Kinetic studies of compatible simultaneous interpenetrating polymer networks based on poly(poly(ethylene glycol) maleate) and epoxy resin

Mu-Shih Lin*, Timothy Yang and Kun-Yui Huang
Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30050
(Received 1 June 1993)

A simultaneous interpenetrating polymer network (SIN) based on diglycidyl ether of bisphenol A (DGEBA) and poly(poly(ethylene glycol) maleate) (PPEGMA) in a 50/50 weight ratio was blended and was cured simultaneously by using benzoyl peroxide and *m*-xylenediamine as curing agents. Kinetic studies during SIN formation were carried out at 50, 60, 65 and 70°C. Concentration changes of both epoxide and double bonds were monitored with Fourier-transform infra-red spectroscopy. Rate expressions were established with model reactions. Experimental results revealed that lower rate constants and higher activation energies for SIN were found compared with those for the formation of the respective component networks. A network interlock effect was proposed to account for this phenomenon. During simultaneous cure of DGEBA and PPEGMA, network interlock must provide a sterically hindered environment, which subsequently increased activation energies and reduced cure rates for both DGEBA and PPEGMA.

(Keywords: interpenetrating networks; kinetics; network interlock)

INTRODUCTION

Although interpenetrating polymer networks (IPN) have been extensively studied in recent years, most reports[1–6] are related to synthesis, morphology and/or mechanical behaviour. Detailed analyses of the polymerization kinetics involved have not been reported in the literature. Jin and Meyer[7], in their kinetic study of polyurethane/poly(methyl methacrylate) IPN, reported the validity of the Beer–Lambert law, but did not calculate the kinetic parameters. Xue and coworkers[8] reported the kinetics of polyurethane/polystyrene (PU/PS) IPNs by infra-red (i.r.) spectroscopy. They found 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.

In our previous studies on optically-clear simultaneous interpenetrating polymer network (SIN) materials[9–11], we found that the curing behaviours of SINs indicated much lower viscosity increases compared with that of single-component network formation. We proposed that the mutual entanglement of the two networks (network interlock) probably played an important role in governing the viscosity changes, and that this network interlock should affect the kinetics during SIN formation. In order to understand this possible effect, we carefully analysed the kinetic data, and checked the results with model reactions. Indeed, we found the existence of this effect on the SIN kinetics. In this paper, we would like to report detailed kinetic studies and compare the kinetic parameters for different compositions.

EXPERIMENTAL

Analytical grades of phenyl glycidyl ether (PGE) and benzylamine were purchased from Merck Co. and were used directly. Model reactions were carried out at 50, 57, 61 and 67°C by reacting PGE (3.75 g) and benzylamine (2.68 g) in 10 ml of dichloroethane.

Preparation of poly(poly(ethylene glycol) maleate) (PPEGMA)

Into a 500 ml four-necked flask, equipped with a mechanical stirrer and a nitrogen inlet and outlet, 0.2 mol of poly(ethylene glycol) ($\bar{M}_n = 200$) and 0.2 mol of maleic anhydride were charged, and heated to 120°C under nitrogen atmosphere. Esterification proceeded at 120°C for 24 h. The viscous product was diluted with methylene chloride, and the unreacted poly(ethylene glycol) and maleic anhydride were removed by extraction with distilled water. The methylene chloride was then evaporated with a rotary evaporator. A syrup PPEGMA with a number-average molecular weight of 1470 (determined by end-group analysis) was obtained in quantitative yield. Its i.r. and ^{1}H nuclear magnetic resonance (n.m.r.) spectra are given in *Figures 1* and *2*.

Diglycidyl ether of bisphenol A (DGEBA; Epikote 815) was obtained from Shell Co. An epoxy equivalent weight (*EEW*) of 194.5 was found by titration. Weight ratios of PPEGMA/DGEBA in 100/0, 50/50 (mixture), 50/50 (SIN) and 0/100 were blended. Benzoyl peroxide (BPO) (1.0 phr based on PPEGMA) and *m*-xylenediamine (*m*XDA) (reagent grade, based on stoichiometric epoxide equivalent weight) were mixed into the blends as curing agents. SIN formations were induced at 50, 60, 65 and

---

* To whom correspondence should be addressed

0032-3861/94/030594-06

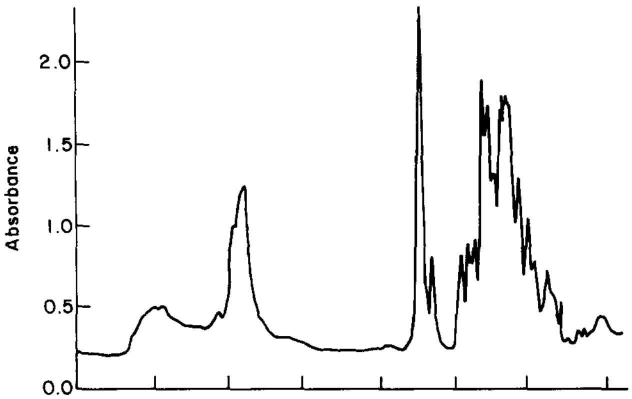


Figure 1 I.r. spectrum of PPEGMA

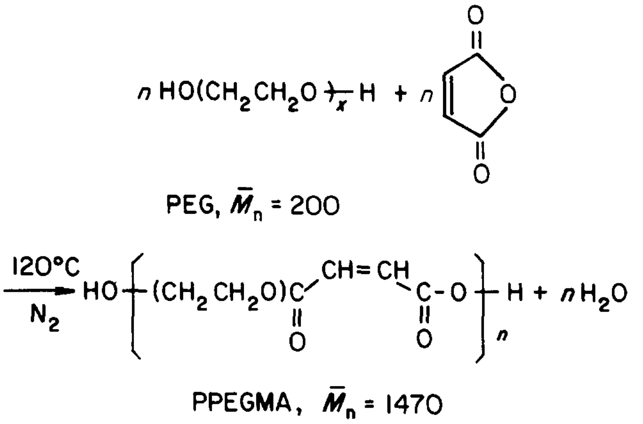
70°C. Samples were cast on KBr plates and were sandwiched and mounted on a sample holder. Changes of concentrations in epoxide groups and double bonds were monitored with a Nicolet model 520 Fourier-transform infra-red (*FT*i.r.) spectrometer. The resolution of *FT*i.r. was set at $1\,cm^{-1}$. Difference spectra were obtained by subtracting the absorbance at time zero from those at time t, using the benzene absorbance at $1602\,cm^{-1}$ as internal standard. Integration of peak areas at 915 and $1644\,cm^{-1}$ from the difference spectra were related to the changes of concentrations for epoxide and double bond. The conversion α is defined as:

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

where A_0, A_t and A_∞ are peak areas of difference spectra for the epoxide (or the C=C) at initial time, time t and after post-cure, respectively; and C_0, C_t and C_∞ are the concentrations of the epoxide (or the C=C) at the corresponding times.

RESULTS AND DISCUSSION

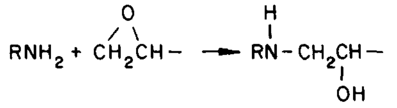
PPEGMA was prepared according to the reaction:



Its i.r. and ¹H n.m.r. spectra (*Figures 1* and *2*) confirm the structure.

Many studies on the kinetics of DGEBA cured by diamines have been reported in the literature[12–18], and several rate expressions proposed. The epoxy/amine reactions would be expected via:

(i) Primary amine/epoxide reaction



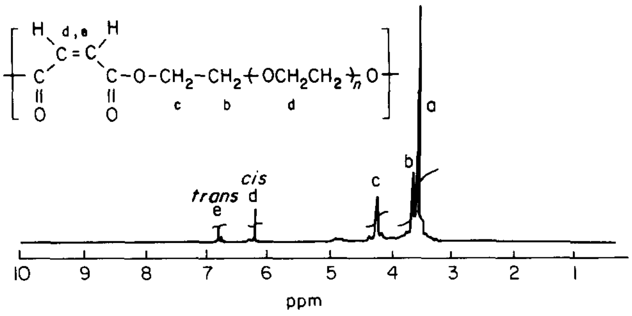
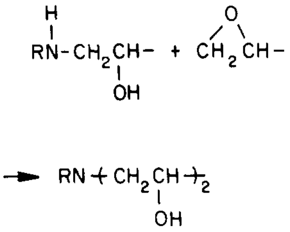
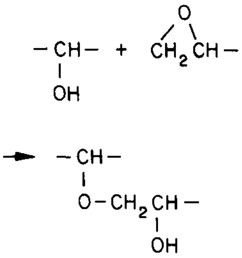


Figure 2 ¹H n.m.r. spectrum of PPEGMA

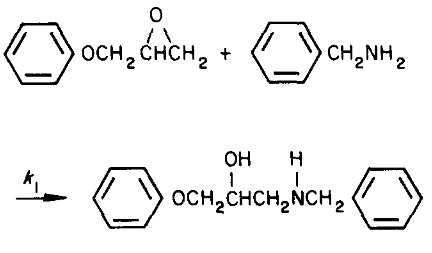
(ii) Secondary amine/epoxide reaction



(iii) Hydroxy/epoxide reaction



However, Schechter *et al.*[12], in their study of epoxide reaction with amine, concluded that there was no great selectivity in a primary amine and a secondary amine reaction with an epoxide, and that the hydroxyl group served 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 the accelerating effect of the hydroxyl group[12]. Adabbo and Williams[14], in their studies of the curing reaction of epoxy with diamine, revealed that the experimental data are consistent with a single activation energy and heat of reaction for both primary and secondary amino hydrogens. In order to clarify the exact rate expression in the literature, we carried out a model reaction, which deals with the spontaneous reaction between phenyl glycidyl ether (PGE) and benzylamine:



I (1)

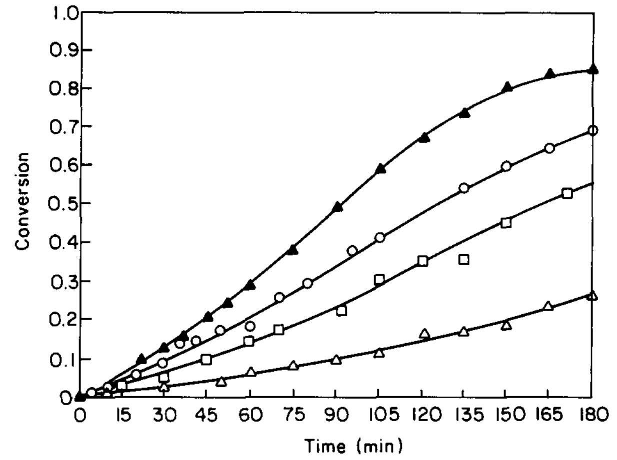
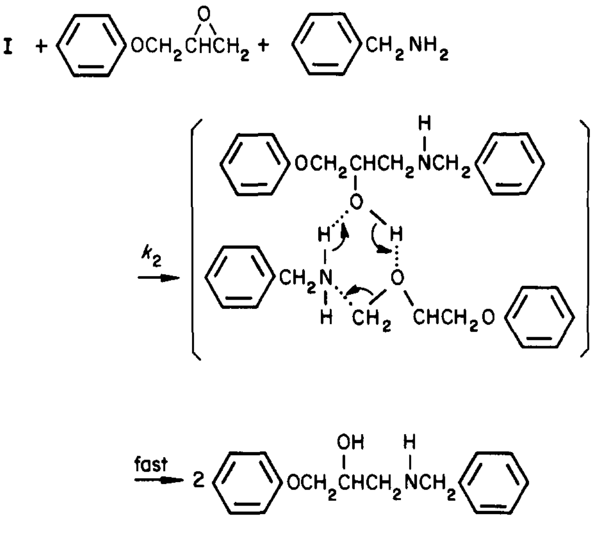


Figure 3 Plots of conversions α vs. time for model reactions at various temperatures: △, 50°C; □, 58°C; ○, 61°C; ▲, 67°C

However, the newly produced hydroxy group in I further catalyses the model reaction, according to the equation:



(2)

Let [E] and [A] be the concentrations of epoxide and amine at time t, which are related to their initial concentrations $[E]_0$ and $[A]_0$ by:

$$[E] = [E]_0(1-\alpha) \tag{3}$$

$$[A] = [A]_0(1-\alpha) \tag{4}$$

Here α is the conversion of epoxide. The conversions were monitored with *FT*i.r. In recent years *FT*i.r. has been extensively used in solving analytical problems. The advantage of *FT*i.r. was discussed by Koenig[19]. Typical changes of conversions with time are given in *Figure 3*.

Since new OH is produced for every epoxide consumed, according to equation (1), so:

$$[OH] = [E]_0\alpha \tag{5}$$

Stoichiometric *EEW* for benzylamine was maintained in our experiment, i.e.

$$[E] = [A] = [E]_0(1-\alpha) \tag{6}$$

So from reactions (1) and (2):

$$-\frac{d[E]}{dt} = k_1[E][A] + k_2[E][A][OH] \tag{7}$$

where k_1 and k_2 are the rate constants for spontaneous and catalytic reactions, respectively. By combining equations (1) to (7), the following equation is obtained:

$$\dot{\alpha} = \frac{d\alpha}{dt} = k_1[E]_0(1-\alpha)^2 + k_2[E]_0^2(1-\alpha)^2\alpha \tag{8}$$

i.e.

$$\dot{\alpha}/(1-\alpha)^2 = k_1[E]_0 + k_2[E]_0^2\alpha \tag{9}$$

The value of $\dot{\alpha}$ can be measured from the slope of conversion *versus* t (*Figure 3*). The plot of $\dot{\alpha}/(1-\alpha)^2$ *versus* α gives a straight line, with an intercept of $k_1[E]_0$ and a slope of $k_2[E]_0^2$, as shown in *Figure 4*. Plots of $\ln k_1$ and $\ln k_2$ *versus* reciprocal absolute temperatures give the corresponding activation energies, E_{a1} and E_{a2}, according to the Arrhenius equation. The resultant rate constants and corresponding activation energies for various temperatures are listed in *Table 1*. It is noted that the rate constant for catalytic reaction (k_2) is about 10 times faster than that for spontaneous reaction (k_1) and the activation energy for catalytic reaction (E_{a2}) is less than that for spontaneous reaction (E_{a1}). From the kinetic studies of model reactions, it was found that the catalytic effect always occurs even if the initial reactants contain no OH groups, because newly produced OH groups are continuously generated during reactions.

The experimental data fit equation (9) well in the early stages of reaction, while in the latter stages the data plotted according to equation (9) are significantly non-linear; probably, side reactions occurred, leading to the observed deviation.

Kinetics of epoxide

In fact, the curing of epoxy resin always involves both spontaneous and catalytic reactions, since new hydroxy groups are always produced during reactions (equations (1) and (2)). Therefore, equation (9) should be used as the rate expression for epoxy cure. The first term on the right-hand side of equation (9) relates to the spontaneous reaction (equation (1)); while the second term relates to the catalytic reaction (equation (2)). Typical changes of conversion α *versus* time for DGEBA/*m*XDA system are shown in *Figure 5*. *Figure 6* shows the plots of $\dot{\alpha}/(1-\alpha)^2$ *versus* α, from which the intercept and slope give $k_1[E]_0$ and $k_2[E]_0^2$, according to equation (9). Kinetic parameters

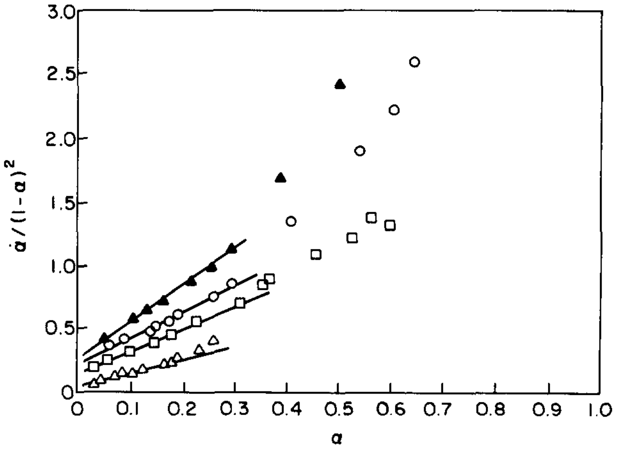


Figure 4 Plots of $\dot{\alpha}/(1-\alpha)$ vs. conversion α for model reactions at various temperatures. Symbols as in *Figure 3*

Table 1 Kinetic parameters for model reactions

Temp. (°C)	$k_1 \times 10^3$ ($\mathrm{l\,mol^{-1}\,min^{-1}}$)	$k_2 \times 10^2$ ($\mathrm{l^2\,mol^{-2}\,min^{-1}}$)	E_{a1} ($\mathrm{kcal\,mol^{-1}}$)	E_{a2} ($\mathrm{kcal\,mol^{-1}}$)
50	0.293	0.491	24.1	19.2
58	0.950	0.666		
61	1.13	0.967		
67	1.82	1.22		

Table 2 Kinetic parameters of epoxide for DGEBA and SINs

PPEGMA/DGEBA	Temp. (°C)	$k_1 \times 10^3$ ($\mathrm{l\,mol^{-1}\,min^{-1}}$)	$k_2 \times 10^2$ ($\mathrm{l^2\,mol^{-2}\,min^{-1}}$)	E_{a1} ($\mathrm{kcal\,mol^{-1}}$)	E_{a2} ($\mathrm{kcal\,mol^{-1}}$)
0/100	50	7.00	2.00	10.2	7.87
	60	11.1	2.53		
	65	14.3	3.22		
	70	17.5	4.06		
50/50[a] (mixture)	50	3.63	1.53	10.3	7.92
	60	5.33	1.93		
	65	7.39	2.58		
	70	9.10	3.15		
	70	8.06	1.61		
60/50[b] (SIN)	50	2.10	1.41	15.4	8.28
	60	2.84	1.86		
	65	4.56	2.42		
	70	7.63	2.98		

[a] Without BPO
[b] With 1% BPO (based on PPEGMA)

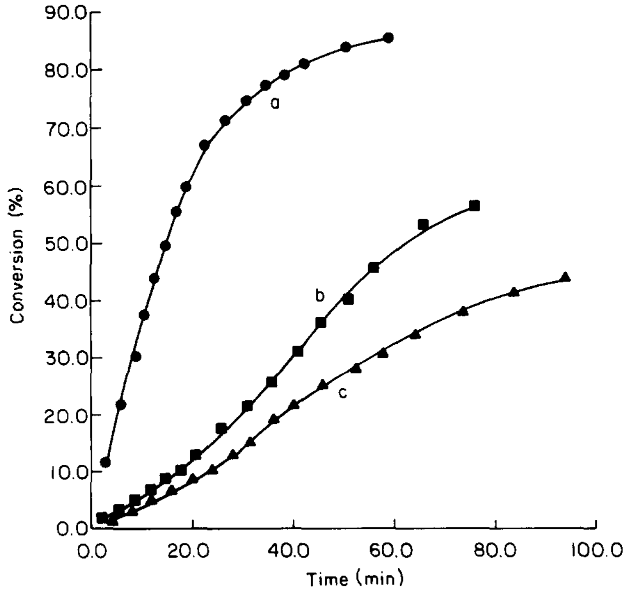


Figure 5 Typical conversions α vs. time for (a) pure DGEBA, (b) epoxide in the mixture of PPEGMA/DGEBA = 50/50 (without BPO), and (c) epoxide in the SIN of PPEGMA/DGEBA (with 1% of BPO)

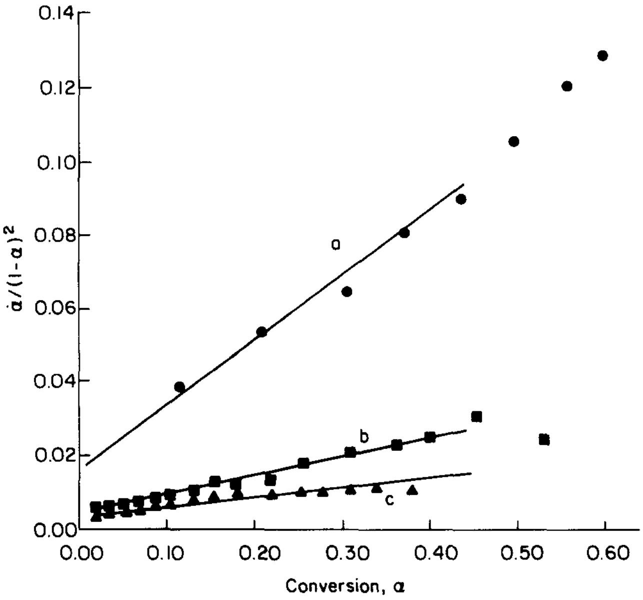


Figure 6 Typical plots of $\dot{\alpha}/(1-\alpha)^2$ vs. α for (a) pure DGEBA, (b) epoxide in the mixture of PPEGMA/DGEBA = 50/50 (without BPO), and (c) epoxide in the SIN of PPEGMA/DGEBA = 50/50 (with 1% of BPO)

are listed in *Table 2*. The activation energies for spontaneous (E_{a1}) and catalytic reactions (E_{a2}) were calculated from the plots of Arrhenius equation. Similar results were found, i.e. that the rate constant for catalytic reaction was about 10 times that of spontaneous reaction, while the activation energy of catalytic reaction was less than that of spontaneous reaction.

Experimental results clearly indicated that the DGEBA/*m*XDA curing reaction followed the same rate expression as the model reactions. In comparison of *Tables 1* and *2*, it is found that both rate constants of spontaneous (k_1) and catalytic (k_2) reactions for DGEBA/*m*XDA are higher than those of the model reactions, and the corresponding activation energies for

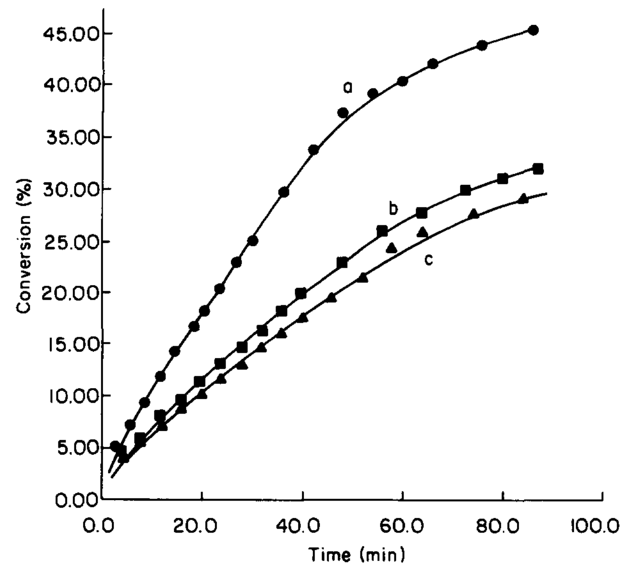
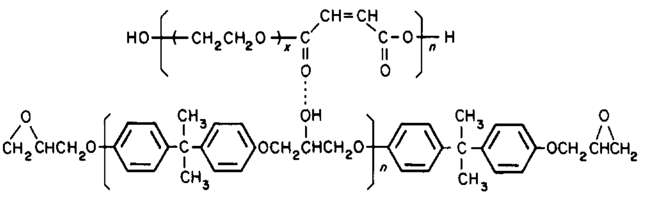


Figure 7 Typical conversions α vs. time for (a) C=C in pure PPEGMA, (b) C=C in the mixture of PPEGMA/DGEBA = 50/50 (without *m*XDA), and (c) C=C in the SIN of PPEGMA/DGEBA = 50/50 (with stoichiometric *EEW* amounts of *m*XDA)

DGEBA/*m*XDA are lower than those of the model reactions, because the DGEBA originally contains OH groups, which were able to catalyse the curing reactions. *Table 2* also clearly shows that the epoxide reaction in the presence of PPEGMA as solvent (without BPO, i.e. the mixture of PPEGMA/DGEBA = 50/50) indicates slightly lower rate constants but somewhat higher activation energies than the pure DGEBA, while the epoxide reaction in the SIN (in the presence of both PPEGMA and BPO, i.e. the SIN of PPEGMA/DGEBA = 50/50) indicates even lower rate constants and even higher activation energies than the pure DGEBA. It appears reasonable to infer that the solvent effect of PPEGMA in the DGEBA/*m*XDA reaction seems to retard the curing reactions via hydrogen bonding:



This hydrogen bonding was evidenced from the shift of $\nu_{C=O}$ to lower frequencies in the i.r. spectra, as reported in our previous paper[10]. Similar hydrogen bonding between DGEBA and unsaturated polyester was reported in the literature[11]. The hydrogen bonding between DGEBA and PPEGMA probably reduced the DGEBA chain mobility slightly, leading to lower rate constants and slightly higher activation energies. On the other hand, the DGEBA/*m*XDA reactions in SIN formation exhibited even lower rate constants and even higher activation energies. This was presumably because, in addition to the H-bonding effect in DGEBA/PPEGMA mixture, mutual entanglement between DGEBA and PPEGMA networks is believed not only to provide an extra sterically hindered environment to the reactions, but also to restrain extensively the DGEBA chain mobility, thus significantly increasing the activation energies during SIN formation. The data plotted according to equation (9) are linear in the early stages of curing reactions. However, in the latter stages, deviation occurred; presumably because of high viscosity, the kinetics became diffusion-controlled.

Kinetics of PPEGMA

Free-radical polymerization of vinyl compounds normally follows first-order reaction kinetics[20,21]:

$$-\frac{d[M]}{dt}=k_p(k_d f[I]/k_t)^{1/2}[M] \qquad (10)$$

where $[M]_0$ and $[M]$ are, respectively, the initial concentration in the C=C and the concentration at time t, in PPEGMA; k_p, k_d and k_t are rate constants for the chain propagation, initiator dissociation and chain termination; and f and $[I]$ are the initiator efficiency and initiator concentration. Integration of equation (10) gives:

$$-\int_{[M]_0}^{[M]}\frac{d[M]}{[M]}=\int_0^t k_p(k_d f[I]/k_t)^{1/2}\,dt \qquad (11)$$

Assume that f and $[I]$ do not change too much in the early stages of curing reactions such that $k_p(k_d f[I]/k_t)^{1/2}$ is nearly constant and is equal to k. The result of equation (11) becomes:

$$-\ln(1-\alpha)=kt \qquad (12)$$

with $[M]=[M]_0(1-\alpha)$, by neglecting the C=C concentration after post-cure $[M]_\infty$. *Figure 7* shows the typical C=C conversion α *versus* time for (a) PPEGMA, (b) a mixture of PPEGMA/DGEBA = 50/50 (without *m*XDA) and (c) the SIN of PPEGMA/DGEBA = 50/50 (with stoichiometric amounts of *m*XDA). *Figure 8* shows the plots of $-\ln(1-\alpha)$ *versus* t for the above compositions. Slopes of the straight lines give the values of apparent rate constant k. The corresponding apparent activation energies were found from the plots of Arrhenius equation. Kinetic parameters for PPEGA, the mixture of PPEGMA/DGEBA = 50/50 and the SIN of PPEGMA/DGEBA = 50/50 are summarized in *Table 3*. Experimental data fit equation (12) well in the early stages

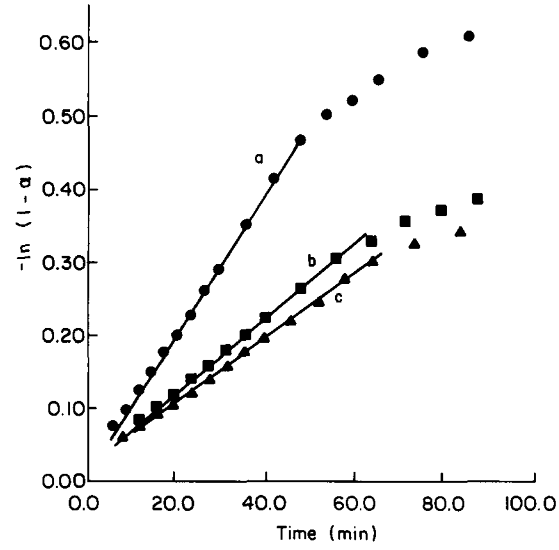


Figure 8 Plots of $-\ln(1-\alpha)$ vs. time for (a) C=C in pure PPEGMA, (b) C=C in the mixture of PPEGMA/DGEBA = 50/50 (without *m*XDA), and (c) C=C in the SIN of PPEGMA/DGEBA = 50/50 (with stoichiometric *EEW* amounts of *m*XDA). PPEGMA charged in different environments at 65°C

Table 3 Kinetic parameters of C=C

PPEGMA/DGEBA	Temp. (°C)	$k \times 10^3$ (min^{-1})	E_a (kcal mol^{-1})
100/0	50	5.18	8.07
	60	6.17	
	65	9.03	
	70	10.6	
50/50[a] (mixture)	50	2.90	8.86
	60	3.79	
	65	4.89	
	70	6.64	
50/50[b] (SIN)	50	2.37	10.4
	60	3.14	
	65	4.32	
	70	6.24	

[a] Without *m*XDA
[b] With stoichiometric amounts of *m*XDA (based on DGEBA)

of reaction, while in the latter stages deviation was observed; presumably *f* and [I] changed too much in the latter stages of reactions and/or viscosity increased continuously, and gradually its kinetics became diffusion-controlled[21].

It is clear from *Table 3* that, compared with the pure PPEGMA, the mixture of PPEGMA/DGEBA = 50/50 (without *m*XDA) indicated a lower apparent rate constant but a slightly higher apparent activation energy, while the SIN of PPEMA/DGEBA = 50/50 (with *m*XDA) indicated even lower apparent rate constant and even higher apparent activation energy. Similar results to the DGEBA cure kinetics were found. The existence of DGEBA network probably provided extra steric hindrance to the growing of PPEGMA network. Again, network interlock played a significant role in the curing of PPEGMA during SIN formation.

CONCLUSIONS

Kinetic studies on the formation of DGEBA/PPEGMA SIN showed that the SIN exhibited lower rate constants and higher activation energies compared with those of the respective components. This phenomenon can be interpreted in terms of a network interlock effect. Network interlock not only gave an additional sterically hindered environment to the curing reactions, but also restrained the mobilities of both DGEBA and PPEGMA, thus accounting for the experimental results.

ACKNOWLEDGEMENT

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

REFERENCES

1 Sperling, L. H. 'Interpenetrating Polymer Networks and Related Materials', Plenum Press, New York, 1981
2 Frisch, K. C., Klempner, D. and Frisch, H. L. *Mater. Des.* 1983, **4**, 855
3 Nishi, S. and Kotoks, T. *Macromolecules* 1985, **18** (8), 1519
4 Siefried, D. L., Thomas, D. A. and Sperling, L. H. *Polym. Eng. Sci.* 1981, **21**, 39
5 Hourston, D. J. and Satgurunatham, R. *J. Appl. Polym. Sci.* 1984, **29**, 2969
6 Hourston, D. J., Satgurunatham, R. and Verma, H. *J. Appl. Polym. Sci.* 1987, **39**, 215
7 Jin, S. R. and Meyer, G. C. *Polymer* 1986, **27**, 592
8 Xue, S.-C., Zhang, Z.-P. and Ying, S.-K. *Polymer* 1989, **30**, 1271
9 Lin, M.-S. and Jeng, K.-T. *J. Polym. Sci., Polym. Chem. Edn.* 1992, **30**, 1941
10 Lin, M.-S., Jeng, K.-T. and Yang, T. *Polymer* 1993, **34**, 3538
11 Lin, M.-S. and Chang, R.-J. *J. Appl. Polym. Sci.* 1992, **46**, 815
12 Schechter, L., Wynstra, J. and Kurkyiy, R. E. *Ind. Eng. Chem.* 1956, **48**, 94
13 King, J. J. and Bell, J. P. 'Epoxy Resin Chemistry' (Ed. R. S. Bauer) American Chemical Society, Washington, DC, Vol. 114, Ch. 16, pp. 2223–62
14 Riccardi, C. C., Adabbo, H. E. and Williams, J. J. *J. Appl. Polym. Sci.* 1984, **29**, 2481
15 Moroni, A., Mijiovic, J., Pearce, E. M. and Foun, C. C. *J. Appl. Polym. Sci.* 1986, **32**, 3761
16 Dutta, A. and Ryan, M. E. *J. Appl. Polym. Sci.* 1979, **24**, 635
17 Golub, M. A. and Lerner, N. R. *J. Appl. Polym. Sci.* 1986, **32**, 5215
18 Mijovic, J., Kim, J. and Slaby, J. *J. Appl. Polym. Sci.* 1984, **29**, 1449
19 Koenig, L. *Appl. Spectrosc.* 1975, **29**, 295
20 Enikolopiyan, N. S. *Pure Appl. Chem.* 1976, **18**, 317
21 Odian, G. 'Principles of Polymerization', 2nd Edn., Wiley, New York, 1981, Ch. 3