

Cure Properties of Methacrylate-Type Prepolymer That Include Cyclohexane Moiety

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ABSTRACT: New methacrylate-type prepolymers including a cyclohexane moiety, which may be used as binder resins for the color filter resist of liquid crystal display, were synthesized by the reaction with methacrylic acid (MA) and epoxy resins. Their photo- and thermal cure properties were investigated using Fourier transform infrared spectroscopy and DSC, respectively. Their photocure reaction rates and the extent of reaction conversion increased with the concentration of photoinitiator and intensity of UV irradiation. An increase of photocure reaction temperature was attributed to the increase of photocure reaction rate and the degree of reaction conversion for EHPE-3150-MA prepolymer. Thermal stability was studied by observing changes in the transmittance of the photocured polymer film upon heating. The

polymer was extremely stable, showing almost no transmittance change in the visible range even after being heated at 250°C for 1 h. We also investigated thermal cure reaction using a DSC technique. An autocatalytic kinetic reaction occurs in these systems, and the kinetic parameters of all systems were reported in terms of a generalized kinetic equation that considered the diffusion term. It can be shown that the reaction conversion rate of NC-9110-MA is faster than that of EHPE-3150-MA, regardless of the kind of thermal initiator. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 43–52, 2004

Key words: photopolymer; cure reaction; LCD; color filter resist

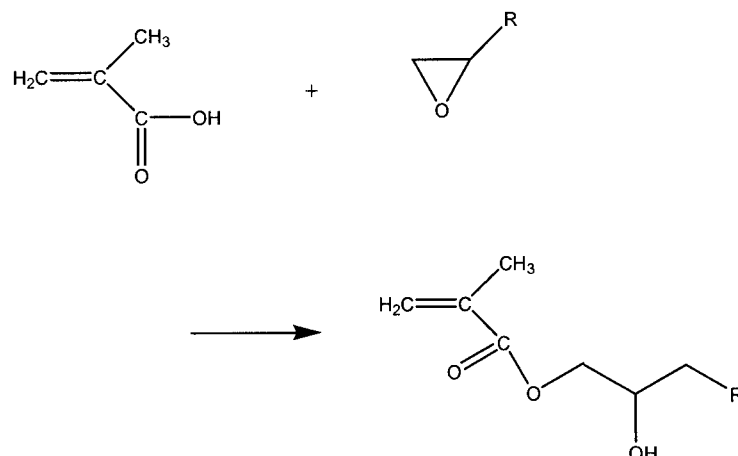
INTRODUCTION

As the need for high resolution, large panel size, and high reliability of liquid crystal display is growing, the improvement of color filter resist is progressing fast.^{1,2} In particular, the most significant challenges have been in the area of improving the thermal resistance and transparency of color filter resist.^{3–5} Various methods to solve these problems have been presented, although to date the most economical and effective method has been the modification of binder resin for color filter resist. Light resistance, heat resistance, and chemical resistance are good for the polyimide resin systems, but these resin systems cannot be satisfied with the properties of transparency and dispersion of pigment. For the acrylic resin systems, good results can be shown in optical properties and pigment dispersion; however, serious problems have occurred in the process of top coating and indium tin oxide coating in color filter process because of low heat resistance.^{6,7}

In this study, new methacrylate-type prepolymers including a cyclohexane moiety are synthesized and

characterized to improve the heat resistance and transparency of the binder resin systems for color filter resist. These prepolymers were synthesized by reaction with epoxy resins and methacrylic acid. We expected that the rigid cyclic moieties from the epoxy resin and double bonds from a methacrylic acid would give rise to thermal stability and photoreactivity, respectively.⁸ These prepolymers are expected to possess high heat resistance and transparency because of a rigid cyclohexane group with no unsaturated carbon. To investigate their photo- and thermal cure properties, we studied the photocure behaviors and thermal stability using UV-visible spectroscopy and Fourier transform infrared (FT-IR) spectroscopy. We also investigated the effects of the photocure conditions such as the concentration of the photoinitiator, the intensity of UV light, and the photocuring temperature on the photocure behavior of the prepolymers. The thermal curing characteristics of such new methacrylate-type prepolymers were investigated using a DSC technique. The curing mechanism of these systems with different thermal initiators was interpreted by means of *n*th order and an autocatalytic mechanism, and the curing kinetics in the overall conversion region were analyzed using the kinetic and diffusion model.

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Scheme 1. Synthetic reaction of methacrylate-type prepolymer

EXPERIMENTAL

Synthesis of a methacrylate-type prepolymer

The synthesis of a methacrylate-type prepolymer has been performed by reacting a methacrylic acid (MA) with an epoxy resin with a cyclohexane moiety, which is described in Scheme 1. The epoxy resins used in this experiment are NC-9110 and EHPE-3150 grade obtained from Nippon Kayaku Co. (Japan) and Dicel Chemical Co. (Japan). Detailed chemical structure descriptions of epoxy resins used in this study are summarized in Table I. As shown in Table I, NC-9110 is an epoxy resin with cyclohexane and aromatic groups and EHPE-3150 is an

epoxy resin including only cyclohexane groups. MA was received from Aldrich Chemical Co. (Milwaukee, WI). An epoxy resin was dissolved in methylethyl ketone (MEK) solvent, and a MA with a weight equivalent to that of an epoxy resin was dropped into the mixture. After 0.5 wt % of tetramethylammonium chloride as a catalyst to total weight was added, the reaction was performed under reflux at 70°C for 72 h. After this solution was evaporated, washed in distilled water, and dried under vacuum, the acid value of this resin was measured.⁹ The acid value of NC-9110-MA (the methacrylate-type prepolymer obtained by reacting NC-9110 with MA) and EHPE-3150-MA (the methacrylate-type

TABLE I
Description of Raw Materials Used in This Study

Grade name	Structure	Remarks
NC-9110		EEW ^a = 231
EHPE-3150		EEW = 182

^a EEW: Epoxy equivalent weight (g/equiv).

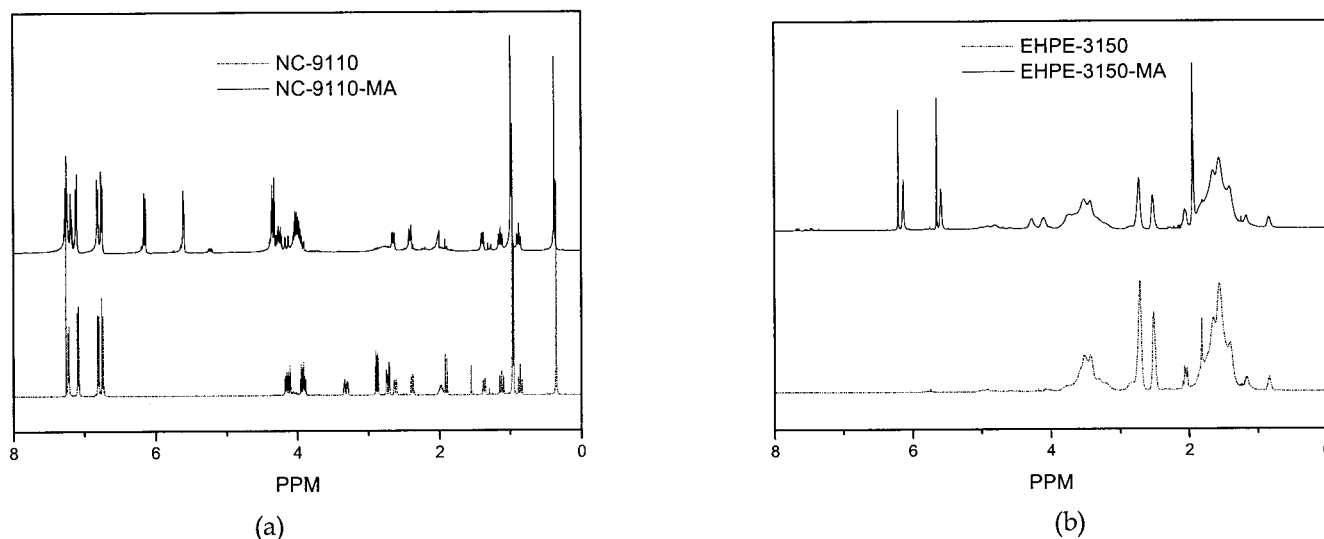


Figure 1 $^1\text{H-NMR}$ spectra of new methacrylate-type prepolymers: (a) NC-9110-MA; (b) EHPE-3150-MA

prepolymer obtained by reacting EHPE-3150 with MA) is 0.97 KOH mg/g and 1.42 KOH mg/g, respectively. Nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 300 MHz, Lake Forest, CA) and FT-IR spectroscopy (Perkin-Elmer Spectrum-2000, Wellesley, MA) were used to characterize these resins. As shown in Figure 1(a), methylene peaks of the cyclohexane group (1.00~1.50 ppm) and methylene and methine peaks of the glycidyl group (2.50~3.50 ppm) of the NC-9110 epoxy resin can be observed. In NC-9110-MA prepolymer, proton peaks of the glycidyl group in NC-9110 epoxy resin disappeared with methacrylation reaction, and proton NMR peaks of 5.60 and 6.15 ppm corresponding to the protons of the methacrylate vinyl group can be measured. A typical FT-IR peak of 1715 cm^{-1} corresponding to the carboxylate group of methacrylate can be

observed in Figure 2. As shown in Figure 1b, it is very difficult to assign methylene and methine peaks of glycidyl group of EHPE-3150 epoxy resin because they overlapped with methylene peaks of the cyclohexane group linked by an ether bond. However, in EHPE-3150-MA prepolymer, the decrease of peaks of the glycidyl group and typical doublet peaks corresponding to the protons of the methacrylate vinyl group (5.60 and 6.15 ppm) can be observed. The peak of the methyl group in methacrylate (1.93 ppm) can also be measured.

Fabrication and characterization of a photopolymer system

This prepolymer was dissolved in a solvent such as chlorobenzene-toluene mixture with a photoinitiator

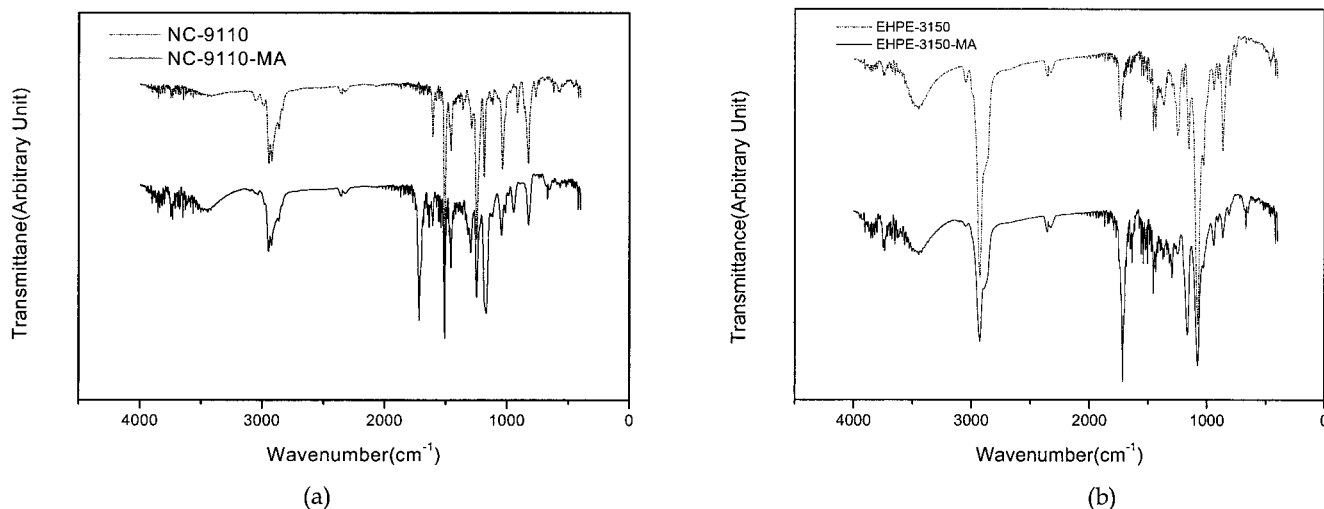


Figure 2 FT-IR spectra of new methacrylate-type prepolymers: (a) NC-9110-MA; (b) EHPE-3150-MA

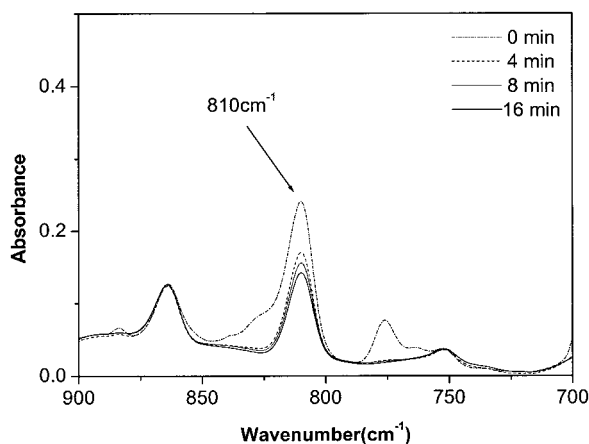


Figure 3 The change in absorbance of the prepolymer at 810 cm^{-1} with UV irradiation time.

(2(2'-furylethylidene)-4,6-bis(trichloromethyl)-s-triazine). The solution was then filtered and spin-coated on a glass substrate at 1500 rpm for 90 s, resulting in good quality of the film with thickness of about $1\ \mu\text{m}$. The film was dried at 80°C for 10 min and exposed to UV (365 nm) with various intensities. We studied the photocure behavior and thermal stability using UV-visible spectroscopy and FT-IR spectroscopy. We measured the relative residual functional peak ratio (R_p) to compare the photocure conversion of this resin system according to the irradiation time as follows,

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

where A_f is the absorption peak height of the C = C double bond (810 cm^{-1}) to be polymerized and A_r is the absorption peak height of the reference group, which is not changed during UV irradiation (1715 cm^{-1} , which represents the absorption peak of the carboxylate group in methacrylate); and subscripts t and s are UV irradiation time after t minutes and reference irradiation time (where $s = 0\text{ min}$), respectively. A typical FT-IR spectrum of this prepolymer according to the UV irradiation time is shown in Figure 3. A photocure reaction conversion (α_t) at each UV irradiation time is obtained by the equation

$$\alpha_t = 1 - \frac{(A_f/A_r)_t}{(A_f/A_r)_s} \quad (2)$$

Sample preparation for thermal cure system

A methacrylate-type resin was dissolved in MEK solvent at room temperature to make a resin composition for the curing reaction study. After a homogeneous solution was obtained, a thermal initiator was added

and fully stirred. Thermal initiators used in the curing reaction of methacrylate-type resin were 2,2'-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO), which were obtained from Aldrich Chemical Co. The thermal initiator concentration was fixed at $6.0 \times 10^{-6}\text{ mol/g}$ with respect to the total amount of resin. Each sample was evaporated under vacuum at room temperature to eliminate solvent and stored in a refrigerator at 4°C . Thermal analyses were performed using a TA-2020 differential scanning calorimeter (TA Instruments, New Castle, DE). Isothermal and dynamic-heating experiments were conducted under a nitrogen flow of 60 mL/min . For dynamic cure, the sample was heated at a rate of 5°C/min from -10 to 300°C , beyond which decomposition was observed. A set of isothermal cure curves was obtained to evaluate the kinetic parameter for the curing reactions.

RESULTS AND DISCUSSION

The changes in degree of photocure conversion with a concentration of photoinitiator in EHPE-3150-MA and NC-9110-MA prepolymer system under constant UV intensity (13 mW/cm^2) are shown in Figure 4. As shown in Figure 4, photocure reaction rates and extent of conversion reaction increased with the concentration of the photoinitiator. Although the differences in photocure reaction conversion between EHPE-3150-MA and NC-9110-MA prepolymer system were small at 5 wt % ($1.2 \times 10^{-4}\text{ mol/g}$) photoinitiator concentration, a big difference can be observed at higher photoinitiator concentration. A sharp increase in photocure reaction rate can be seen for the EHPE-3150-MA system with a high concentration of photoinitiator.

Figure 5 shows the change of the degree of conversion with the radiation time at different UV intensities under constant photoinitiator concentration (15 wt %, $3.6 \times 10^{-4}\text{ mol/g}$). The degree of conversion increased with UV radiation intensity, and especially this effect can be observed more clearly in the EHPE-3150-MA system. The degree of conversion increased rapidly during the early radiation period and then slowly decreased with exposure time. This implies that the photopolymerization reaction takes place very extensively in the early stage to a high conversion. The photopolymerization seems to end within 10 min since little change in conversion was observed after 10 min.

An increase of photocuring temperature under conditions of constant UV radiation intensity (9.0 mW/cm^2) resulted in an increase of cure conversion reaction as shown in Figure 6. Especially, the high degree of cure conversion (85% at 105°C) for the EHPE-3150-MA system can be obtained compared with the NC-9110-MA system.

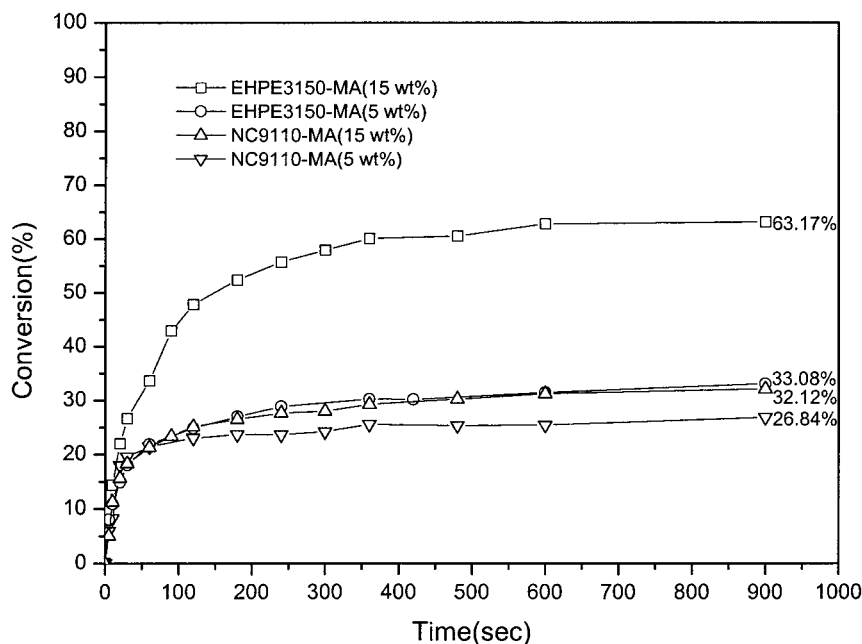


Figure 4 The change in photocure reaction conversion of new methacrylate-type prepolymers with UV irradiation time according to the content of photoinitiator.

These polymers obtained by UV photopolymerization exhibited extreme thermal stability, as seen in Figure 7. We observed changes in the transmittance of the photocured polymer film upon heating. The photocured film showed almost no change in transmittance in the visible region even after being heated at 250°C for 1 h compared with the transmittance of the unheated photocured film.

The thermal cure reaction conversion changes of each methacrylate-type prepolymer system were investigated according to the thermal initiator changes. The reaction conversion rate changes of each resin system with BPO as thermal initiator are plotted as a function of reaction conversion in Figure 8. Figure 9 represents the reaction conversion rate changes of each resin system with AIBN as thermal initiator. As

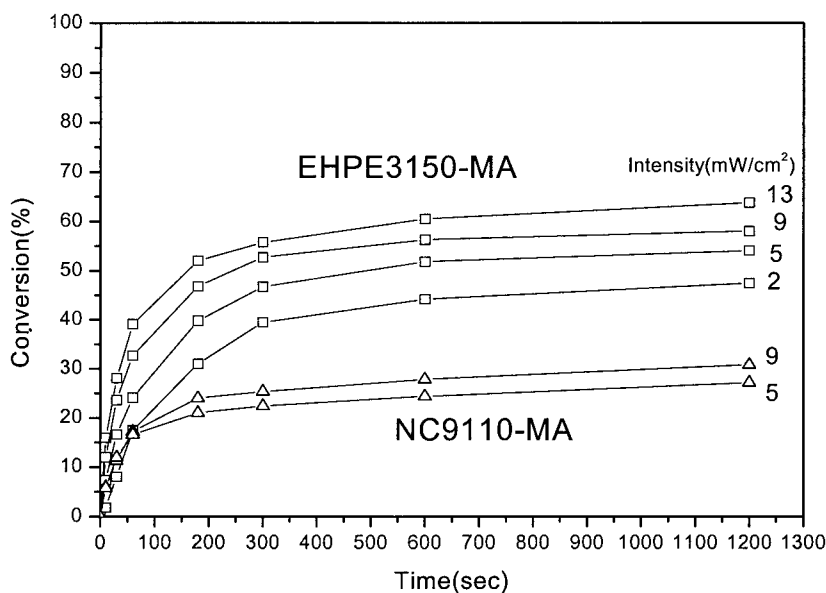


Figure 5 The change in photocure reaction conversion of new methacrylate-type prepolymers with UV irradiation time at different UV intensity.

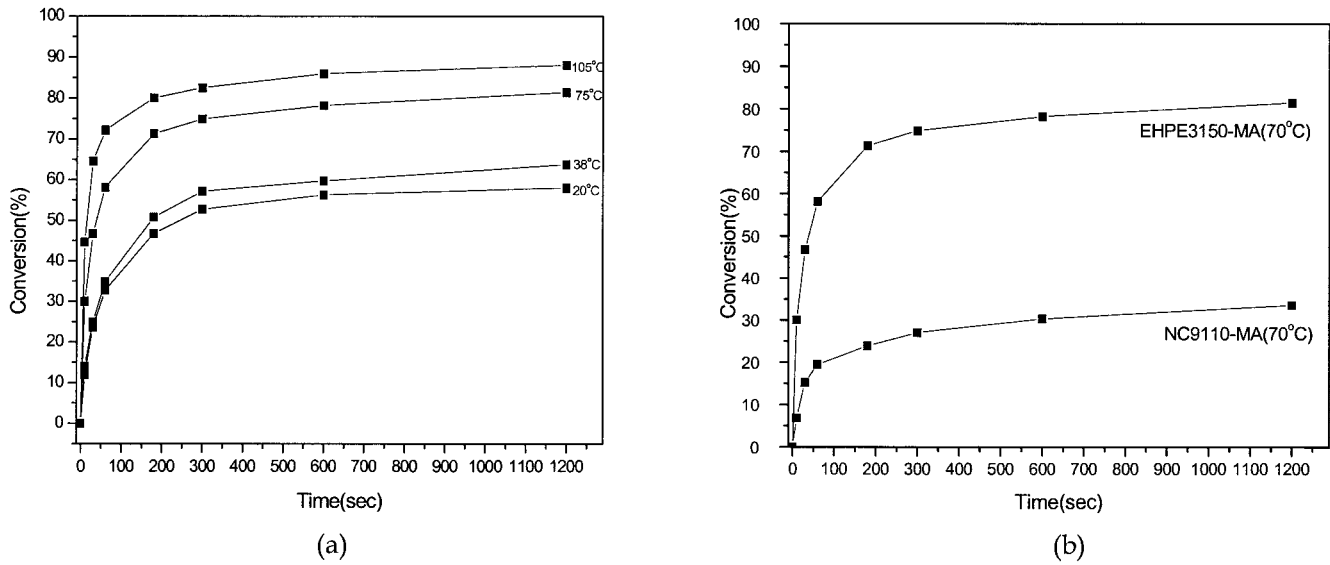


Figure 6 The change in photocure reaction conversion of new methacrylate prepolymers with the change in photocure temperature under a constant UV radiation intensity (9.0 mW/cm²): (a) EHPE-3150-MA; (b) EHPE-3150-MA and NC-9110-MA at 70°C.

demonstrated in these figures, these resin systems follow an autocatalytic cure reaction as described in Eq. (3),

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (3)$$

where α is the reaction conversion, t is time, m and n are the reaction order of the system, and k_1 and k_2 are kinetic rate constants of the system. As shown in Figures 8 and 9, the initial rate of reaction k_1 can be

negligible as in previous reports,^{10,11} so that the last expression can be reduced to

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \quad (4)$$

To precisely predict the cure kinetics over the whole range of conversion, the autocatalytic model was modified in terms of the introduction of a diffusion term as represented in Eq. (5).¹²

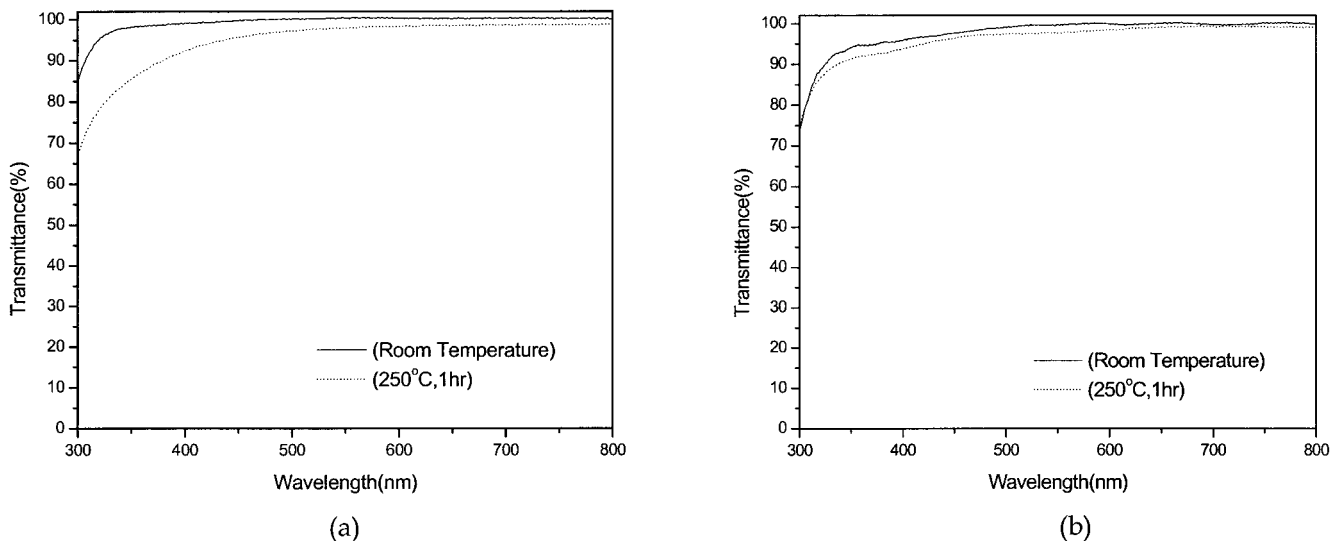


Figure 7 The change in transmittance of photocured prepolymers before and after being heated at 250°C for 1 h: (a) EHPE-3150-MA; (b) NC-9110-MA.

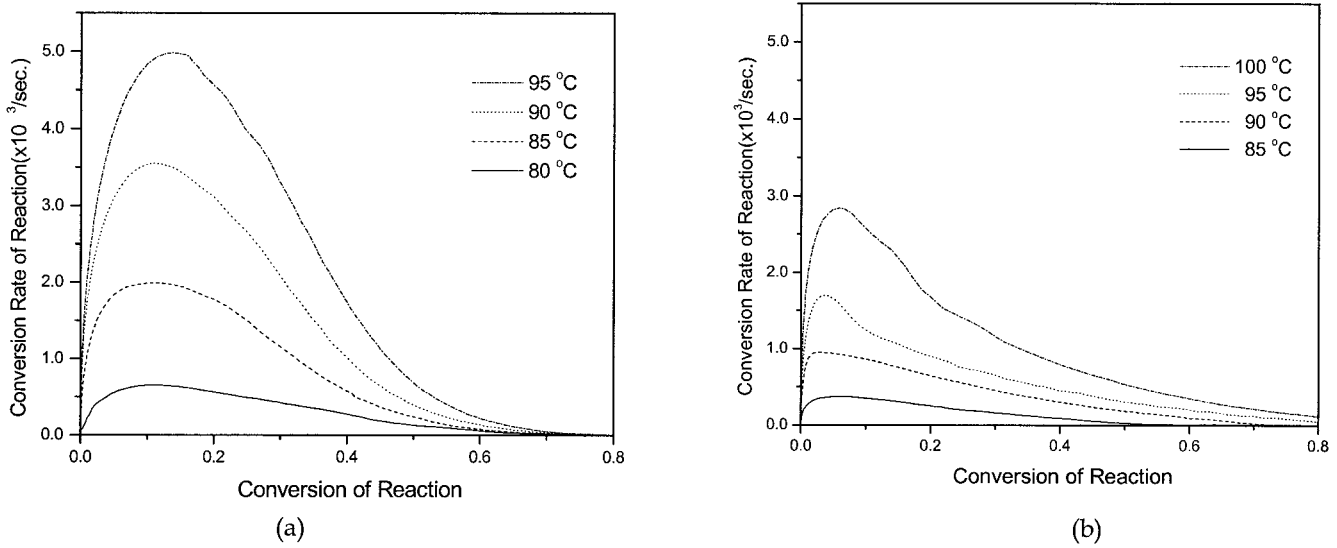


Figure 8 Isothermal conversion rate as a function of the conversion of the resin systems with BPO as thermal initiator: (a) NC-9110-MA; (b) EHPE-3150-MA.

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (5)$$

In this equation, C is a constant and α_c is the critical conversion. For $\alpha \ll \alpha_c$, $f(\alpha)$ is approximately equal to unity and the effect of diffusion is negligible, so that the reaction is kinetically controlled. Considering the diffusion effect, Eq. (4) can be rewritten as Eq. (6).^{13,14}

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \quad (6)$$

All kinetic constants in this equation of each resin system were obtained by taking advantage of a previous method.¹⁵ Figure 10 shows the comparisons between the experimental values of reaction conversion and the values calculated by a generalized autocatalytic model for resin systems with BPO as thermal initiator. The values of reaction conversion with AIBN as thermal initiator are demonstrated in Figure 11. Good agreements were found over the whole curing temperature range for all resin systems. As shown in these figures, the reaction conversion of these prepolymers was dependent upon thermal initiator, and a

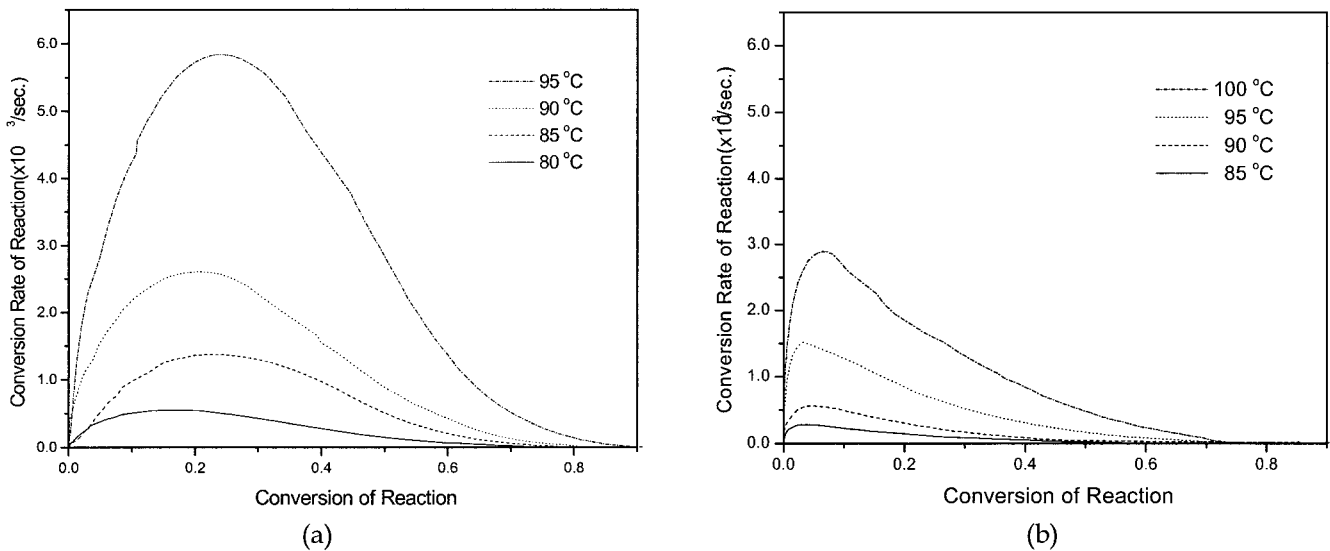


Figure 9 Isothermal conversion rate as a function of the conversion of the resin systems with AIBN as thermal initiator: (a) NC-9110-MA; (b) EHPE-3150-MA.

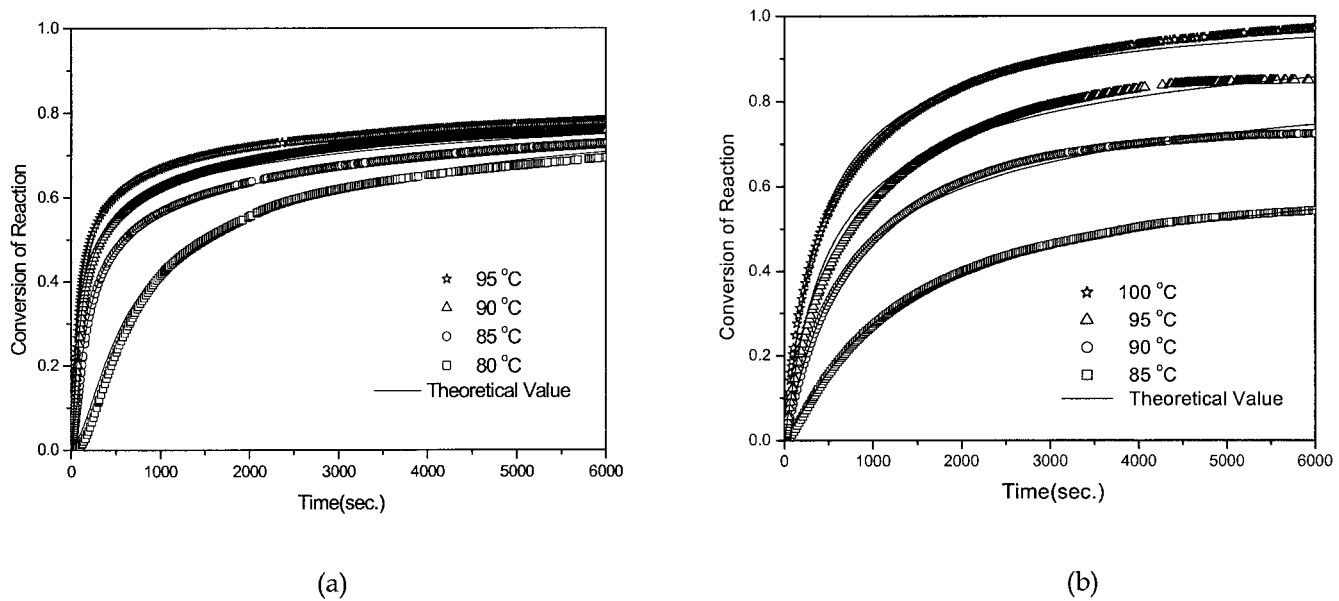


Figure 10 Comparisons between the experimental values of α and theoretical values obtained from the generalized autocatalytic model for the resin systems with BPO as thermal initiator: (a) NC-9110-MA; (b) EHPE-3150-MA.

higher reaction conversion of EHPE-3150-MA system was observed in the system with BPO as thermal initiator.

The kinetic parameters are reported in Tables II and III for the resin systems with BPO as thermal initiator that follow the autocatalytic curing reaction. It can be seen that the reaction rate of NC-9110-MA system is faster than that of EHPE-3150-MA, as shown in Figure 8. It is postulated that the increased rate in NC-9110-MA system should be attributable to its higher reaction rate constant k values compared with EHPE-3150-MA, even if the reaction order of NC-9110-MA was higher than that of EHPE-3150-MA, as summa-

rized in Table II. In particular, the notable increase in reaction rate constant k in the NC-9110-MA system can be observed, which would be attributed to the lower value of its activation energy. The constant, C , and the critical conversion of reaction, α_c in the generalized autocatalytic kinetic equation, Eq. (6), for resin systems with BPO as thermal initiator are reported in Table III. Generally, the α_c increased with temperature but C showed no discernible trend in these systems.

The kinetic parameters for resin systems with AIBN as thermal initiator are summarized in Tables IV and V. As shown in Figure 9, the reaction conversion rate of the NC-9110-MA system is faster than that of the

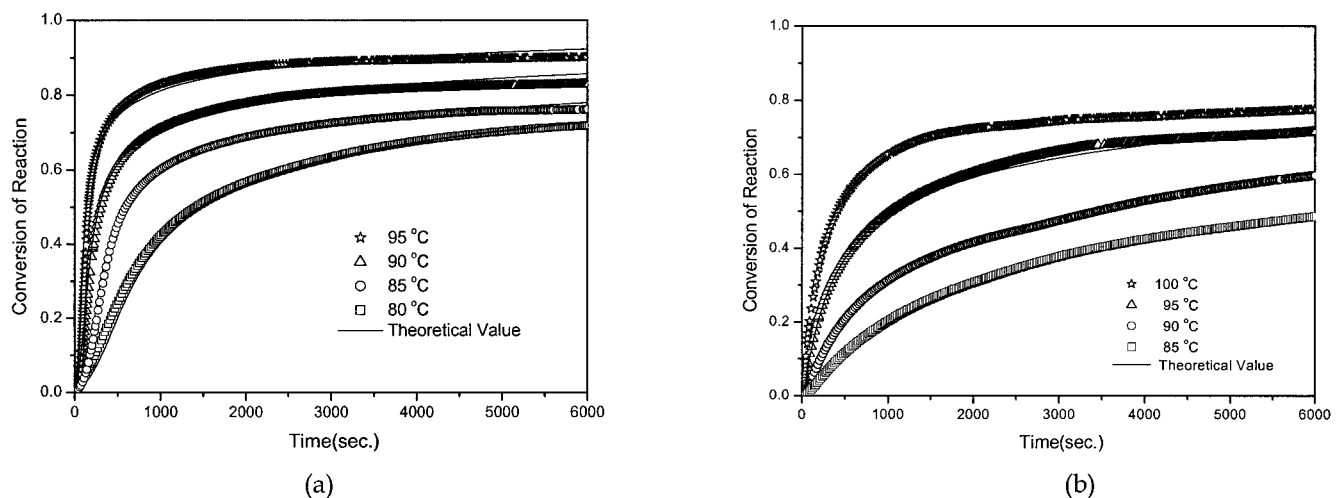


Figure 11 Comparisons between the experimental values of α and theoretical values obtained from the generalized autocatalytic model for the resin systems with AIBN as thermal initiator: (a) NC-9110-MA; (b) EHPE-3150-MA.

TABLE II
Kinetic Parameters of New Methacrylate-Type Prepolymers with BPO as Thermal Initiator

Prepolymer	Temperature (°C)	k (s ⁻¹)	m	n	Temperature dependency of the rate constant	Average $m + n$ value
NC-9110-MA	80	0.75×10^{-2}	0.6	3.7	$k_2 = 7.47 \times 10^8 \exp(-7.46 \times 10^4/RT)$	3.3
	85	0.82×10^{-2}	0.4	2.7		
	90	1.42×10^{-2}	0.4	2.7		
	95	1.98×10^{-2}	0.5	2.3		
	85	0.10×10^{-2}	0.3	2.8		
EHPE-3150-MA	90	0.18×10^{-2}	0.2	1.7	$k_2 = 6.67 \times 10^{11} \exp(-1.01 \times 10^5/RT)$	2.0
	95	0.29×10^{-2}	0.1	1.5		
	100	0.39×10^{-2}	0.2	1.3		

EHPE-3150-MA system. This is caused by the higher value of reaction rate constant k of NC-9110-MA than that of EHPE-3150-MA. Differently, with resin systems with BPO as thermal initiator, an increase of total reaction order cannot be found in the NC-9110-MA system compared with the EHPE-3150-MA system. It is postulated that the increased rate in the NC-9110-MA system with AIBN as thermal initiator should be attributable to an increase of reaction rate constant k with the lower activation energy and a decrease of total reaction order in the NC-9110-MA system (because $0 < \alpha < 1$). Similarly, with resin systems with BPO as thermal initiator, the α_c in the

generalized autocatalytic kinetic equation increased with temperature, although a unique tendency cannot be found in C of Eq. (6) for these systems. However, it can be shown that the value of α_c in NC-9110-MA with BPO as thermal initiator is lower than that with AIBN, and the opposite results can be observed for EHPE-3150-MA. As shown in Tables II and IV, total reaction order of the NC-9110-MA with BPO as thermal initiator is higher than that with AIBN, whereas that of EHPE-3150-MA with BPO is lower than that with AIBN. Therefore, it can be considered that an increase in total reaction order would give rise to a decrease in critical conversion α_c .

TABLE III
Values of the Constant C and Critical Conversion at Different Temperatures of New Methacrylate-Type Prepolymers with BPO as Thermal Initiator

Prepolymer	Temperature (°C)	C	α_c
NC-9110-MA	80	1.62	0.12
	85	8.08	0.36
	90	8.59	0.37
	95	8.59	0.38
	85	6.28	0.34
EHPE-3150-MA	90	5.28	0.35
	95	4.02	0.35
	100	3.75	0.43

In general, lumped rate constant $k_p/k_t^{0.5}$ for radical polymerization using BPO as thermal initiator would represent a higher value than that with AIBN.^{16,17} Considering these initiators with respect to the initiator decomposition rate constant k_d , it is reported that an activation energy and a frequency factor in the Arrhenius equation of BPO are lower than those of AIBN.¹⁸ These phenomena can be also observed in the reaction rate constant of curing reaction k , as shown in Tables II and IV.

In this study we introduced a cyclohexane group with no double bond in methacrylate-type prepolymer in order to improve the transparency and heat resistance of the photopolymer system so that we

TABLE IV
Kinetic Parameters of New Methacrylate-Type Prepolymers with AIBN as Thermal Initiator

Prepolymer	Temperature (°C)	k (s ⁻¹)	m	n	Temperature dependency of the rate constant	Average $m + n$ value
NC-9110-MA	80	0.43×10^{-2}	0.7	1.7	$k_2 = 2.28 \times 10^{17} \exp(-1.34 \times 10^5/RT)$	2.5
	85	0.64×10^{-2}	0.7	1.7		
	90	1.18×10^{-2}	0.6	2.0		
	95	2.77×10^{-2}	0.7	1.8		
	85	0.12×10^{-2}	0.3	2.6		
	90	0.23×10^{-2}	0.2	3.0		
EHPE-3150-MA	95	0.41×10^{-2}	0.2	2.4	$k_2 = 3.27 \times 10^{19} \exp(-1.54 \times 10^5/RT)$	2.9
	100	1.00×10^{-2}	0.3	2.7		

TABLE V
Values of the Constant C and Critical Conversion at Different Temperatures of New Methacrylate-Type Prepolymers with AIBN as Thermal Initiator

Prepolymer	Temperature (°C)	C	α_c
NC-9110-MA	80	5.92	0.25
	85	10.02	0.43
	90	8.20	0.48
	95	8.36	0.50
	85	4.86	0.07
EHPE-3150-MA	90	3.78	0.12
	95	4.40	0.21
	100	4.57	0.31

could obtain new prepolymers with good optical and thermal properties. With respect to the molecular structure of these prepolymers, NC-9110-MA is linear with one methacrylate group at each end, and EHPE-3150-MA is a three-arm molecule with at least one methacrylate group per branch. The EHPE-3150-MA prepolymer system shows higher reaction conversion and conversion rates than the NC-9110-MA prepolymer system in photocure reaction; however, the conversion rate of the EHPE-3150-MA prepolymer system is slower than that of NC-9110-MA in the thermal cure reaction. Therefore, it is postulated that the photocure mechanism of these prepolymers is different from the thermal cure mechanism, and the conversion rate of linear type prepolymer is slower than that of branch type prepolymer in the photocure reaction and vice versa in the thermal cure reaction.^{19,20}

CONCLUSION

The novel methacrylate-type prepolymers including a cyclohexane moiety were synthesized by reaction with MA and epoxy resins. We confirmed the chemical structures of the prepolymers by FT-IR and NMR spectroscopy. We found that the photocure of the prepolymers took place rapidly to a very high conversion with UV radiation. The prepolymer manifested thermal stability can be observed. A reaction conversion and conversion rate of the EHPE-3150-MA prepolymer system that is higher than that of the NC-9110-MA system can be observed at high photoinitiator concentration. We also investigated their curing characteristics according to the change in thermal initiators by the thermal analysis method. It can be shown that an autocatalytic kinetic reaction occurs in these systems. Differently with photocure reaction, the conversion rate of the EHPE-3150-MA prepolymer

system is slower than that of NC-9110-MA, regardless of the kinds of thermal initiators. However, the degree of reaction conversion of these prepolymers was dependent upon thermal initiator, so that a higher reaction conversion could be seen in the EHPE-3150-MA prepolymer system with BPO as thermal initiator. It is postulated that the thermal cure mechanism of these prepolymers is different from the photocure mechanism, even if photo- and thermal cure data with the same concentration of initiator cannot be obtained because a photo- and thermal analysis for them should require optimum initiator concentration for each experimental analysis, respectively.

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