive polymer showed a lower transmittance upon heating than the other photoreactive polymers. XP2030-CA among these photoreactive polymers represented the best optical properties with high heat resistances.

The weight loss values of these photocrosslinked polymers are plotted against temperature by means of TGA in Figure 10. These photoreactive polymers showed good thermal stability, exhibiting little weight loss up to about 250°C. The NC3000-CA photoreactive polymer among them represents the high-

est heat-resistant properties, which had a higher photocure conversion rate and high aromaticity.<sup>21</sup> YX4000H-CA, which included only a biphenyl moiety and had a lower photocure conversion rate, and



**Figure 10** Weight loss of the photocured polymers with temperature as measured by TGA.

the XD1000-2L-CA, which had a lower aromaticity, showed more increases in weight loss with temperature than the other photoreactive polymers.

### CONCLUSIONS

Novel photoreactive photopolymers with cinnamate groups that could perform photocure reactions without photoinitiators were synthesized by the reaction of CA and epoxy resins. We confirmed the chemical structures of these photopolymers by FTIR and NMR spectroscopy. Their photocure reaction conversions increased with UV intensity, and their photocure reaction conversion rates were plotted against reaction conversion to investigate their photocure reaction kinetics. The experimental data of these reaction rates showed the characteristics of an  $n$ th-order kinetics reaction, and all kinetic constants of each photoreactive polymer with this equation were summarized; good agreement was found between them over the whole range for all of these photopolymers. YX4000H-CA, with only biphenyl groups, and NC7300L-CA, with naphthalene moieties, were shown to have strong molecular interactions and lower conversion reaction rates and reaction constants compared with the other photoreactive polymers with different aromatic groups. The photocured films exhibited good thermal stability. Among these photoreactive photopolymers, the best optical properties with heating were observed in XP2030-CA, and the highest heat-resistant properties were found out in NC3000-CA, which had the optimum cure reaction space and high aromaticity.

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