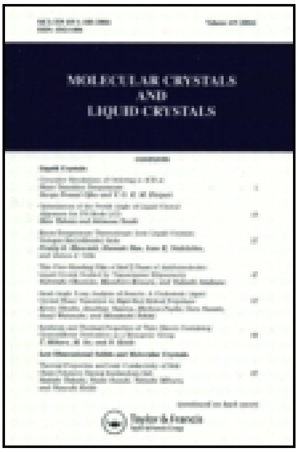

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Photocure Kinetics of Thermally Stable Photoreactive Prepolymers with Cinnamate Moiety

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New thermally stable photoreactive prepolymers were synthesized by the reaction of t-cinnamic acids (CAs) with different functional groups and two kinds of epoxy resins which are a biphenyl type epoxy resin and a novolac type epoxy resin with furan ring. Their photocure reaction rates and the extent of reaction conversion were measured with Fourier transform infrared spectroscopy, and their photocure reactions were analyzed in terms of n*th-order kinetic reaction equation. Their optical and thermal stability were investigated with UV-Visible spectroscopy and thermogravimetric analysis (TGA). Their photocure reaction rates and the extent of reaction conversion increased with the intensity of UV irradiation. The photoreactive cinnamate prepolymers synthesized from FPREP epoxy resin showed a lower reaction conversion rate and a reaction constant than those of the photopolymer systems based on EBPXA epoxy resin. The reaction conversion rates of these photopolymers with hydroxyl group as a functional group of cinnamate were lower than those of only cinnamate moiety. Thermal stability was studied by observing changes in the transmittance of the photocured polymer films upon heating and by measuring weight loss with temperature using TGA. These photoreactive prepolymers with a biphenyl group showed good thermal properties, with almost no transmittance change in the visible range even after they were heated at 250°C for 1 hour, and these cinnamate photopolymer systems exhibited little weight loss up to about 300°C.*

Keywords Biphenyl; furan; photocure kinetics; photopolymerization; photoreactive polymers; thermal properties

Introduction

High heat resistant photopolymer systems have been requested since the rapid progress of the information society has brought about a boost in the dramatic growth of liquid crystal displays and semiconductors [1]. In particular, photopolymer systems for the color filter resist, photoreactive polymers for photo-alignment in liquid crystal display, and the photopolymer systems in optical data storage have been studied for the improvements of display performances [2–6]. The most significant challenges

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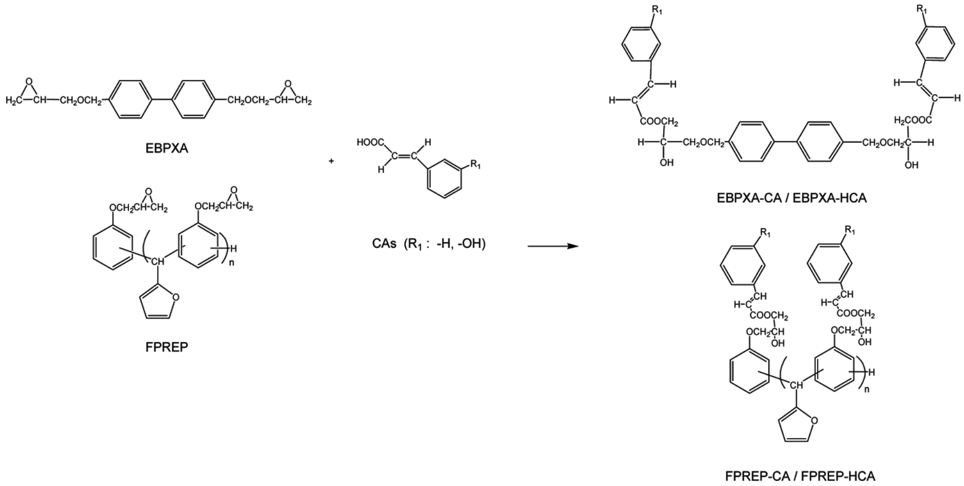
have been in the area of improving the thermal resistance, transparency, and cost effectiveness of color filter resists for color patterning, so we have reported the photocure properties of highly transparent and thermally stable methacrylate type photopolymer systems with cyclohexane moiety [7,8] and photo-cycloaddition type photopolymer systems with various aromatic groups [9,10].

In this study, the new cinnamate photopolymer systems, which include the biphenyl moiety with liquid crystallinity and the furan ring to improve the adhesion with substrates, were synthesized and we investigated their photocure kinetics and thermal properties. The photocure kinetics of the prepolymers were investigated with Fourier transform infrared (FTIR) spectroscopy, and their thermal stability was measured with thermogravimetric analysis (TGA). The changes in the transmittance of the polymer film upon heating were monitored in order to observe their optical thermal stability. The photocure reactions of these prepolymers 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

The synthesis of a photoreactive prepolymer with cinnamate groups was performed by the reaction of cinnamic acids (CAs) including different substitution moieties and two kinds of epoxy resins; EBPXA (Nippon Kayaku Co., Tokyo, Japan) and FPREP (Nippon Kayaku Co., Tokyo, Japan), which is shown in Scheme 1. The CAs with different substitution moieties were t-cinnamic acid (CA) and 3-hydroxy t-cinnamic acid (HCA), and they were received from Aldrich Chemical Co. (Milwaukee, WI). All the epoxy resin and CAs in this study were composed of the same equivalent weight ratio (1:1) of epoxy and carboxyl acid groups with tetramethyl ammonium chloride as a catalyst. The reactions were carried out in the methyl ethyl ketone at 70°C for 80 h. We confirmed the chemical structure of the photoreactive prepolymers using ^{1}H-NMR spectroscopy (Varian Gemini 300-MHz, Lake Forest, CA) and FT-IR spectroscopy (Perkin-Elmer Spectrum-2000, Wellesley, MA). In the ^{1}H-NMR spectra of the Epoxy-CAs polymers, the peak at



Scheme 1. Synthetic scheme of the photoreactive prepolymer with cinnamate moiety.

2.7–2.9 ppm corresponding the epoxide ring proton disappeared and the doublet proton NMR peaks near 6.5 ppm corresponding to the protons of the cinnamate double bond appeared. The typical FT-IR peaks of 1715 cm^{-1} (carbonyl group of cinnamate) and 1635 cm^{-1} (cinnamate double bond) were observed for the Epoxy-CAs polymers.

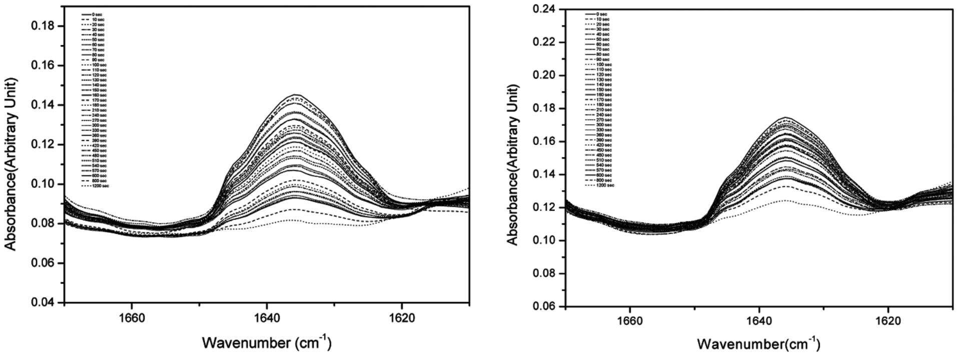
These photoreactive prepolymers were dissolved in the solvents such as monochlorobenzene, tetrahydrofuran, methyl ethyl ketone, and toluene. Each solution was filtered through a 0.2 μm membrane filter and spin-coated on a quartz substrate using spin coater (Brewer Science Cee 100, Rolla, MO). These polymer films were then dried at 70°C for 30 min, which led to excellent quality film with a thickness of about 1 μm. The photocure of the photoreactive prepolymer films was 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 were studied by using FT-IR spectroscopy, UV-visible spectroscopy (Shimatzu UV-1650PC, Tokyo, Japan) and TGA (TA Instrument SDT-2960, New Castle, DE). UV spectra were measured by the films with a thickness of about 1 μm which were prepared by the above mentioned method. The photocure conversions of these photoreactive prepolymers were determined by the normalization of the FT-IR peak area of the cinnamate double bond at 1635 cm^{-1} with respect to the peak area of the aromatic double bond at 1450 cm^{-1} as a reference with the following equation:

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

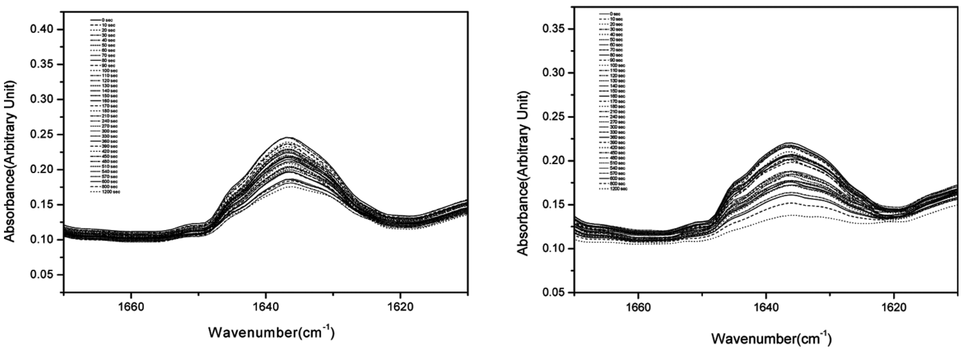
where α_t is the photocure reaction conversion at each UV irradiation time; $\mathrm{A_f}$ is the absorption peak area of the cinnamate double bond at 1635 cm^{-1}; $\mathrm{A_r}$ is the absorption peak area of the reference group, which did not change during UV irradiation (1450 cm^{-1}, which represents the absorption peak of the aromatic double bond); and subscript t and s are the UV irradiation time after t minutes and the reference irradiation time (where s = 0 min), respectively. The FT-IR spectrum of these photoreactive prepolymers according to the UV irradiation time is shown in Figure 1. Thermal stability was investigated with TGA and the changes in the transmittance of the photocured polymer film upon heating at 250°C for 1 h were observed by UV-visible spectroscopy for optical thermal stability.

Results and Discussion

These photoreactive prepolymers 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 Epoxy-CAs photoreactive polymers with different functional group of CA are shown in Figure 2. As shown in Figure 2, the extent of photocure reaction conversion increased with UV intensity in these photoreactive prepolymers. 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 [11], the rate constant in cinnamate photoreactions such as with these photoreactive prepolymers without photoinitiators is linearly dependent on the intensity of incident light [12,13].



(a) EBPXA-CA (b) EBPXA-HCA



(c) FPREP-CA (d) FPREP-HCA

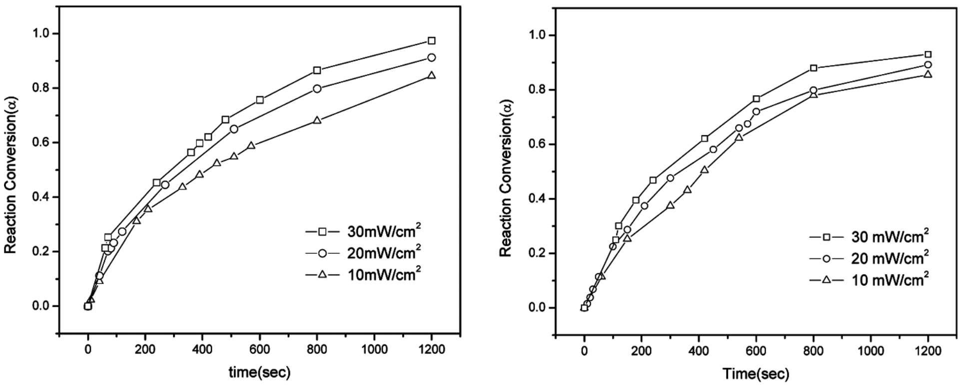
Figure 1. Changes in the FT-IR absorbance of the photoreactive prepolymers at 1635 cm^{-1} with the UV irradiation time: (a) EBPXA-CA (b) EBPXA-HCA (c) FPREP-CA (d) FPREP-HCA.

The reaction conversion rates of these photopolymers are presented in Figure 3 to illustrate the photocure reaction kinetics. As shown in Figure 3, the experimental data of these reaction rates show the behavior of *n*th-order kinetics reaction as described in the following equation [14]:

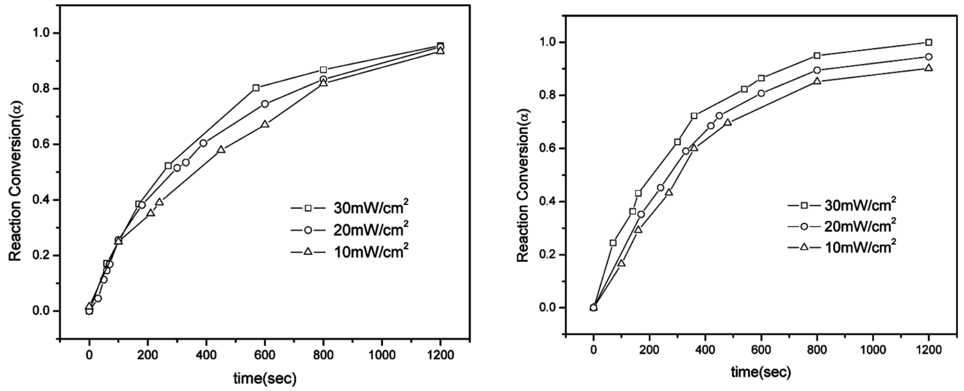
$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{2}$$

where α 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 prepolymer calculated with this equation are summarized in Table I.

For the EBPXA-CAs photoreactive prepolymers that included biphenyl cinnamate groups, the conversion rate and rate constant of EBPXA-HCA with hydroxyl group were lower than those of EBPXA-CA in the below 20 mW/cm^2 of UV intensity, as shown in Figure 3 and Table 1. 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 [15,16]. Therefore, the EBPXA-HCA photopolymer



(a) EBPXA-CA (b) EBPXA-HCA

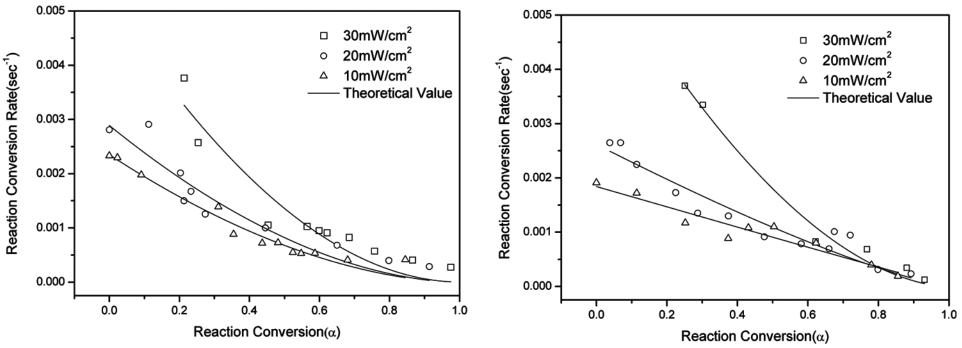


(c) FPREP-CA (d) FPREP-HCA

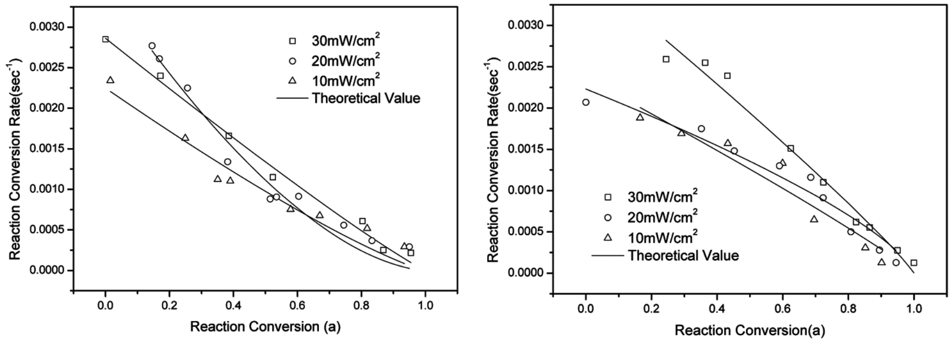
Figure 2. Change in the photocure reaction conversion of the photoreactive prepolymers with cinnamate groups according to the UV irradiation time at different UV intensities: (a) EBPXA-CA (b) EBPXA-HCA (c) FPREP-CA (d) FPREP-HCA.

with strong intermolecular interactions, such as a hydrogen bond, is less reactive, and a lower conversion rate and a rate constant are obtained in this photoreactive prepolymer. However, these phenomena disappeared under high UV intensity such as 30 mW/cm^2 of UV intensity. Similar results were observed in FPREP-CAs photoreactive prepolymers containing furan ring with cinnamate moiety. The conversion rate and rate constant of FPREP-HCA with hydroxyl group were lower than those of FPREP-CA in the below 20 mW/cm^2 of UV intensity, as shown in Figure 3 and Table 1. This implies that there are decreases in the reaction conversion rate and conversion in accordance with the decreases of mobility for the photoreactions due to the molecular interactions between the hydroxyl groups such as the hydrogen bond. These phenomena also disappeared under high UV intensity such as 30 mW/cm^2 of UV intensity as shown in EBPXA-CAs systems. It can be thought that these inverse phenomena at high UV intensity are due to the increases of segmental chain mobility with high power energy.

The reaction conversion rates of the EBPXA-CAs photoreactive prepolymers containing biphenyl type cinnamate groups were higher than those of FPREP-CAs,



(a) EBPXA-CA (b) EBPXA-HCA



(c) FPREP-CA (d) FPREP-HCA

Figure 3. Comparisons between the experimental and theoretical photocure conversion rates as a function of the conversion of the photoreactive prepolymers with cinnamate groups in terms of *n*th-order equation: (a) EBPXA-CA (b) EBPXA-HCA (c) FPREP-CA (d) FPREP-HCA.

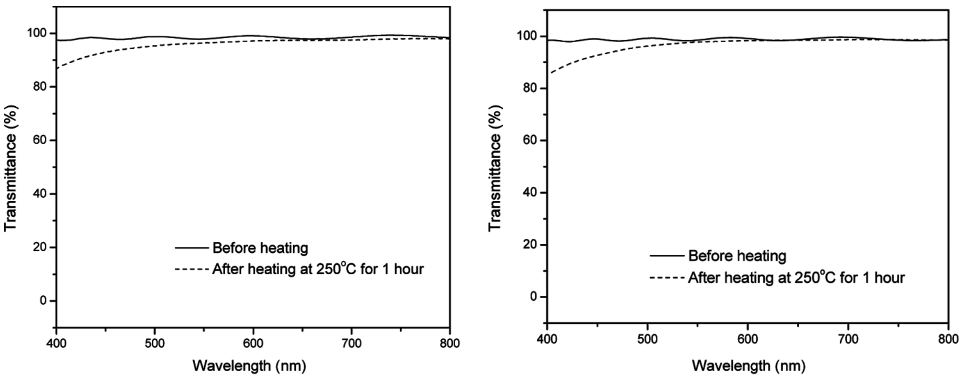
Table 1. Kinetic parameters of the photoreactive prepolymers with cinnamate groups

Photoreactive polymer	Intensity (mW/cm^2)	k	n
EBPXA-CA	30	4.78×10^{-3}	1.94
	20	2.89×10^{-3}	1.82
	10	2.35×10^{-3}	1.79
EBPXA-HCA	30	6.22×10^{-3}	1.79
	20	2.62×10^{-3}	1.26
	10	1.84×10^{-3}	1.02
FPREP-CA	30	2.86×10^{-3}	1.10
	20	3.52×10^{-3}	1.66
	10	2.25×10^{-3}	1.20
FPREP-HCA	30	3.64×10^{-3}	0.91
	20	2.23×10^{-3}	0.72
	10	2.37×10^{-3}	0.91

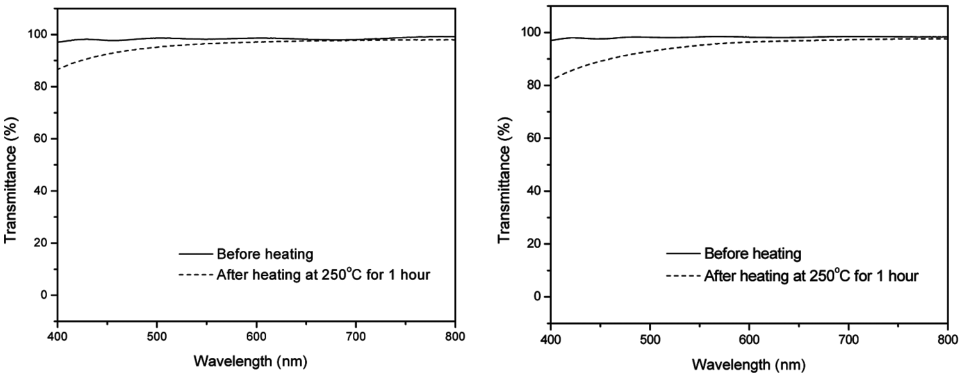
which include the furan ring with cinnamate groups. This can be attributed to the increase of molecular orientation for [2 + 2] cycloaddition of cinnamates according to the introduction of the biphenyl group [17].

To investigate optical properties with heating of these photoreactive prepolymers, the transmittance changes upon heating of these photocured films are shown in Figure 4. As shown in Figure 4, the photocured films showed almost no change in transmittance in the 500–800 nm region of wavelength even after they were heated at 250°C for 1 h compared with the unheated photocured film. These high heat resistant and good optical properties are attributed to the biphenyl group of EBPXA-CAs and the furan ring of FPREP-CAs with high aromaticity and no light absorption in the 500–800 nm region of wavelength.

The weight loss values of these photocrosslinked polymers are plotted against temperature by means of TGA in Figure 5. For the all Epoxy-CAs, the weight loss approaches 10% before 300°C. Therefore, these polymers show high heat resistant properties, and the EBPXA-CAs resin systems show better overall stability than FPREP-CAs systems as shown in Figure 5. Among them, EBPXA-CA photoreactive polymer represents the highest heat-resistant properties, which shows the small



(a) EBPXA-CA (b) EBPXA-HCA



(c) FPREP-CA (d) FPREP-HCA

Figure 4. Change in the transmittance of the photocured films before heating and after heating at 250°C for 1 h: (a) EBPXA-CA (b) EBPXA-HCA (c) FPREP-CA (d) FPREP-HCA.

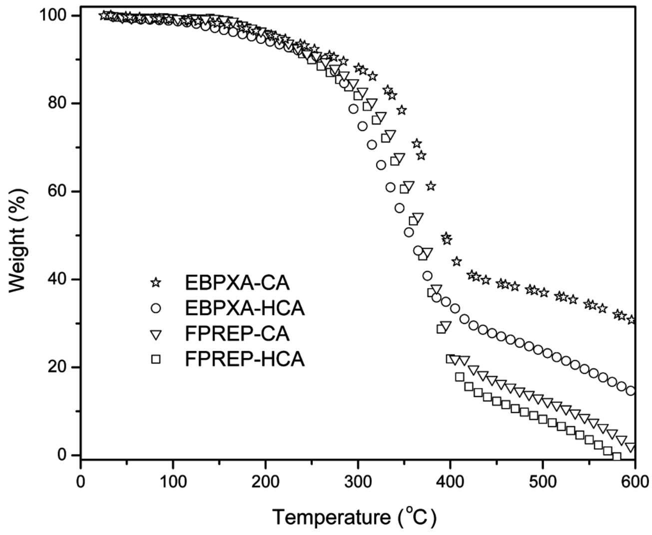


Figure 5. Weight loss of the photocured polymers with temperature as measured by TGA.

weight loss before 300°C. The FPREP-CAs, which included a furan ring with cinnamate moiety, showed more increases in weight loss with temperature than the EBPXA-CAs with a biphenyl type cinnamate group. It can be thought that the molecular orientation for photocure reaction make a major contribution to the high heat resistant photopolymers.

Conclusions

The photoreactive photopolymers with biphenyl group and furan ring that could perform photodimerization were designed and synthesized by the reaction of CA and epoxy resins, which may be applied as the base resin of color filter resist for LCD. We confirmed the chemical structures of these photopolymers by FT-IR and NMR spectroscopy. The photo-cure reaction conversions of these systems with UV irradiation time were investigated using FT-IR spectroscopy, and thermal stability and transparency with high temperatures were measured by TGA and UV. 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 *n*th-order kinetics reaction, and all kinetic constants of each photoreactive polymer with this equation were summarized. EBPXA-HCA and FPREP-HCA, with hydroxyl groups as a substituent, were shown to have strong molecular interactions such as the hydrogen bond and lower conversion reaction rates and reaction constants under the low UV irradiation intensity compared with the other photoreactive prepolymers without substituent group. The photocured films exhibited good thermal stability and optical properties with heating. The highest heat- resistant properties were represented in EBPXA-CA, which had the optimum molecular orientation of cure reaction by biphenyl group and a high reaction conversion rate.

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