

Optically Clear Simultaneous Interpenetrating Polymer Networks Based on Poly(ethylene glycol) Diacrylate and Epoxy. II. Kinetic Study

MU-SHIH LIN,* KUEN-TAY JENG, KUN-YUI HUANG, and YEN-FONG SHIH†

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050, Republic of China

SYNOPSIS

Simultaneous interpenetrating polymer networks (SINs) based on diglycidyl ether of bisphenol A (DGEBA) and poly(ethylene glycol) diacrylate (PEGDA) in weight ratios of 100/0, 50/50, and 0/100 were blended and cured simultaneously by using benzoyl peroxide (BPO) and *m*-xylenediamine (MXDA) as curing agents. A kinetic study during SIN formation was carried out at 45, 55, 63, and 70°C. Concentration changes for both the epoxide and C=C bond were monitored with FTIR. A rate expression for DGEBA cure kinetics was established with a model reaction of phenyl glycidyl ether (PGE) and benzylamine. Experimental results revealed that lower rate constants and higher activation energy for the SIN were found, compared with those for the constituent DGEBA and PEGDA network formation. A model of network interlock was proposed to account for this phenomenon. During simultaneous cure of DGEBA and PEGDA, the interlock (mutual entanglement) between DGEBA and PEGDA networks provided a sterically hindered environment, which subsequently increased the activation energy and reduced cure rates for both DGEBA and PEGDA. © 1993 John Wiley & Sons, Inc.

Keywords: simultaneous interpenetrating polymer network (SIN) • kinetic parameter • network interlock

INTRODUCTION

In our previous report on the preparation and characterization of optically clear, simultaneous interpenetrating polymer networks based on PEGDA and an epoxy,¹ we reported such intermolecular interactions in PEGDA/DGEBA and PEGDA/diamine on the curing behavior of PEGDA/epoxy SINs. It was noted that the unusually slow increase in viscosity for a composition of PEGDA/EGDBA = 50/50 was mainly attributed to H bonding between PEGDA and DGEBA.¹ We then found that this generally slow viscosity increase could be possibly, in part, due to the effect of mutual entanglement between PEGDA and DGEBA networks, i.e., an ef-

fect of network interlock.² We then searched the literature and found Xue et al.'s report on the kinetic study of polyurethane (PU) and styrene (St) IPN.³ They found that there was no interference between the reaction mechanisms and that increasing the PU/St proportion enhanced the rate of PU formation, but lessened the rate of PS formation. We were interested in these results and thought that there might be some factor governing the cure rate of each network. In this article, we would like to report on the detailed kinetic analyses, including the model reaction of the epoxy cure to elucidate the implied factors governing the cure behavior of SIN formation.

EXPERIMENTAL

Analytical grade of phenyl glycidyl ether (PGE) and benzylamine were purchased from Merck Co. and were used as received. The model reaction was car-

* To whom all correspondence should be addressed.

† Present address: Department of Chemical Engineering, Shu-Teh Junior College of Technology, Taichung, Taiwan 40202, Republic of China

ried out at 50, 58, 61, and 67°C by reacting PGE (3.75 g) and benzylamine (2.68 g) in 10 mL of dichloroethane.

PEGDA was prepared according to the previous study.¹ DGEBA (Epikote 826) containing PGE was obtained from Shell Co. An epoxy equivalent weight (EEW) of 185 was found by titration. PEGDA/DGEBA in weight ratios of 100/0, 50/50, and 0/100 were blended. BPO (1.0 phr based on PEGDA) and MXDA (based on stoichiometric EEW) were added to the foregoing compositions as curing agents. SIN formations were induced at 45, 55, 63, and 70°C. Samples were cast on KBr plates and were sandwiched and mounted on a sample holder which was heated electrically. Changes of concentrations in the epoxide group and the C=C bond were monitored with a Nicolet model 520 FTIR. The resolution of FTIR was set at 1 cm⁻¹. Difference spectra were obtained by subtracting the absorbances at time t from that at time zero, using the benzene absorbance at 1608 cm⁻¹ as the internal standard. Integration of peak areas at ca. 915 and 1636 cm⁻¹ from the difference spectra were related to the changes of concentrations for the epoxide and the C=C bond. The conversion, α , is defined as

$$\alpha = (A_0 - A_t)/(A_0 - A_\infty) = (C_0 - C_t)/(C_0 - C_\infty)$$

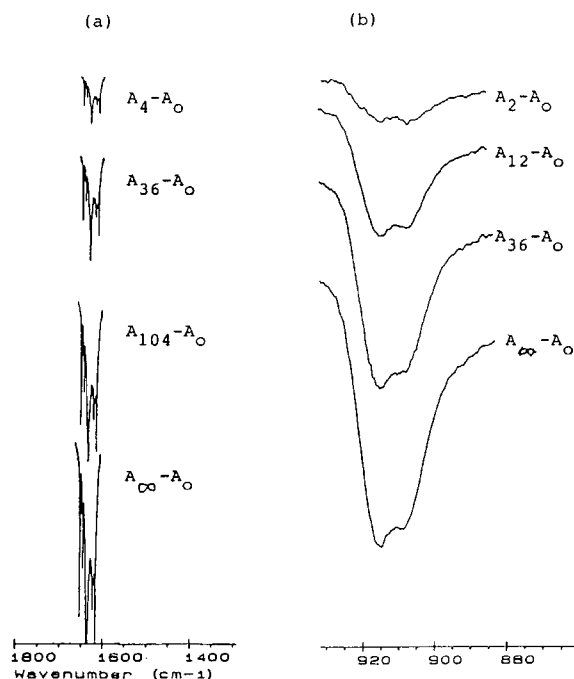


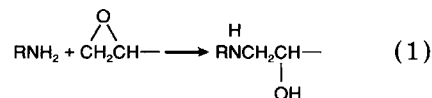
Figure 1. Typical difference spectra (t , in minutes) of: (a) C=C bond in PEGDA and (b) epoxide.

where A_0 , A_t , and A_∞ are peak areas of the specific functional group at the initial time, time t , and after post-cure, respectively; C_0 , C_t , and C_∞ are the corresponding concentrations. Typical difference spectra for the epoxide and the C=C bond are shown in Figure 1.

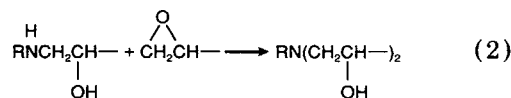
RESULTS AND DISCUSSIONS

Many studies on epoxide cured by diamines were reported in the literature.⁴⁻¹⁶ King and Bell reviewed and discussed the reaction mechanisms extensively in their study on reactions in a typical epoxy-aliphatic diamine system.⁹ The reaction of a primary amine and an epoxide would be expected to lead to the following possibilities:

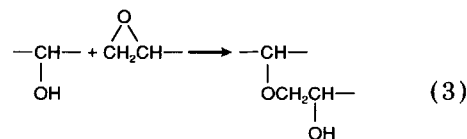
Primary amine-glycidyl ether reaction:



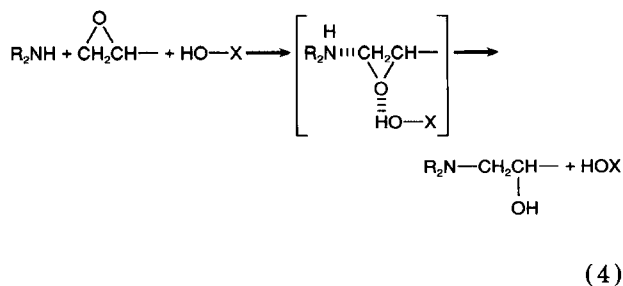
Secondary amine-glycidyl ether reaction:



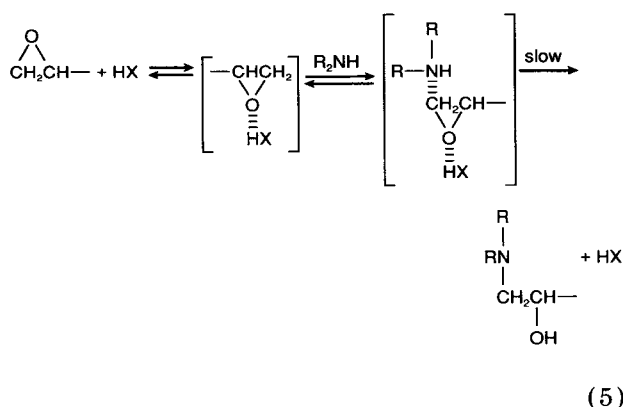
Etherification of primary alcohol-glycidyl ether:



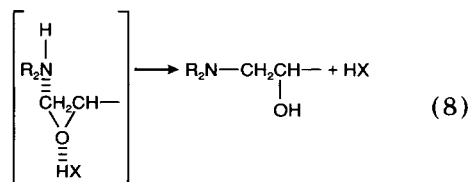
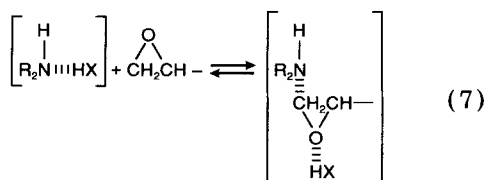
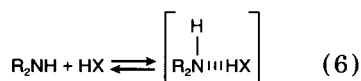
However, Shechter et al.,⁴ in their study of glycidyl ether reaction with amine, came to the conclusion that there was no great selectivity in the reaction of a primary amine with a glycidyl ether successively from secondary to tertiary amine and that, as in the secondary amine-glycidyl ether reactions, the amount of etherification was negligible. In all cases, the hydroxyl groups served only as a catalyst for the reaction and not as a serious contender for epoxide in competition with amine. They proposed a termolecular mechanism to account for this accelerating effect:



A similar mechanism was proposed by Smith⁸ that a hydrogen bond forms between hydrogen donor and the epoxide ring followed by a three molecular transition state which is rate-determining:

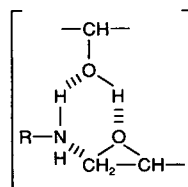


Tanaka and Mika¹⁰ suggested a mechanism based on the hydrogen bonding of amine to a hydrogen donor such as alcohol:



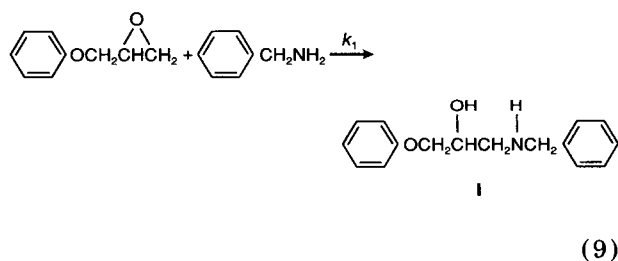
Harrod⁶ and Bellenger et al.¹⁷ observed hydrogen bonding in an epoxy-amine system. We also observed hydrogen bonding in DGEBA-MXDA sys-

tem.¹ King and Bell⁹ argued that equilibrium hydrogen bonding would be more favorable between hydroxyl and amine groups than epoxy and hydroxyls due to the difference in basicity. Nevertheless, in the catalytic reaction, a hypothetical termolecular transition state among secondary alcohol, amine, and an epoxy is generally recognized:

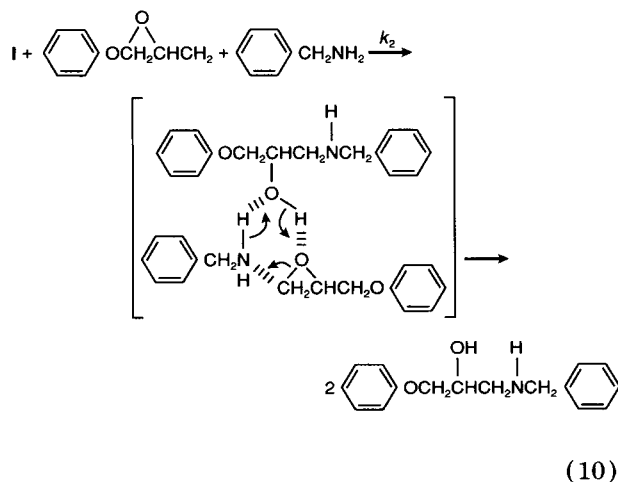


Kinetics of the Model Reaction

To establish the rate expression, we carried out a model reaction, which dealt with the "uncatalytic" reaction between phenyl glycidyl ether (PGE) and benzylamine:



As concluded by Shechter et al.,⁴ there was no great selectivity in the reaction of glycidyl ether with a primary or a secondary amine, the rate constant may be expressed as k_1 . The newly produced hydroxy group in I further "catalyzes" this model reaction, according to reaction (10):



In a typical epoxy-amine cure reaction, both uncatalytic and catalytic reactions are generally recognized in the literature.¹²⁻¹⁶ Let $[E]$ and $[A]$ be concentrations of epoxide and amine at time t and are related to their initial concentrations of $[E]_0$ and $[A]_0$ by

$$[E] = [E]_0(1 - \alpha) \quad (11)$$

$$[A] = [A]_0(1 - \alpha) \quad (12)$$

Here α is the conversion of epoxide. Since new OH is produced for every epoxide consumed, according to reaction (9), so

$$[OH] = [E]_0\alpha \quad (13)$$

Typical changes of conversions with time for the model reaction are given in Figure 2. From reactions (9) and (10), the rate of disappearance of the epoxide is given by

$$-\frac{d[E]}{dt} = k_1[E][A] + k_2[E][A][OH] \quad (14)$$

where k_1 and k_2 are rate constants for uncatalytic and catalytic reactions, respectively. By combining eqs. (11)–(14), eq. (15) is obtained:

$$\dot{\alpha} = \frac{d\alpha}{dt} = k_1[A]_0(1 - \alpha)^2 + k_2[E]_0[A]_0(1 - \alpha)^2\alpha \quad (15)$$

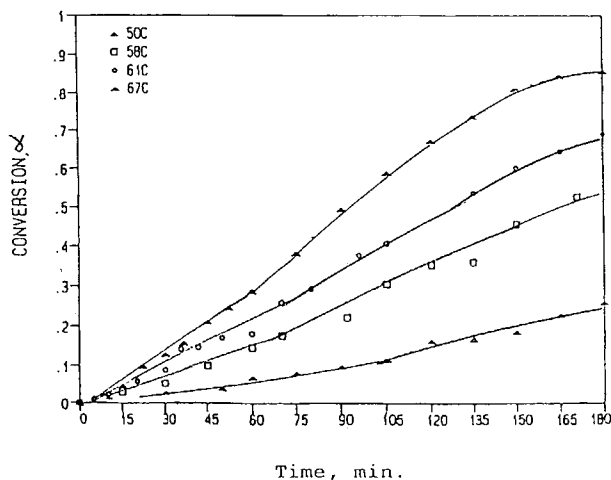


Figure 2. Plots of conversions of epoxide versus time for the model reaction at various temperatures.

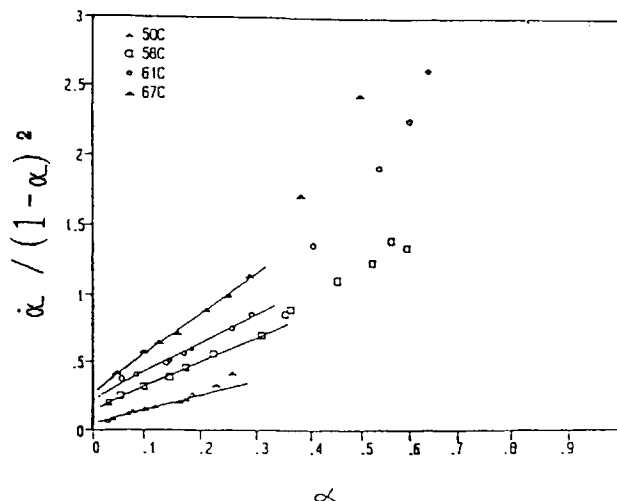


Figure 3. Plots of $\dot{\alpha}/(1 - \alpha)^2$ vs. α for the model reaction at various temperatures.

i.e.,

$$\dot{\alpha}/(1 - \alpha)^2 = k_1[A]_0 + k_2[E]_0[A]_0\alpha \quad (16)$$

where $\dot{\alpha}$ can be found from the slopes of the conversion curves α vs. t (Fig. 2). A plot of $\dot{\alpha}/(1 - \alpha)^2$ vs. α gives a straight line, with an intercept of $k_1[A]_0$ and a slope of $k_2[E]_0[A]_0$, as shown in Figure 3. Plots of $\ln k_1$ and $\ln k_2$ versus reciprocal absolute temperatures $1/T$ give the activation energies of uncatalytic (E_1) and catalytic (E_2) reactions (Fig. 4). The resultant rate constants and corresponding activation energies for the model reaction are listed

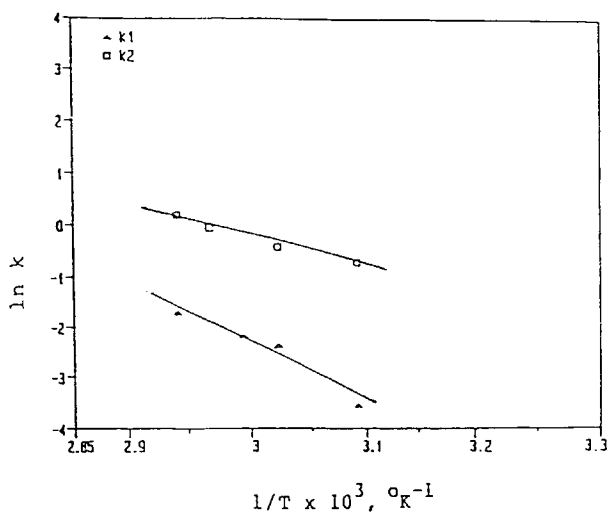


Figure 4. Plots of: (a) $\ln k_1$ vs. $1/T$ and (b) $\ln k_2$ vs. $1/T$ for the model reaction.

in Table I. It is noted that the rate constant (k_2) for the catalytic reaction is about 10 times faster than that for the uncatalytic reaction (k_1) and, the activation energy of the catalytic reaction (E_2) is less than that of the uncatalytic reaction (E_1). From the study of the model reaction, it is found that the catalytic effect is always there even if the initial reactants contain no OH group, because the newly produced OH group is always present in the course of the reaction.

Kinetics of the DGEBA Cure

From the study of the model reaction, it is known that both the uncatalytic and catalytic reactions always get involved in the cure reaction of epoxide since a new hydroxy group is always produced [reactions (9) and (10)]. The reactivities of the two amino hydrogens may be similar in dilute solution as concluded by Shecheter et al.,⁴ while the reactivities of these two amino hydrogens may be different in bulk. Analyses of the secondary amine concentrations done by King and Bell⁹ indicated that at the early stages of curing reaction only primary amine were consumed quickly; the secondary amine participated in the reaction at latter stages. Therefore, it appears reasonable to assume that in a DGEBA-MXDA curing reaction, the primary amino hydrogen predominately reacts with the epoxide at the early stages, and eq. (16) may be properly used for the rate expression for epoxy-diamine cure kinetics. The first term on the right side of eq. (16) relates to the uncatalytic reaction [reaction (9)] while the second term relates to the catalytic reaction [reaction (10)]. An alternate expression was proposed in the literature:¹²⁻¹⁶

$$\frac{d\alpha}{dt} = k'_1(1 - \alpha)^n + k'_2\alpha^m(1 - \alpha)^n \quad (17)$$

where k'_1 and k'_2 are apparent rate constants for the uncatalytic and the catalytic reactions, and $m + n$

= 2. Generally, the reported m and n values are not integers, probably due to diffusion and other unknown factors. By comparing eqs. (16) and (17), it is clear that $k'_1 = k_1[A]_0$ and $k'_2 = k_2[E]_0[A]_0$. Here k_1 and k_2 are real rate constants, while k'_1 and k'_2 are only the "apparent rate constants." Furthermore, this rate expression has little direct relationship to the reaction mechanisms, as it is only an empirical equation.

Typical changes of conversions α vs. time are shown in Figures 5(a) and 5(b) for pure DGEBA and SIN of PEGDA/DGEBA = 50/50. Figures 6(a) and 6(b) show the plots of $\dot{\alpha}/(1 - \alpha)^2$ vs. α for pure DGEBA and SIN of PEGDA/DGEBA = 50/50, from which the intercept and slope give $k_1[A]_0$ and $k_2[E]_0[A]_0$ as known from eq. (16). It is noted that at early stages of curing reactions, the data nicely fits eq. (16), while at the latter stages, deviation is observed, presumably because diffusion control and/or complicated reactions got involved in the curing behavior. Kinetic parameters are listed in Table II. The activation energy for the uncatalytic (E_1) and the catalytic (E_2) reactions were calculated from Arrhenius plots [Figs. 7(a) and 7(b)]. Results similar to the model reaction were found. The rate constant for the uncatalytic reaction (k_1) was generally lower than that of the catalytic reaction (k_2) while the activation energy of the uncatalytic reaction (E_1) was generally higher than that of the catalytic reaction (E_2). Comparing Tables I and II, DGEBA exhibited higher rate constants than PGE, presumably because the original OH group in DGEBA provided a catalytic environment for the cure reaction. Similar results were found for other SIN systems in our laboratory.^{2,18} Ohashi and co-workers recently reported a similar effect by curing epoxy resin having hydroxymethyl groups.¹⁹ In addition, experimental results also clearly indicated that the rate constants k_1 and k_2 for SIN are generally lower than the corresponding ones of the pure DGEBA. On the other hand, the corresponding activation energies for SIN are generally higher than

Table I. Kinetic Parameters for the Model Reaction: $[E]_0 = [A]_0 = 1.55$ mol/L

Temperature (°C)	$k_1 \times 10^3$ (L/mol min)	$k_2 \times 10^2$ (L ² /mol ² min)	E_1 (kcal/mol)	E_2 (kcal/mol)
50	0.293	0.491	24.13	19.16
58	0.950	0.666	24.13	19.16
61	1.128	0.967	24.13	19.16
67	1.821	1.223	24.13	19.16

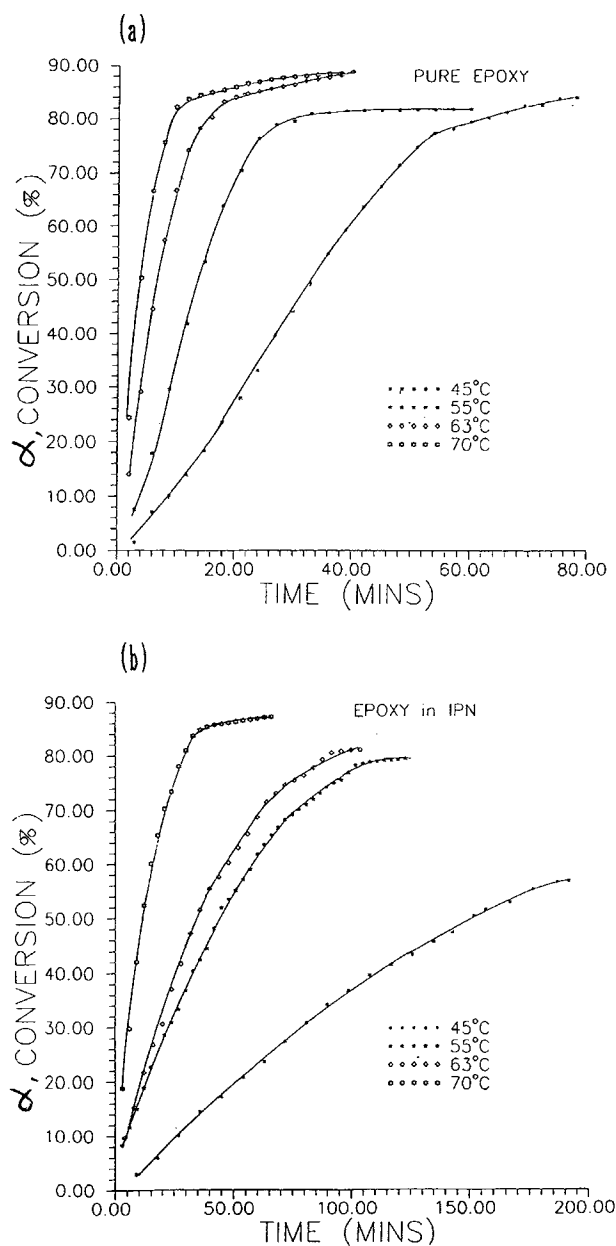


Figure 5. Plots of conversions versus time for: (a) DGEBA and (b) epoxide in SIN of PEGDA/DGEBA = 50/50.

those of pure DGEBA. From the above findings, it appears that network interlock does exist. Here the network interlock means the mutual entanglement between the epoxy network and the PEGDA network. During SIN formation, the presence of one network, e.g., the epoxy network, would provide an additional sterically hindered environment to the growth of the other network, i.e., the PEGDA network, and vice versa. The network interlock not only

gives additional steric hindrance but also restrains chain mobility of the reactants, leading to a lower rate constant and a higher activation energy for SIN.

Kinetics of the PEGDA Cure

Free radical polymerization of vinyl compounds normally follows a first-order reaction,²⁰ assuming the homolysis of the initiator is the rate-determining

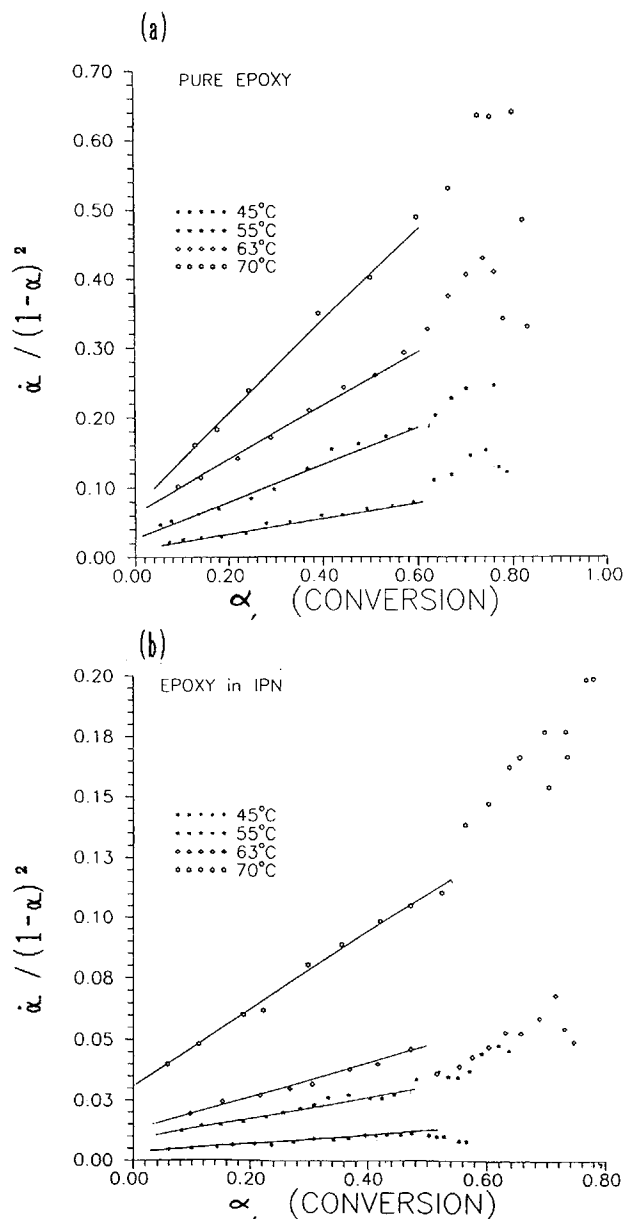


Figure 6. Plots of $\dot{\alpha}/(1-\alpha)^2$ vs. α for: (a) DGEBA and (b) SIN of PEGDA/DGEBA = 50/50 at various temperatures.

Table II. Kinetic Parameters of Epoxy for DGEBA and SIN: $[E]_0 = 5.02 \text{ mol/L}$, $[A]_0 = 0.329 \text{ mol/L}$

Sample	Temperature (°C)	$k_1 \times 10^3$ (L/mol min)	$k_2 \times 10^2$ (L ² /mol ² min)	E_1 (kcal/mol)	E_2 (kcal/mol)
DGEBA	45	0.375	0.750	16.63	15.15
	55	0.800	1.663	16.63	15.15
	63	1.671	2.535	16.63	15.15
	70	2.224	4.142	16.63	15.15
SIN	45	0.179	0.344	23.77	19.14
	55	0.488	0.898	23.77	19.14
	63	0.701	1.358	23.77	19.14
	70	1.702	3.152	23.77	19.14

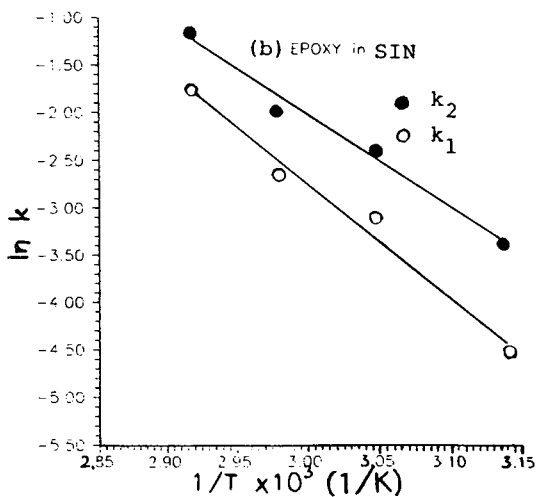
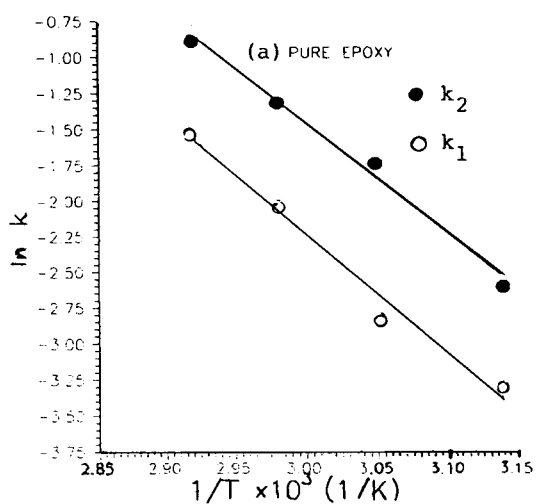


Figure 7. Plots of $\ln k_1$ and $\ln k_2$ versus reciprocal absolute temperature $1/T$ for: (a) DGEBA and (b) SIN of PEGDA/EGDBA = 50/50.

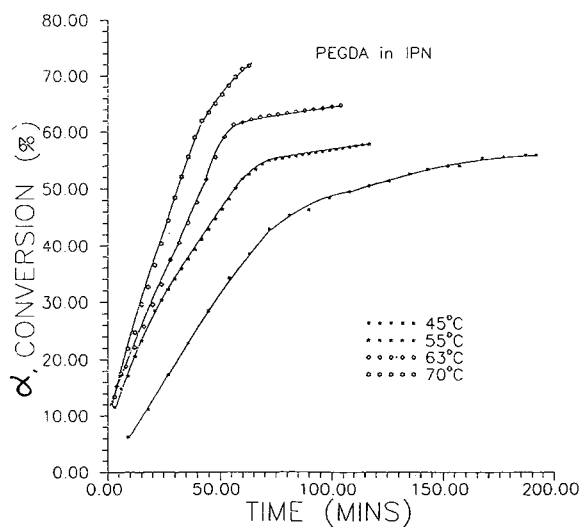
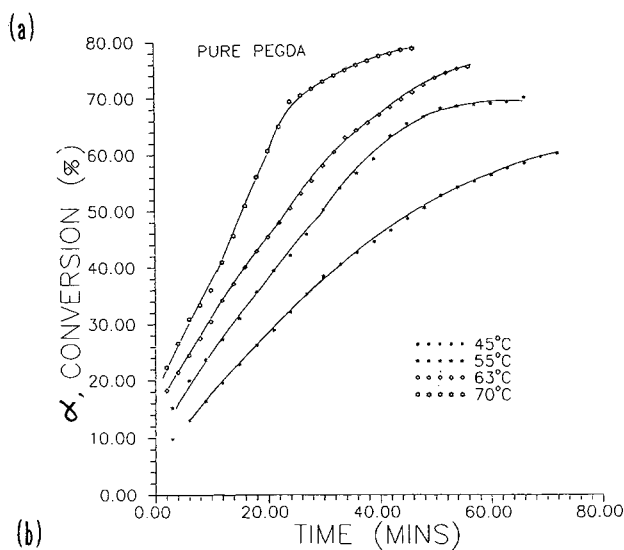


Figure 8. Plots of conversions versus time for C=C in: (a) PEGDA and (b) PEGDA/DGEBA = 50/50.

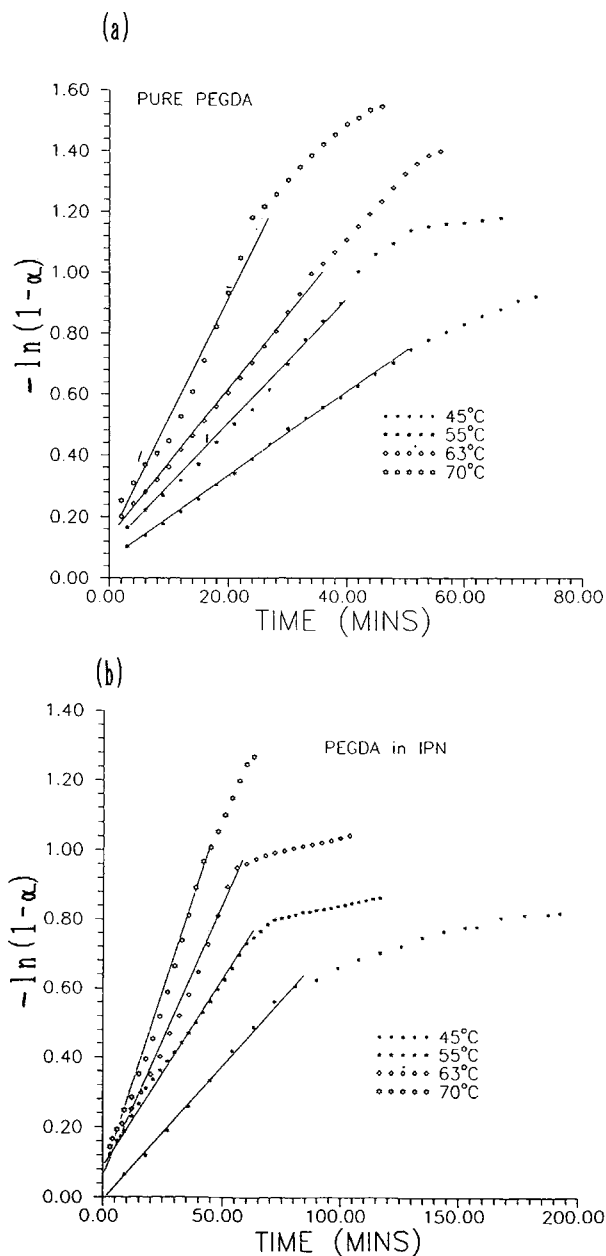


Figure 9. Plots of $-\ln(1 - \alpha)$ vs. time for C=C in: (a) PEGDA and (b) SIN of PEGDA/DGEBA = 50/50.

step for the initiation, and steady-state is reached:

$$-\frac{d[M]}{dt} = k_p(k_{df}[I]/k_t)^{1/2}[M] \quad (18)$$

Integration of eq. (18) gives

$$-\int_{[M]_0}^{[M]} \frac{d[M]}{[M]} = \int_0^t k_p(k_{df}[I]/k_t)^{1/2} dt \quad (19)$$

where $[M]_0$ and $[M]$ are the concentrations of the C=C bond in PEGDA at the beginning and time t , f is the initiator efficiency, $[I]$ is the initiator concentrations, k_d is the dissociation constant of the initiator, and k_p and k_t are rate constants of chain propagation and chain termination. Assume that f and $[I]$ do not change too much at early stages of cure such that $k_p(k_{df}[I]/k_t)^{1/2}$ is nearly constant and equal to k . The result of eq. (19) can be expressed as

$$-\ln(1 - \alpha) = kt \quad (20)$$

with $[M] = [M]_0(1 - \alpha)$ by neglecting the C=C concentration after postcure ($[M]_\infty$). Figures 8(a) and 8(b) show the conversions α vs. time t for PEGDA and for a SIN of PPEGMA/DGEBA = 50/50. Figure 9(a) shows the plot of $-\ln(1 - \alpha)$ vs. t for PEGDA cured by BPO at various temperatures. Figure 9(b) shows a similar plot for SIN of PEGDA/DGEBA = 50/50. Slopes of straight lines give the values of the apparent rate constant k at various temperatures. The corresponding apparent activation energies were calculated from the plots of $\ln k$ vs. reciprocal absolute temperature $1/T$ [Figs. 10(a) and 10(b)]. Kinetic parameters for PEGDA and SIN are summarized in Table III. Similarly, the data closely fit eq. (20) at early stages of cure while at latter stages, deviation is generally observed, presumably because of the gel effect.²⁰

It is clear from Table III that the SIN shows lower apparent rate constants and higher apparent activation energies than pure PEGDA. Again, the net-

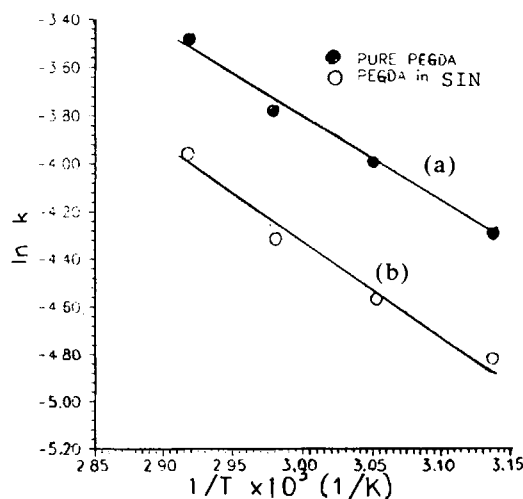


Figure 10. Plots of $\ln k$ vs. $1/T$ for C=C for: (a) PEGDA and (b) SIN of PEGDA/EGDBA = 50/50.

Table III. Kinetic Parameters of C=C for PEGDA and SIN

Sample	Temperature (°C)	$k \times 10^2$ (min ⁻¹)	E (kcal/mol)
PEGDA	45	1.40	7.03
	55	1.86	7.03
	63	2.30	7.03
	70	3.11	7.03
SIN	45	0.79	7.99
	55	1.02	7.99
	63	1.34	7.99
	70	1.95	7.99

work interlock appears to have a significant effect on the curing behavior of SIN.

CONCLUSIONS

In a kinetic study of DGEBA/PEGDA SIN, it was found that the SIN resulted in lower rate constants and higher activation energies, compared with those of the respective components. This phenomenon can be interpreted by an effect of the network interlock. The network interlock apparently not only gave additional sterically hindered environment to the curing reactions, but also restrained the mobilities of both DGEBA and PEGDA, thus accounting for the observed phenomenon.

The authors are grateful to the National Science Council of ROC for financial support under Contract Number NSC-82-0405-E009-095.

REFERENCES AND NOTES

- M. S. Lin and K. T. Jeng, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 1941-1951 (1992).
- M. S. Lin and C. C. Yeh, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 2093 (1993).
- S.-C. Xue, Z.-P. Zhang, and S.-K. Ying, *Polymer*, **30**, 1271 (1989).
- L. Shechter, J. Wynstra, and R. E. Kurkiy, *Ind. Eng. Chem.*, **48**, 94 (1956).
- A. K. Ingberman and R. K. Walton, *J. Polym. Sci.*, **28**, 468 (1958).
- (a) J. F. Harrod, *J. Appl. Polym. Sci.*, **6**, S63 (1962); (b) J. F. Harrod, *J. Polym. Sci.*, **A1**, 385 (1963).
- N. S. Isaacs and R. E. Parker, *J. Chem. Soc.*, 3497 (1960).
- I. T. Smith, *Polymer*, **2**, 95 (1961).
- J. J. King and J. P. Bell, *Reactions in a Typical Epoxy-Aliphatic Diamine System*, in *Epoxy Resin Chemistry*, R. S. Bauer, Ed., ACS Symposium Series, Vol. 114, American Chemical Society, Washington, DC, pp. 223-262.
- Y. Tanaka and T. F. Mika, in *Epoxy Resins Chemistry and Technology*, C. A. May and Y. Tanaka, Eds., Dekker, New York, 1973, p. 135.
- K. Horie, H. Hiura, M. Sawada, I. Mita, and H. Kambe, *J. Polym. Sci. A-1*, **8**, 1357-1372 (1970).
- O. A. Moroni, J. Mijovic, E. M. Pearce, and C. C. Foun, *J. Appl. Polym. Sci.*, **32**, 3761-3773 (1986).
- C. C. Riccardi, H. E. Adabbo, and J. J. Williams, *J. Appl. Polym. Sci.*, **29**, 2481-2492 (1984).
- A. Dutta and M. E. Ryan, *J. Appl. Polym. Sci.*, **24**, 635-649 (1979).
- M. A. Golub and N. R. Lerner, *J. Appl. Polym. Sci.*, **32**, 5215-5229 (1986).
- J. Mijovic, J. Kim, and J. Slaby, *J. Appl. Polym. Sci.*, **29**, 1449 (1984).
- V. Bellenger, J. Vender, J. Francillette, P. Hoarau, and E. Morel, *Polymer*, **28**, 1079 (1987).
- (a) M. S. Lin and R. J. Chang, *J. Appl. Polym. Sci.*, **46**, 815-827 (1992); (b) M. S. Lin, Timothy Yang, and Kun-Yui Huang, *Polymer*, in press.
- K. Ohashi, K. Hasegawa, A. Fukuda, and K. Uede, *J. Appl. Polym. Sci.*, **44**, 419-423 (1992).
- (a) George Odian, *Principles of Polymerization*, 2nd ed., Wiley, New York, 1981, chapter 3; (b) T. R. Cuadrado, J. Baanajo, and R. J. J. Williams, *J. Appl. Polym. Sci.*, **28**, 485-499 (1983).

Received December 21, 1992

Accepted May 25, 1993