

## Photocure Reactions of Photoreactive Prepolymers with Cinnamate Groups

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The photoreactive prepolymers with multifunctional cinnamate and bisphenol A type cinnamate groups that could perform photodimerization without photoinitiators were synthesized by the reaction of *t*-cinnamic acids (CAs) and epoxy resins. Their photocure reaction rates and the extent of reaction conversion were measured with Fourier transform infrared spectroscopy, and these increased with the intensity of UV irradiation. The experimental data of these reaction rates showed the characteristics of *n*th-order kinetics reaction, and all kinetic constants of each photoreactive polymer with this equation were summarized. Although the GTR-1800-HCA and KWG1-EP-HCA with hydroxyl group substituted cinnamate showed lower reaction conversion rates and rate constant than GTR-1800-CA and KWG1-EP-CA with an unsubstituted cinnamate group, GTR-1800-MCA and KWG1-EP-MCA with methoxy group substituted cinnamate showed similar and higher reaction conversion rates than the former, respectively. These results were explained in terms of segmental mobility for photopolymerization by molecular interactions.

**Key Words** : Curing of polymers, Kinetics (polym.), Photopolymerization, Thermal properties, Epoxy resin

### Introduction

High heat resistant photopolymer systems have been requested since the rapid progress of the electronic industries including semiconductor and liquid crystal displays.<sup>1</sup> In particular, the color filters (CF) in liquid crystal displays, which are a key component for the production of color images, require low power consumption, high color purity and transmittance, high contrast, low reflection, and high stability against heat, light, and chemicals. The most significant challenges have been in the area of improving the thermal resistance, transparency, and cost effectiveness of CF resists for color patterning, because the pigment dispersion method, which is the widely used CF manufacturing process, requires these properties.<sup>2-4</sup> In previous reports,<sup>5,6</sup> new methacrylate-type pre-polymers including a cyclohexane moiety and biphenyl group, and new cinnamate-type photoreactive pre-polymers with a cyclopentadiene moiety and various aromatic groups were synthesized in order to improve the heat resistance and transparency of photopolymer systems.

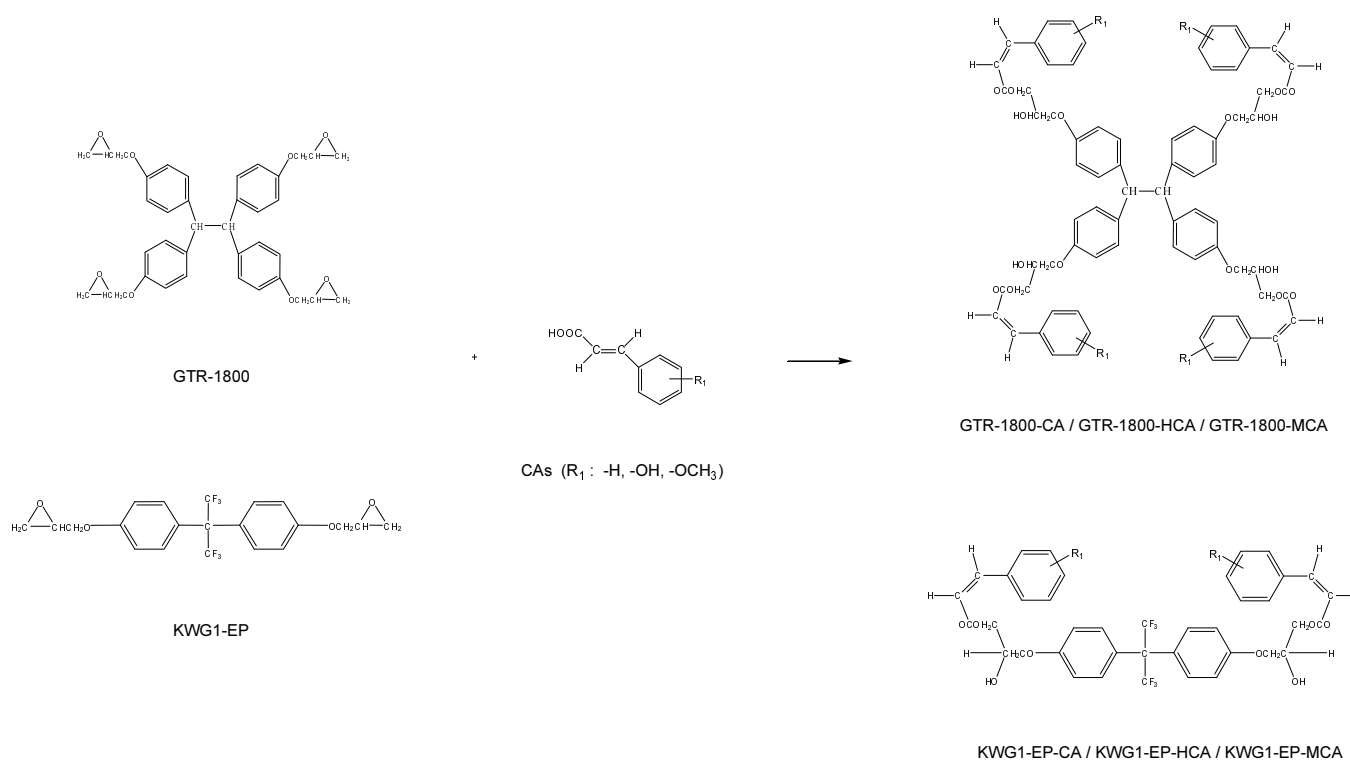
In this study, the new multifunctional cinnamate photoreactive prepolymer systems with tetraphenyl ethane moiety, and the bisphenol A type cinnamate photopolymer systems with trifluoro methyl group were synthesized and their photocure properties were investigated. It can be expected that the multifunctional cinnamate prepolymer including tetraphenyl ethane unit and a bisphenol A type with trifluoro methyl group cinnamate photoreactive pre-polymers, which show good electrical insulation performance and lower moisture absorption properties, would give rise to good thermal stability, optical properties, and photocrosslinking without photoinitiators.<sup>7-9</sup> The photocure kinetics of these prepolymers were investigated using Fourier transform infrared (FTIR) spectroscopy, and their thermal stability was measured with thermogravimetric analysis (TGA). The photocure reactions of them with light intensity were interpreted by means of the *n*th-order mechanism and the

curing kinetics in the overall conversion region were analyzed with this kinetic model.

### Experimental

The synthesis of a photoreactive pre-polymer with cinnamate groups was performed by reacting cinnamic acids (CAs), including different substitution groups, with two kinds of epoxy resins, GTR-1800 (Nippon Kayaku Co., Tokyo, Japan) and KWG1-EP (Nippon Kayaku Co., Tokyo, Japan) as shown in Figure 1. The detailed chemical structures of epoxy resins used in this study are summarized in Table 1. The CAs with different substitution groups were *t*-cinnamic acid (CA), 3-hydroxy *t*-cinnamic acid (HCA) and 4-methoxy *t*-cinnamic acid (MCA), and they were received from Aldrich Chemical Co. (Milwaukee, WI). All the photoreactive prepolymers in this study were synthesized by maintaining a 1:1 ratio of equivalent weight of epoxy and carboxyl acid groups with 0.04 *m* of tetramethyl ammonium chloride as a catalyst based on epoxy resin. The reactions were carried out in the methyl ethyl ketone at 70 °C for 80 h. The acid values of these synthesized photoreactive polymers were controlled below 1.00 KOH mg/g in order to maintain constant initial CA double bond concentration of photoreactive prepolymers synthesized from each base epoxy resin.<sup>5,6</sup>

These photoreactive prepolymers were dissolved in the solvents including monochlorobenzene, tetrahydrofuran, methyl ethyl ketone and toluene to have optimum viscosity for spin coating. Each solution was filtered through a 0.2 μm membrane filter and spin-coated on a quartz substrate using a spin coater. These polymer films were then dried at 70 °C for 30 min, which led to a good quality film with a thickness of about 1 μm. The photocure of these were carried out by exposure to UV light radiated from a high-pressure mercury lamp at various intensities using UV exposure system (Nanotech NLS-HG50, Seoul, Korea). The photocure behavior and thermal stability of the

**Figure 1.** Synthetic reactions of the photoreactive prepolymers with cinnamate groups.**Table 1.** Description of Raw Materials Used in This Study

Grade Name	Structure	Remarks
GTR-1800		<sup>1</sup> EEW = 171
KWG1-EP		<sup>1</sup> EEW = 235
<i>t</i> -Cinnamic Acid (CA)		
3-Hydroxy <i>t</i> -Cinnamic Acid (HCA)		
4-Methoxy <i>t</i> -Cinnamic Acid (MCA)		

<sup>1</sup>EEW: Epoxy Equivalent Weight (g/equiv.)

films were studied using FTIR spectroscopy and TGA. The photocure conversions of the films 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 ( $1715\text{ cm}^{-1}$  and represents the absorption peak of the carbonyl group in the cinnamate group); and subscripts  $t$  and  $s$  are the UV irradiation time after  $t$  minutes and the reference irradiation time (where  $s = 0\text{ min}$ ), respectively.

### Results and Discussion

It was represented that GTR-1800-CA, GTR-1800-HCA, and GTR-1800-MCA were the reaction products of GTR-1800 epoxy resin with CAs and also stated that KWG1-EP-CA, KWG1-EP-HCA, and KWG1-EP-MCA were the reaction products of KWG1-EP epoxy resin with CAs, as shown Figure 1. These

products performed photocure reactions by intermolecular or intramolecular photocycloaddition reactions.

The chemical structures of the photoreactive prepolymers were confirmed using  $^1\text{H-NMR}$  spectroscopy and FTIR spectroscopy. As shown in Figure 2(a) and Figure 3(a), the doublet proton NMR peaks near 6.5 ppm corresponding to the protons of the cinnamate double bond for the GTR-1800-CA and KWG1-EP-CA, respectively, and the typical FTIR peaks of  $1715\text{ cm}^{-1}$  (carbonyl group of cinnamate) and  $1635\text{ cm}^{-1}$  (cinnamate double bond) were observed for the GTR-1800-CA and KWG1-EP-CA, respectively, which are shown in Figure 2(b) and Figure 3(b). The doublet proton NMR peaks near 6.5 ppm and the FTIR peaks of  $1635\text{ cm}^{-1}$  were observed in other photoreactive prepolymers with cinnamate groups (GTR-1800-HCA, GTR-1800-MCA, KWG1-EP-HCA, and KWG1-EP-MCA).

The changes in the degree of photocure conversion with the change of UV intensity in the GTR-1800-CAs photoreactive polymers with different functional group of CA are shown in Figure 4, and those in KWG1-EP-CAs are represented in Figure 5. As shown in Figure 4 and 5, the extent of 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>10</sup> the rate constant in cinnamate photocure reactions

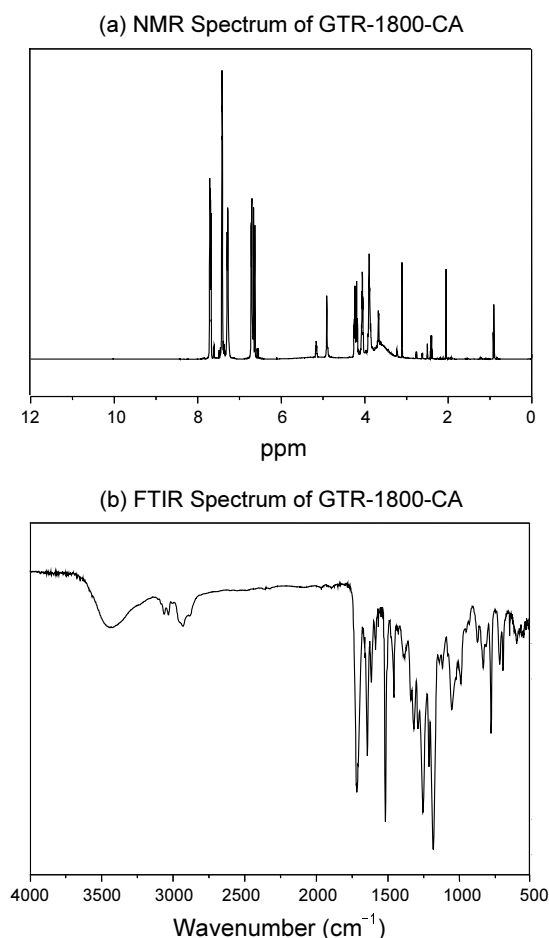


Figure 2. (a)  $^1\text{H-NMR}$  and (b) FTIR Spectra of GTR-1800-CA.

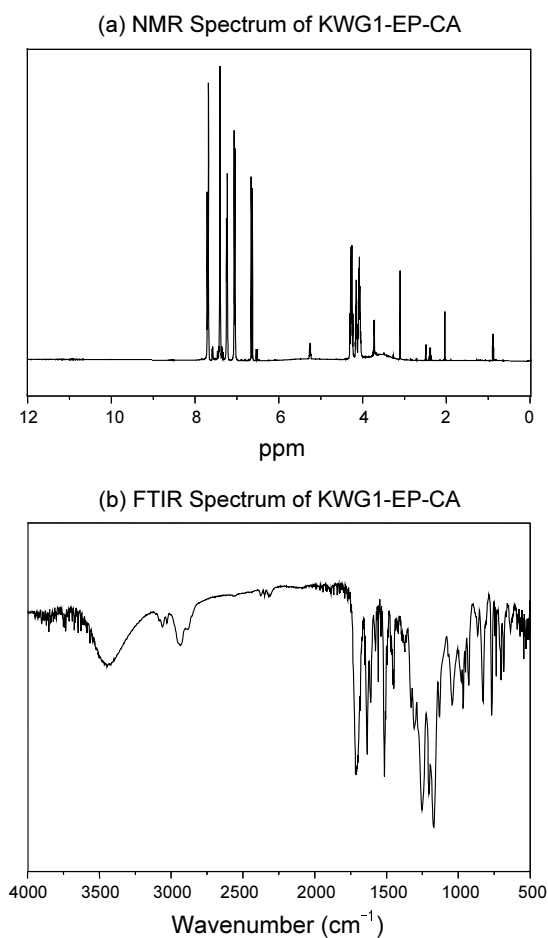
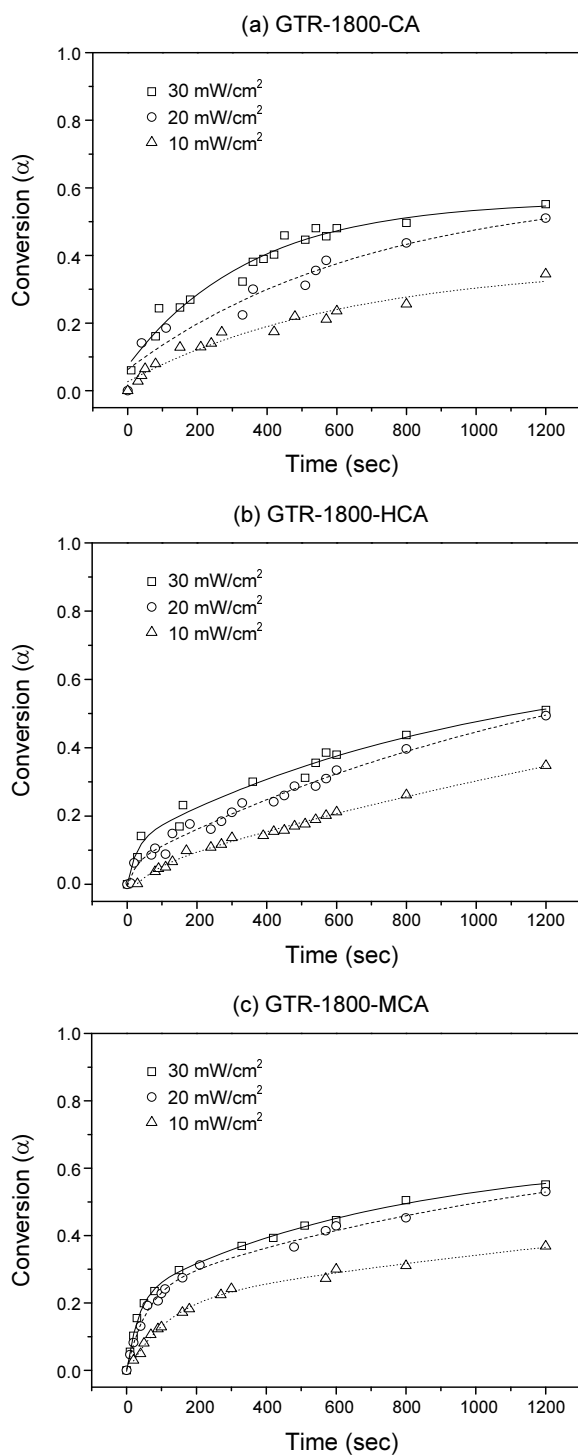
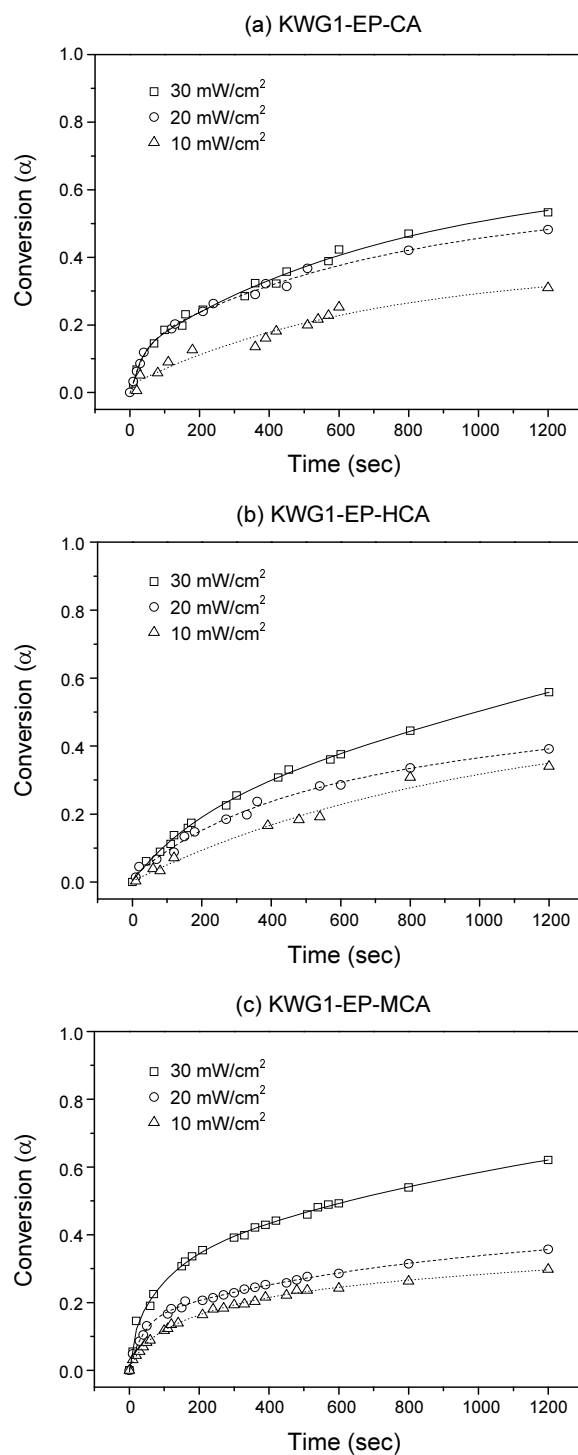


Figure 3. (a)  $^1\text{H-NMR}$  and (b) FTIR Spectra of KWG1-EP-CA.



**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) GTR-1800-CA, (b) GTR-1800-HCA, and (c) GTR-1800-MCA.



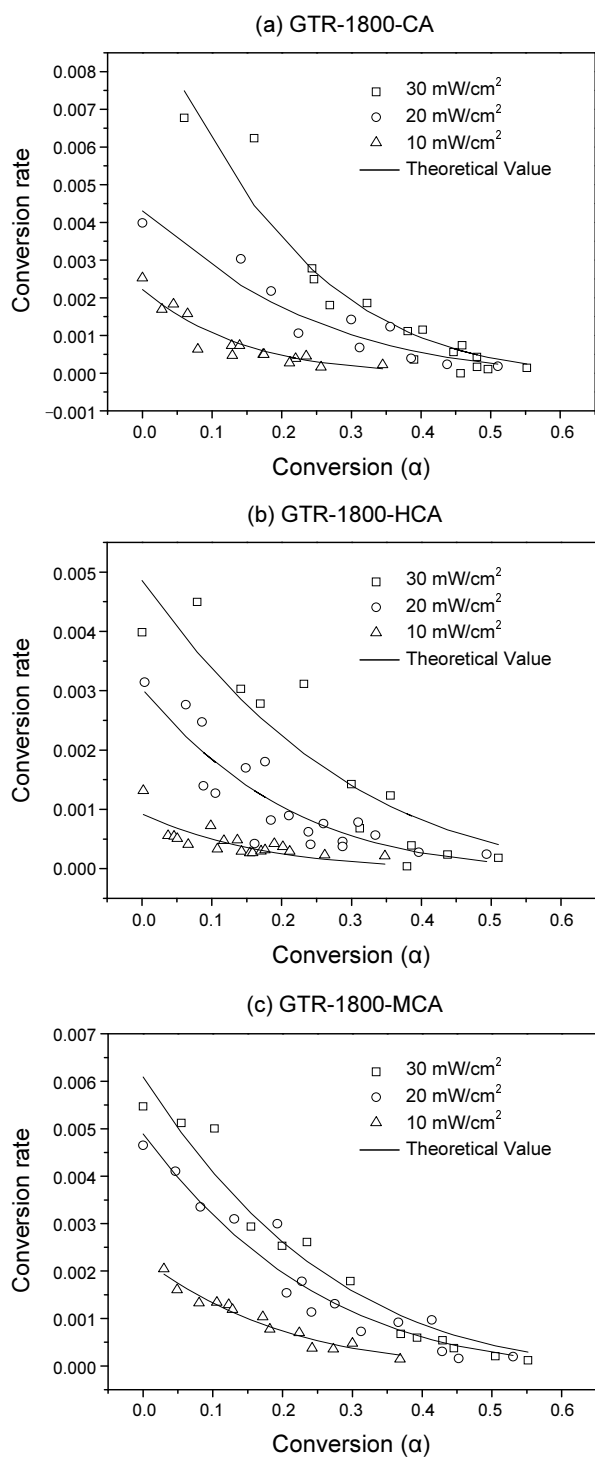
**Figure 5.** Change in photocure reaction conversion of the photoreactive polymers with cinnamate groups according to the UV irradiation time at different UV intensities: (a) KWG1-EP-CA, (b) KWG1-EP-HCA, and (c) KWG1-EP-MCA.

such as these photoreactive polymers without photoinitiators is linearly dependent on the intensity of incident light.<sup>11-12</sup>

The reaction conversion rates of the GTR-1800-CAs photoreactive prepolymers with different functional groups of CA are shown in Figure 6, and those of KWG1-EP-CAs are plotted against reaction conversion in Figure 7. As shown in Figure 6

and 7, the experimental data of these reaction rates show the behavior of  $n$ th-order kinetics reaction as described in the following equation:<sup>13,14</sup>

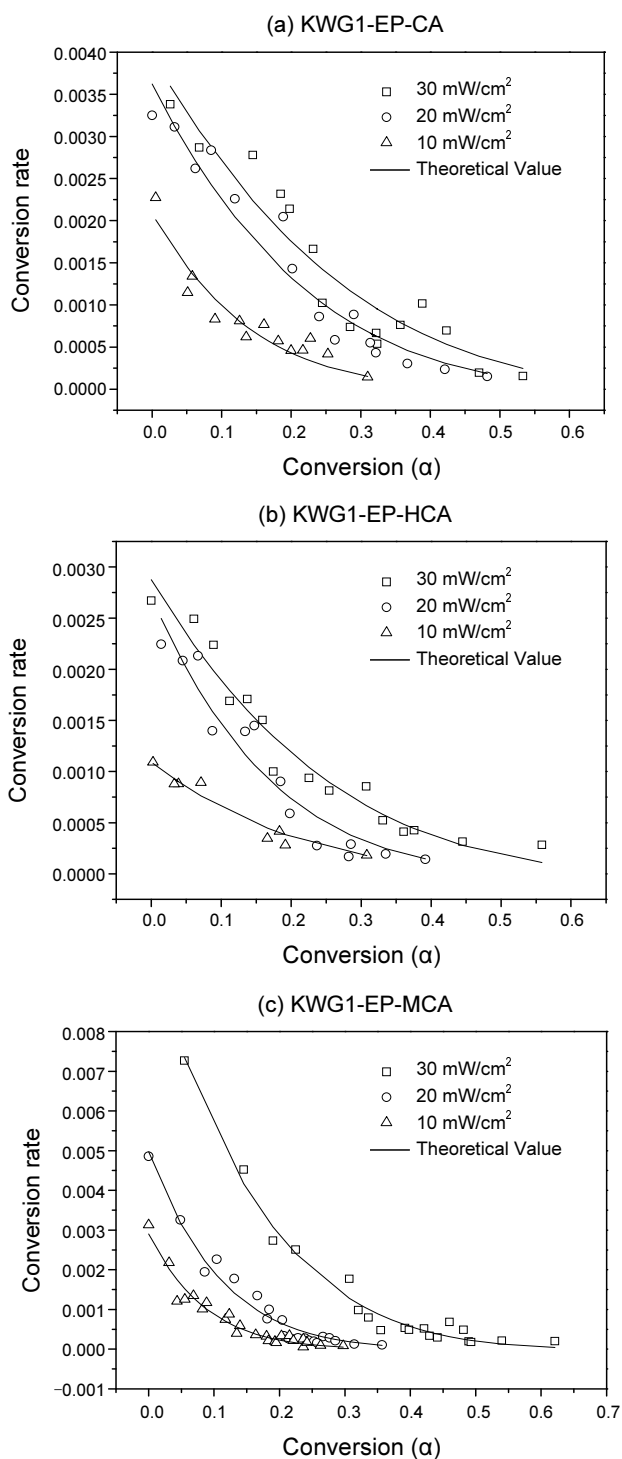
$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (2)$$



**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  $n$ th-order equation: (a) GTR-1800-CA, (b) GTR-1800-HCA, and (c) GTR-1800-MCA.

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 2.

For the GTR-1800-CAs photoreactive prepolymers that included multifunctional cinnamate groups, the conversion rate



**Figure 7.** 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  $n$ th-order equation: (a) KWG1-EP-CA, (b) KWG1-EP-HCA, and (c) KWG1-EP-MCA.

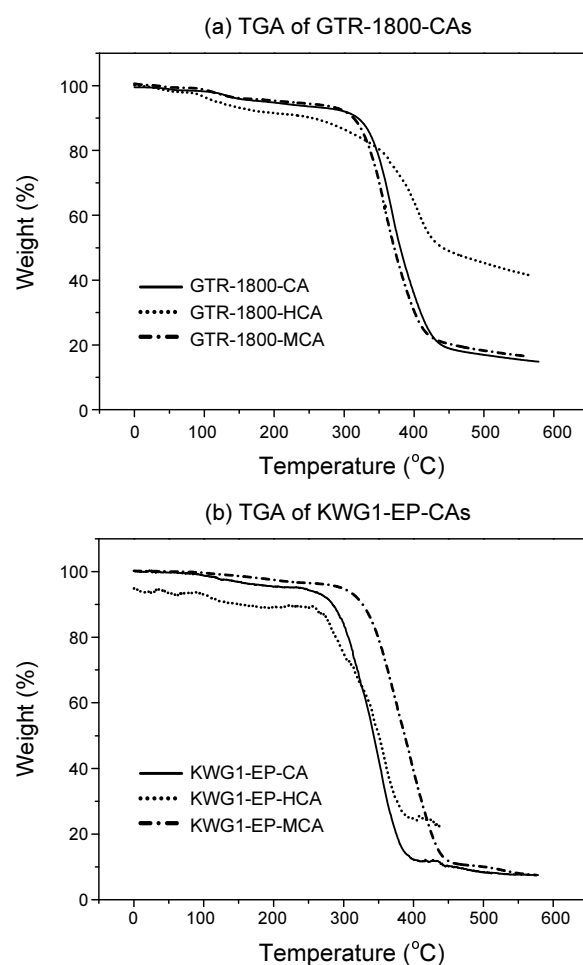
and rate constant of GTR-1800-HCA were lower than those of GTR-1800-CA and GTR-1800-MCA, as shown in Figure 6 and Table 2. For the photodimerization of cinnamate groups, a particular spatial conformation is required so that cyclobutane rings can be formed. Photoreactive polymers have a certain degree of mobility to perform the photoreaction in the solid

**Table 2.** Kinetic Parameters of the Photoreactive Polymers with Cinnamate Groups

Photoreactive Prepolymer	Intensity (mW/cm <sup>2</sup> )	k	n
GTR-1800-CA	30	$9.97 \times 10^{-3}$	4.61
	20	$4.31 \times 10^{-3}$	4.03
	10	$2.22 \times 10^{-3}$	6.92
GTR-1800-HCA	30	$4.86 \times 10^{-3}$	3.49
	20	$3.41 \times 10^{-3}$	4.76
	10	$0.92 \times 10^{-3}$	5.84
GTR-1800-MCA	30	$6.09 \times 10^{-3}$	3.79
	20	$4.89 \times 10^{-3}$	4.08
	10	$2.26 \times 10^{-3}$	5.02
KWG1-EP-CA	30	$3.96 \times 10^{-3}$	3.65
	20	$3.62 \times 10^{-3}$	4.51
	10	$2.09 \times 10^{-3}$	7.08
KWG1-EP-HCA	30	$2.88 \times 10^{-3}$	3.98
	20	$2.72 \times 10^{-3}$	5.87
	10	$1.09 \times 10^{-3}$	4.94
KWG1-EP-MCA	30	$10.10 \times 10^{-3}$	5.63
	20	$4.97 \times 10^{-3}$	8.97
	10	$2.90 \times 10^{-3}$	11.40

state.<sup>15,16</sup> Therefore, the GTR-1800-HCA with strong intermolecular interactions such as a hydrogen bond is less reactive due to the decrease of mobility, and thus, the lowest conversion rate and rate constant are obtained in this pre-polymer. Similar results were observed in KWG1-EP-CAs photoreactive prepolymers. The conversion rate and rate constant of KWG1-EP-HCA were lower than those of KWG1-EP-CA and KWG1-EP-MCA, as shown in Figure 7 and Table 2. This also implies that the decrease in the reaction conversion rate and conversion in the KWG1-EP-HCA are in accordance with the decrease of mobility of chain segment due to the molecular interactions between the hydroxyl groups such as a hydrogen bond.

Comparing GTR-1800-CAs with KWG1-EP-CAs, the reaction conversion rates and rate constant of GTR-1800-CAs are larger than those of KWG1-EP-CAs except for the methoxy group substituted pre-polymer systems, GTR-1800-MCA and KWG1-EP-MCA. These increases of GTR-1800-CAs are due to the multifunctional cinnamate group of GTR-1800-CAs, because the conversion rates generally increase with photopolymerizable functional group density. However, a small decrease of reaction conversion rate and rate constant of GTR-1800-MCA compared to that of KWG1-EP-MCA can be observed as shown in Figure 6 and Figure 7. Although a similar reaction conversion rate can be seen in the GTR-1800-MCA compared to that of the GTR-1800-CA as shown in Figure 6, a larger increase can be observed in the KWG1-EP-MCA compared to that of the KWG1-EP-CA as shown in Figure 7. The increase of reaction rates according to the introduction of methoxy group can be remarkably found in a bisphenol A type backbone structure with trifluoromethyl group than multifunctional cinnamate with tetraphenyl ethane structure. Therefore, it can be considered that the introduction of methoxy group contributed to the increase of mobility of the chain segments along with a decrease

**Figure 8.** Weight loss of the photocured polymers with temperature as measured by TGA: (a) TGA of GTR-1800-CAs, and (b) TGA of KWG1-EP-CAs.

of molecular interactions between the backbone chains; however, the decrease of reaction conversion rates and rate constant according to these effects diminished with photopolymerizable functional group density.

The weight loss values of these photocrosslinked polymers are plotted against temperature by means of TGA in Figure 8. For the GTR-1800-CAs, the weight loss doesn't approach 10% until about 300 °C in all cases. The KWG1-EP-CAs resin systems show better overall stability with the exception of the KWG1-EP-HCA, which also shows 10% weight loss before 300 °C. Therefore, KWG1-EP-MCA photoreactive prepolymer represents the highest heat-resistant properties, which had a higher photocure conversion rate and reaction conversion.<sup>17</sup> The GTR-1800-HCA and KWG1-EP-HCA, which included a hydroxyl cinnamate moiety and had a lower photocure conversion rate, showed more increase in weight loss with temperature than the other photoreactive polymers. The improvements of cure reaction conversion in CA double bond are required in order to obtain more high heat resistant photopolymers.

## Conclusions

New photoreactive prepolymers were synthesized by the

reaction of CAs with different functional groups and two kinds of epoxy resins which are a multifunctional epoxy resin (GTR-1800) and a bisphenol A type epoxy resin with trifluoro methyl group (KWG1-EP). The chemical structures of these photopolymers were confirmed by FTIR and NMR spectroscopy, and their photocure reactions were analyzed in terms of  $n$ th-order kinetic reaction equation. 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. GTR-1800-HCA and KWG1-EP-HCA prepolymers containing hydroxyl group substituted cinnamate were shown to have strong molecular interactions such as a hydrogen bond and represented lower conversion reaction rates and reaction constants than the other photoreactive prepolymers. These phenomena can be explained by photopolymerizable functional group density and segmental mobility. The photocured films exhibited good thermal stability, and the highest heat-resistant properties were found in KWG1-EP-MCA.

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