Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 6303–6309

polymer

www.elsevier.com/locate/polymer

Cure kinetics of methacrylate-type resin that include cyclohexane moiety

Whan Gun Kim[a,*], Jun Young Lee[b]

[a]Department of Applied Chemistry, Seokyeong University, 16-1 Jeongneung-Dong, Seongbuk-Ku, Seoul 136-704, South Korea
[b]Department of Textile Engineering, Sungkyunkwan University, 300, Chunchun-Dong, Jangan-gu, Suwon, Kyunggi-Do 440-746, South Korea

Received 23 April 2003; received in revised form 14 July 2003; accepted 15 July 2003

Abstract

Two methacrylate-type resin including cyclohexane moiety were synthesized and characterized. The curing characteristics of these resins were investigated according to the change of thermal initiator. An autocatalytic kinetic reaction occurs in these systems, and the kinetic parameters of all systems were reported in terms of generalized kinetic equation that considered the diffusion term. It can be shown that the reaction conversion rate of one methacrylate-type resin (NC-9110-MA) is faster than another resin (EHPE-3150-MA), regardless of the kinds of thermal initiator, which is attributed to the reaction rate constant increases of NC-9110-MA with lower activation energy compared with EHPE-3150-MA. It can be seen that the conversion reaction rate of these resin systems with BPO as thermal initiator at low temperature is higher than those with AIBN. A main factor of reaction conversion rate increase for the NC-9110-MA resin system is a reaction rate constant; however, that for the EHPE-3150-MA resin system is a total reaction order. These resin with BPO as thermal initiator represent a lower cure reaction activation energy and collision frequency factor than those with AIBN.

Keywords: Methacrylate-type resin; Cure kinetics; Thermal initiator

---

1. Introduction

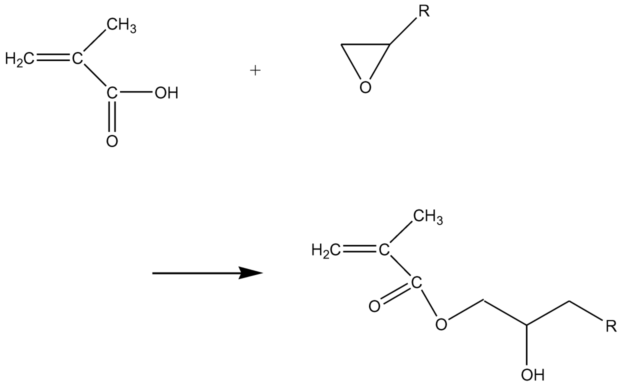
Because of the growing need for high resolution, large panel size and high reliability of liquid crystal display (LCD), the performance improvement of color filter resist is progressing fast [1]. In particular, the most significant challenges have been in the area of improving the thermal resistance and transparency of color filter resist [2,3]. Various methods to solve these problems has 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 (ITO) coating in color filter process due to the low heat resistance of them [4,5].

In this study, new methacrylate-type resins including cyclohexane moiety are synthesized and characterized in order to improve the heat resistance and transparency of the acrylic resin systems. Free-radical bulk polymerization of multifunctional methacrylate-type resins is one of the most efficient methods of synthesizing a highly cross-linked polymer with high mechanical properties [6,7]. Generally, an aromatic group has been introduced to main chain or side-chain unit of acrylic resin to increase the heat resistance, but the introduction of it would bring acrylic resin systems to decrease a transparency. Therefore, the methacrylate-type resins that include cyclohexane moiety were synthesized, so that the multifunctionality and cyclohexane group of them can contribute to both of high heat resistance and transparency. The curing characteristics of such new methacrylate type resins were investigated using DSC. The cure kinetics of these resin systems show autocatalytic cure reaction irrespective of thermal initiator change. The kinetic parameters of all resin systems were reported in terms of a generalized kinetic equation that considered the diffusion term.

---

* Corresponding author. Tel.: +82-2-940-7167; fax: +82-2-919-0345.
E-mail address: whgunkim@unitel.co.kr (W.G. Kim).

0032-3861/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00647-5



Scheme 1. Synthetic reaction of methacrylate type resin.

2. Experimental

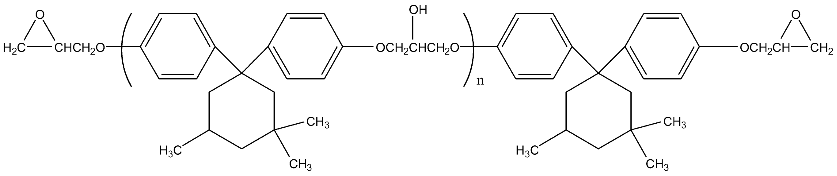
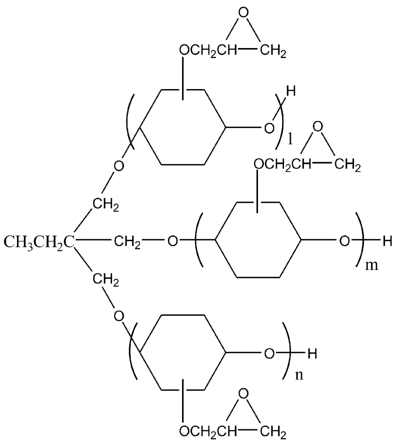
2.1. Synthesis of a methacrylate-type resin

The synthesis of a methacrylate-type resin has been performed by reacting a methacrylic acid (MA) with an epoxy resin with 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 1. As shown in Table 1, NC-9110 is an epoxy resin with cyclohexane and aromatic groups and EHPE-3150 is an epoxy resin including only cyclohexane groups. Methacrylic acid (MA) was received from Aldrich Chemical Co. (Milwaukee, WI). An epoxy resin was dissolved in methylethylketone (MEK) solvent, and a MA with same equivalent weight to an epoxy resin was dropped in them. After 0.5 wt% of tetra methyl ammonium chloride (TMAC) as catalyst was added, the reaction was performed under the reflux at 70 °C for 72 h. After this solution was evaporated, washed in distilled water, and dried under vacuum, an acid value of this resin was measured [8]. That of NC-9110-MA (the methacrylate-type resin obtained by reacting NC-9110 with MA) and EHPE-3150-MA (the methacrylate-type resin 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 Fourier transform infrared (FT-IR) spectroscopy (Perkin–Elmer Spectrum-2000, Wellesley, MA) were used to characterize these resins. The proton NMR peaks of 5.60 and 6.15 ppm in Fig. 1 correspond to the protons of the methacrylate vinyl group, and a typical FT-IR peak of 1715 cm^{-1} corresponded to the carboxylate group of methacrylate can be observed in Fig. 2.

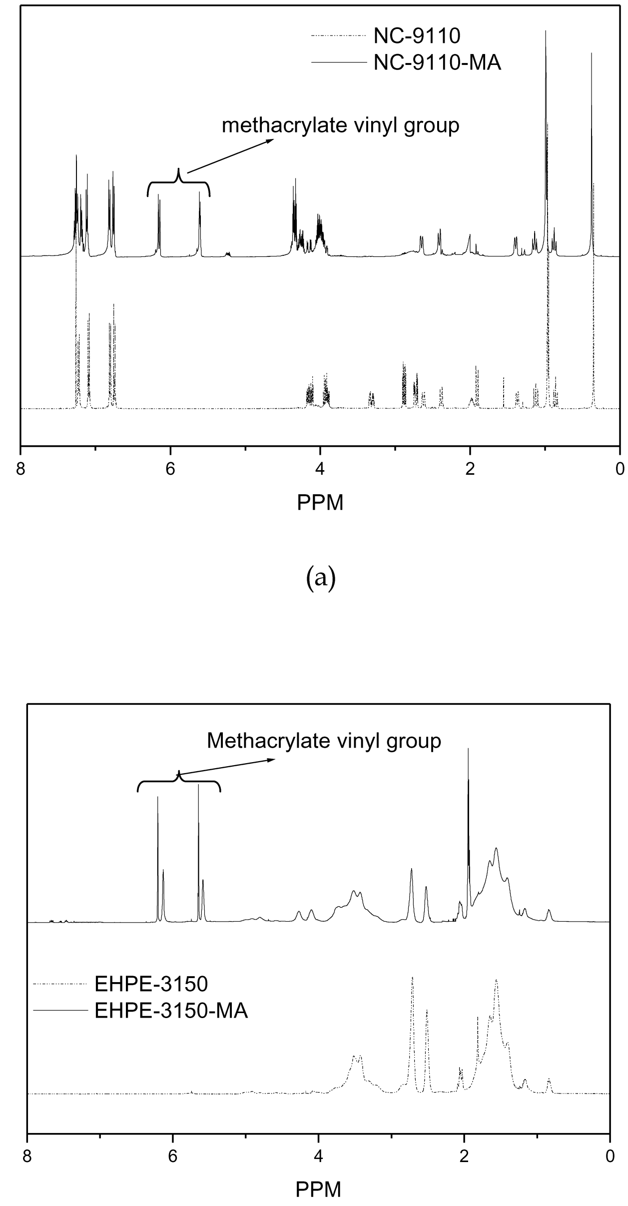
2.2. Sample preparation

A methacrylate type resin was dissolved in MEK solvent at room temperature to make a resin composition for curing reaction study. After a homogeneous solution was obtained, a thermal initiator was added and fully stirred. Thermal initiators used in curing reaction of methacrylate-type resin

Table 1
Description of raw materials used in this study

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

[a] EEW, epoxy equivalent weight (g/equiv.).



(a)

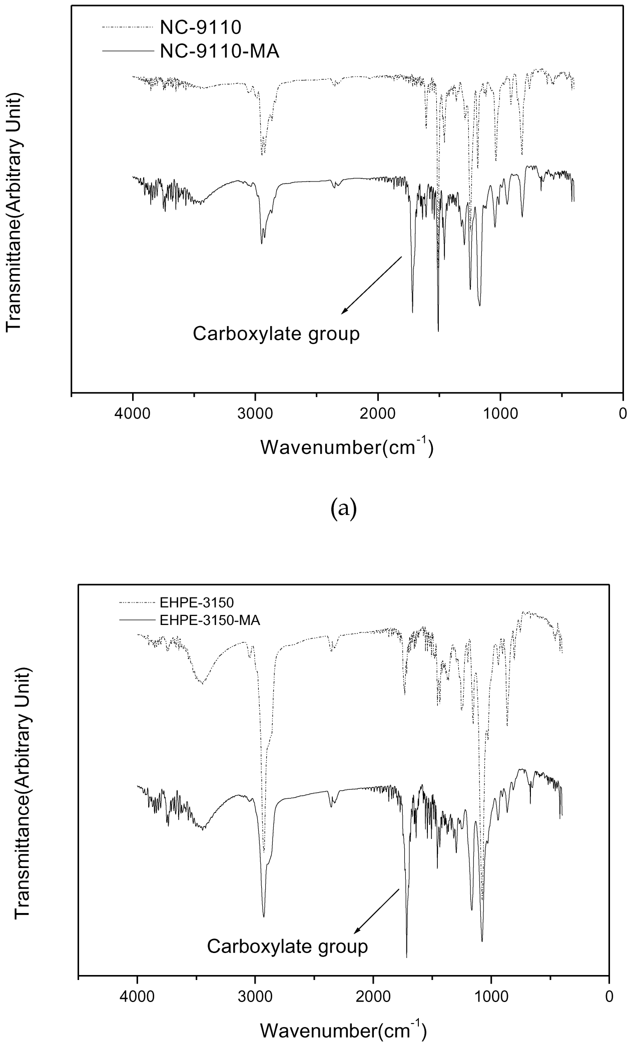
(b)

Fig. 1. ^{1}H NMR spectrums of new methacrylate-type resins: (a) NC-9110-MA, (b) EHPE-3150-MA.

were 2,2′-azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO), which were obtained from Aldrich Chemical Co. The thermal initiator concentration was fixed at 6×10^{-6} mol with respect to the total amount of resin. Each sample was evaporated under vacuum at room temperature to eliminate solvent and stored in refrigerator at 4 °C.

2.3. DSC measurement

Calorimetric measurements were performed using a TA-2020 differential scanning calorimeter (TA Instruments, New Castle, DE). This was calibrated in the region from −40 to 450 °C. 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.



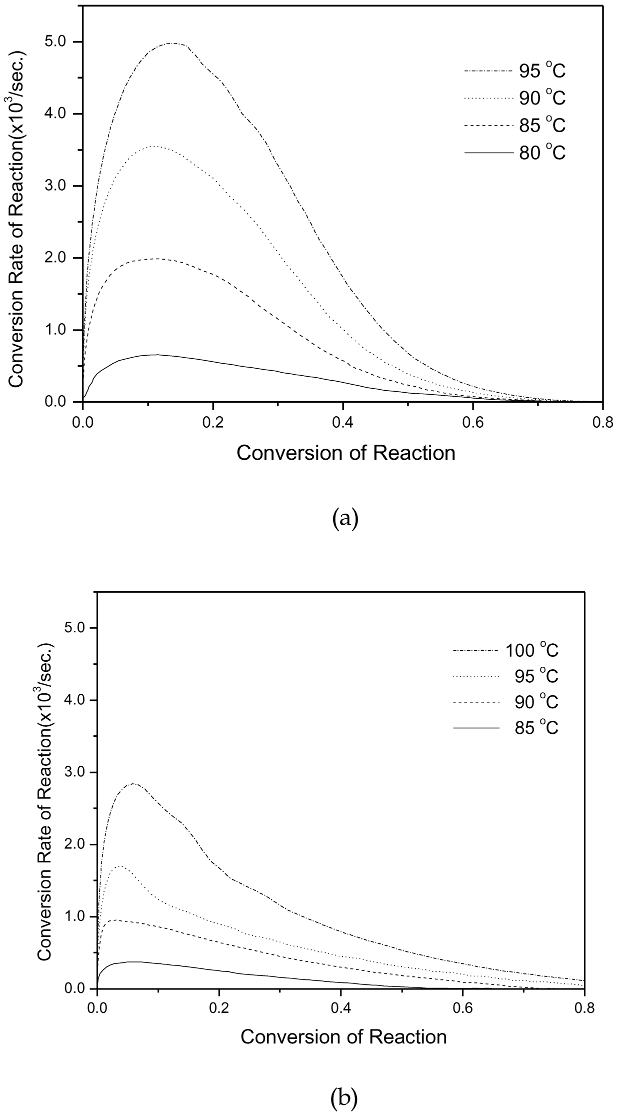
(a)

(b)

Fig. 2. FT-IR spectrums of new methacrylate-type resins: (a) NC-9110-MA, (b) EHPE-3150-MA.

3. Results and discussion

The curing reaction conversion changes of each methacrylate-type resin 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 Fig. 3.



(a)

(b)

Fig. 3. 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.

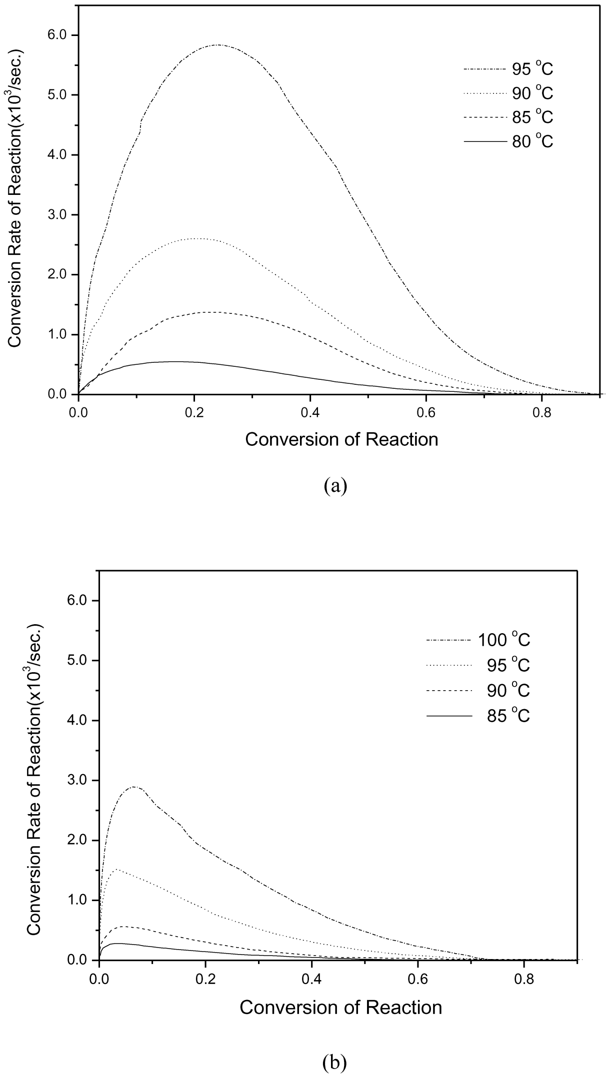
Fig. 4 represents them for AIBN as thermal initiator. As seen in these figures, it can be found that these resin systems follow an autocatalytic cure reaction as described in Eq. (1).

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

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 Figs. 3 and 4, the initial rate of reaction k_1 can be negligible as in previous reports [9,10], so that the last expression can be reduced to

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

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. (3) [11]:



(a)

(b)

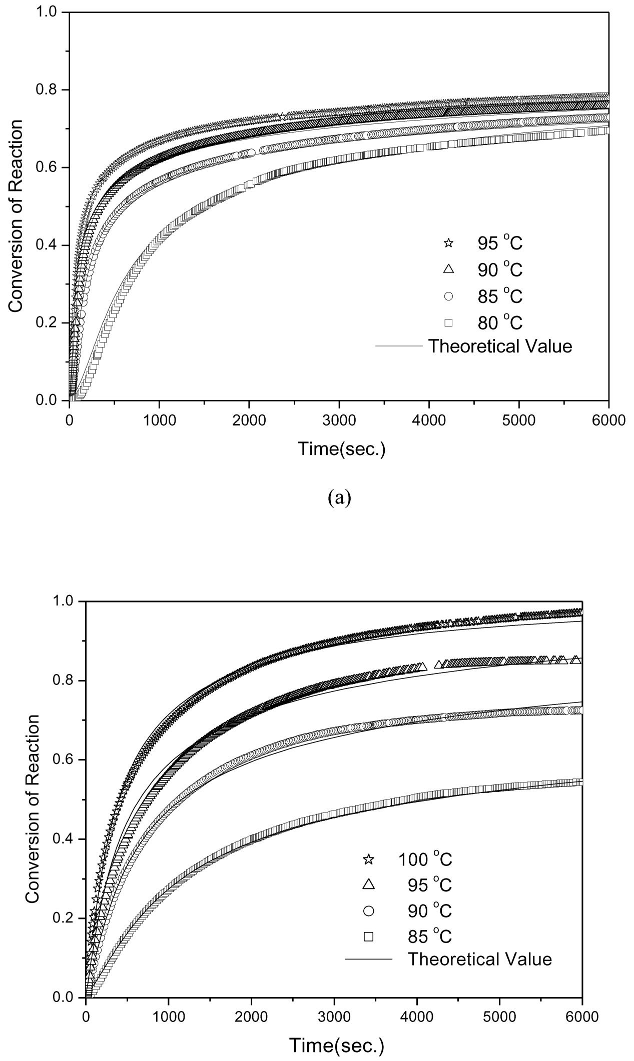
Fig. 4. Isothermal conversion rate as a function of the conversion of the resin systems with AIBN as thermal initiator: (a) NC-9110-MA, (b) EHPE-3150-MA.

$$f(\alpha) = \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{3}$$

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. (2) can be rewritten as Eq. (4) [12,13]:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n \frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{4}$$

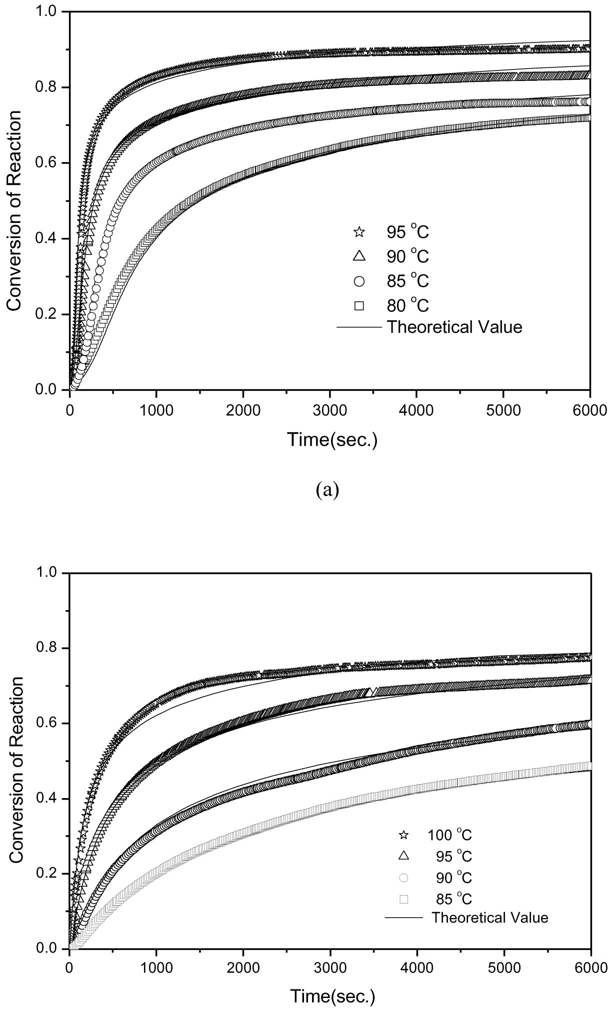
All kinetic constants in this equation of each resin system were obtained by taking advantage of a previous method [14]. Fig. 5 shows the comparisons between the experimental values of reaction conversion and the values calculated by generalized autocatalytic model for resin systems with BPO as thermal initiator. They with AIBN as thermal



(a)

(b)

Fig. 5. 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.



(a)

(b)

Fig. 6. 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.

initiator were represented in Fig. 6. Good agreements were found over the whole curing temperature range for all resin systems.

The kinetic parameters are reported in Tables 2 and 3 for the resin systems with BPO as thermal initiator that follow

Table 2
Kinetic parameters of new methacrylate-type resins using BPO as thermal initiator

Resin	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		
EHPE-3150-MA	85	0.10×10^{-2}	0.3	2.8	$k_2 = 6.67 \times 10^{11} \exp(-1.01 \times 10^5/RT)$	2.0
	90	0.18×10^{-2}	0.2	1.7		
	95	0.29×10^{-2}	0.1	1.5		
	100	0.39×10^{-2}	0.2	1.3		

Table 3
Values of the constant C and critical conversion at different temperature of new methacrylate-type resins using BPO as thermal initiator

Resin	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
EHPE-3150-MA	85	6.28	0.34
	90	5.28	0.35
	95	4.02	0.35
	100	3.75	0.43

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 Fig. 3. It is postulated that the increase of rate in NC-9110-MA system should be attributable to its higher values of the reaction rate constant k compared with EHPE-3150-MA, even if reaction order of NC-9110-MA was higher than that of EHPE-3150-MA, as summarized in Table 2. In particular, the notable increase of reaction rate constant k in NC-9110-MA system can be observed, which would be attributed to the lower value of activation energy of it. It can be considered that these phenomena are caused by the bulky structures of EHPE-3150-MA according to the increase of multifunctionality of it, so that steric hindrances between them could make an increase of activation energy of EHPE-3150-MA compared with NC-9110-MA. The constant, C and the critical conversion of reaction, α_c in the generalized autocatalytic kinetic equation, Eq. (4) for resin system with BPO as thermal initiator are reported in Table 3. 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 4 and 5. As shown in Fig. 4, the reaction conversion rate of NC-9110-MA system is faster than that of EHPE-3150-MA system. That is caused by the higher value of reaction rate constant k of the 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 NC-9110-MA system compared with EHPE-3150-MA system. It is postulated that the increase of rate in 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 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 out in C of Eq. (4) for these systems. However, it can be shown that the value of α_c in the NC-9110-MA with BPO as thermal initiator is lower than that with AIBN, and the opposite results can be observed for the EHPE-3150-MA. As shown in Tables 2 and 4, total reaction order of the NC-9110-MA with BPO as thermal initiator is higher than that with AIBN, whereas that of the EHPE-3150-MA with BPO is lower than that with AIBN. Therefore, it can be considered that an increase of the total reaction order would give rise to a decrease of critical conversion α_c.

As shown in Figs. 3 and 4, the conversion rate of NC-9110-MA system with BPO as thermal initiator represents higher value than that with AIBN except for 95 °C, and these similar phenomena can be observed in EHPE-3150-MA system, although the differences are small. This increase of NC-9110-MA system with BPO is attributed to the higher reaction rate constant even if this system shows the higher total reaction order. However, this increase of EHPE-3150-MA system with BPO is caused by the lower total reaction order, because its reaction rate constant with BPO is lower than that with AIBN, although these differences are small according to the decrease of a reaction rate constant by introducing bulky group. That is, the reaction conversion rate of NC-9110-MA system is mainly dependent on a reaction rate constant, and a main factor in that of EHPE-3150-MA system is a total reaction order. 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 [15,16]. Considering these initiators with respect to the initiator decomposition rate constant k_d, it is reported that activation energy and frequency factor in Arrhenius equation of BPO are lower than those of AIBN [17]. These phenomena can also be observed in the reaction rate constant of curing reaction k, as

Table 4
Kinetic parameters of new methacrylate-type resins using AIBN as thermal initiator

Resin	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	$k_2 = 2.28\times10^{17}\exp(-1.34\times10^5/RT)$	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		
EHPE-3150-MA	85	0.12×10^{-2}	0.3	2.6	$k_2 = 3.27\times10^{19}\exp(-1.54\times10^5/RT)$	2.9
	90	0.23×10^{-2}	0.2	3.0		
	95	0.41×10^{-2}	0.2	2.4		
	100	1.00×10^{-2}	0.3	2.7		

Table 5
Values of the constant *C* and critical conversion at different temperature of new methacrylate-type resins using AIBN as thermal initiator

Resin	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
EHPE-3150-MA	85	4.86	0.07
	90	3.78	0.12
	95	4.40	0.21
	100	4.57	0.31

shown in Tables 2 and 4. It is postulated that the increase of conversion rate in the systems using BPO at low temperature should be attributable to the lower activation energy of BPO, and that using AIBN at high temperature is caused by the higher value of frequency factor in Arrhenius equation. As a difference of activation energy between BPO and AIBN is smaller by introducing bulky group such as EHPE-3150-MA system, the increase of conversion rate constant can be observed in EHPE-3150-MA system using AIBN with high value of frequency factor even if this difference is small. Therefore, it is postulated that the conversion rate of EHPE-3150-MA system with bulky groups should be depend on more a total reaction order than conversion reaction rate constant.

4. Conclusions

The new methacrylate-type resins that include a cyclohexane moiety were synthesized and characterized. The curing characteristics of them according to the change of thermal initiators were investigated by the thermal analysis method. It can be shown that an autocatalytic kinetic reaction occurs in these systems, and the conversion rate of EHPE-3150-MA system with bulky group is slower than that of NC-9110-MA, regardless of the kinds of thermal initiators. In NC-9110-MA system, it can be observed that this resin with BPO as thermal initiator has higher reaction conversion rate than that with AIBN because of low activation energy of BPO. However, this effect diminishes with a temperature increase, and an increase of conversion rate in this system with AIBN at high temperature can be seen, which is attributed to mainly the higher frequency factor of AIBN. In EHPE-3150-MA system with bulky moiety, these differences between BPO and AIBN are small compared with NC-9110-MA system. It can be considered that the conversion rate of EHPE-3150-MA system should be depend on more a total reaction order than conversion reaction rate constant.

Acknowledgements

This work was supported by grant No. (R01-2000-000-00333-0) from the Basic Research Program of the Korea Science and Engineering Foundation. The authors would like to express their gratitude to Nippon Kayaku Co., for their generous supply of samples and fruitful discussions.

References

[1] Yoon HG, Kim WG. Polymer for electronics. Seoul, Korea: Munundang; 2001.
[2] Kudo T, Nanjo Y, Nozaki Y, Nagao K, Yamaguchi H, Kang W, Pawlowski G. J Photopolym Sci Technol 1996;1:109.
[3] Kudo T, Nanjo Y, Nozaki Y, Yamaguchi H, Kang W, Pawlowski G. Jpn J Appl Phys 1998;37:1010.
[4] Yamaho Y, Asano M. Japan Patent 06-273616; 1994.
[5] Wen C, Cheng S, Wu Y, Liu H, Chao C, Yasukawa J. Proceesings of SPIE optoelectronics materials and devices II. Taiwan: Taipei; 2000. p. 732.
[6] Rey L, Galy J, Sautereau H. Macromolecules 2000;33:6780.
[7] Chiu YY, Lee LJ. J Polym Sci: Part A: Polym Chem 1995;33:257.
[8] Lee JY, Kim WG. Korea Patent, 2002-80433, 2002-80434, 2002-80435; 2002.
[9] Auad ML, Aranguren MI, Elicabe G, Borrajo J. J Appl Polym Sci 1999;74:1044.
[10] Huang C, Sun Y, Huang W. J Polym Sci: Part A: Polym Chem 1997; 35:1873.
[11] Chern CS, Poehlein GW. Polym Engng Sci 1987;27:782.
[12] Kim WG, Yoon HG, Lee JY. J Appl Polym Sci 2001;81:2711.
[13] Kim WG, Lee JY. J Appl Polym Sci 2002;86:1942.
[14] Kim WG, Lee JY. Polymer 2002;43:5713.
[15] Huang N, Sundberg DC. J Polym Sci: Part A: Polym Chem 1995;33: 2571.
[16] Mckenna TF, Villanueva A. J Polym Sci: Part A: Polym Chem 1999; 37:589.
[17] Mckenna TF, Villanueva A, Santos M. J Polym Sci: Part A: Polym Chem 1999;37:571.